Investigation of Optical Effect of Lignin Solution and Determination of $\bar{M}_w$ of Kraft Lignin by LALLS

DAOJIE DONG and ARTHUR L. FRICKE*

Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611

SYNOPSIS

The optical effects (fluorescence, anisotropy, and absorption) of kraft lignin solutions in three different kinds of solvents (0.1*N* NaOH, DMF, and pyridine) on the measurement of the weight-averaged molecular weight of lignin were investigated, and a correction procedure for these optical effects in the determination of the weight-averaged molecular weight of kraft lignin was developed. It was found that the fluorescence effect is the main source of error in the determination of the molecular weight of lignin, and the anisotropy and absorption strongly affect the second virial coefficient. It was also found that the anisotropic effect of kraft lignin dissolved in DMF and pyridine is contributed mainly by the anisotropic solvents rather than by the lignin particles and that the lignin solution in 0.1*N* NaOH is essentially optically isotropic. By using the correction procedure provided, the corrected molecular weight of lignin determined in three kinds of solvents varies only about ±10%, whereas the apparent weight-averaged molecular weight of the same lignin differs by ±57%.

INTRODUCTION

A huge amount of kraft lignin is generated each year as a byproduct in the pulp and paper industry. The behavior of lignin, whether in processing or in end-use applications, is often critically governed by the variety and relative amounts of molecular weight species present. Therefore, considerable effort has been made on the determination of its average molecular weight and molecular weight distribution.[1-6] For the weight-averaged molecular weight ($\bar{M}_w$) determination, a low-angle laser light-scattering photometer (LALLSP) is often employed due to its amenability to absolute calibration in the sense that the Rayleigh factor, R_θ, is computed from geometric parameters and ratios of radiant power measurement[7] and its advantage in permitting observations at smaller scattering angles with a smaller sample volume to be made, which decreases interference from foreign particles.[8,9]

Large variations in the $\bar{M}_w$ of kraft lignin isolated from various black liquors have been reported.[4] For example, values from as low as a few thousands[10,11] to as high as 48×10^6 have been reported.[12,13] The variation may result from different wood species and pulping conditions; however, there are also large differences in the reported molecular weights of lignin separated from the same wood species. It is believed that part of the variation is undoubtedly due to the different isolation methods used and the inadequate techniques in $\bar{M}_w$ determination.[14]

There are two aspects that may give rise to difficulties in the determination of the molecular weight of lignin—its impurity and its solution optical property. Kraft lignin is isolated from black liquor, a byproduct of the pulping process, which is commonly viewed as being an almost hopelessly complicated mixture.[15] It is very important, but difficult, to employ proper isolation procedures to obtain a high-purity sample for determination of molecular weight. The principle of determination of $\bar{M}_w$ by low-angle laser light scattering (LALLS) is based on the fluctuation theory.[16-18] This theory is valid only for optically isotropic particles that do not absorb and fluoresce at the incident wavelength. In fact, light scattering by purified lignin must be corrected for the optical effects of anisotropy, fluorescence, and absorption. Forss[19] reported that the absorption of

* To whom correspondence should be addressed.
Journal of Applied Polymer Science, Vol. 50, 1131–1140 (1993)
 CCC 0021-8995/93/071131-10

light by lignosulfonate interferes with the determination of its molecular weight, but no influence of fluorescence on the measured scattered light can be expected at a wavelength of 546 nm. Kolpak et al.[1] reported a correction for both fluorescence and absorption, and Pla et al.[20] and Kim[21] corrected all three optical effects by using rather different methods. However, no detailed information of the influence of these optical effects on the lignin molecular weight could be found in the literature.

In this work, $\bar{M}_w$ of purified kraft lignin was determined in three different solvents: DMF, pyridine, and 0.1*N* NaOH, and correction for the three optical effects mentioned above were developed. The optical effects of lignin solutions in different solvents were analyzed and compared, and the effects of the optical properties of lignin solution on the determination of $\bar{M}_w$ of lignin are discussed and reported. No attempt has been made in this study to investigate the effect of the pulping conditions on the lignin molecular weight; a four-variable statistical experimental pulping design that produced 25 kraft black liquors with KAPPA numbers ranging from 25 to 110 has been conducted, and the influence of pulping conditions on the molecular weight of lignin will be reported separately.[22]

INSTRUMENTATION

Experiments were performed with a Chromatix KMX-6 LALLSP that uses a 2 mW helium–neon laser as a light source (λ = 632.8 nm) and has a set of auxiliaries consisting of a 632.8 nm narrow-band filter and a polarizing analyzer that can be optionally inserted into the scattered light path. The relatively long wavelength (632.8 nm) reduces the optical effects of sample absorption and fluorescence. The essential features of the KMX-6 LALLSP are approximately the same as those of the LALLSP reported in the literature[7,23] except that the positions of the 632.8 nm narrow-band filter and the polarizing analyzer are inverted.

A Chromatix KMX-16 light differential refractometer (LDRM) that has a 0.5 mW helium–neon laser as light source (λ = 632.8 nm) was employed to measure the specific refractive index increment (SRII). A Perkin-Elmer Lambda 4C dual-beam UV-visible spectrophotometer was used for measurement of transmittance of the lignin solution.

THEORY (A BRIEF SUMMARY)

The quantity used to describe the light-scattering property of a sample is the Rayleigh factor:

$$R_\theta = I_\theta r^2 / I_0 V \tag{1}$$

where I_θ is the intensity measured at a distance r from the sample and at a angle θ from the direction of the incident light; I_0, the intensity of the incident light; and V, the volume of the sample simultaneously illuminated and viewed by the detector.[24] In reality, the Rayleigh factor is determined by eq. (2), because the photomultiplier detector directly measures the radiant power rather than the intensity. Thus:

$$R_\theta = G_\theta / (G_0 \sigma l) \tag{2}$$

where G_θ and G_0 are the radiant powers of the scattered and the incident beams, respectively, and σ and l are the solid angle[7] of the detected scattered light and the distance (parallel to the incident beam) from the scattering volume, respectively.

The principle of the light-scattering method is based on the fluctuation theory,[16–18] which gives the following equation for the relationship between the molecular characteristics, $\bar{M}_w$ and $P(\theta)$, and the scattering characteristic $\bar{R}_\theta$:

$$\frac{KC}{\bar{R}_\theta} = \frac{1}{\bar{M}_w P(\theta)} + 2A_2 \frac{C}{P(\theta)} + 3A_3 \frac{C^2}{P(\theta)} \tag{3}$$

where

$$K = \frac{2\pi^2 n^2}{\lambda^4 N} \left(\frac{dn}{dc}\right)^2 (1 + \cos^2 \theta) \tag{4}$$

$$P(\theta)_{\theta \to 0} = 1 - \frac{16\pi^2}{3\lambda^2} R_g^2 \sin^2\left(\frac{\theta}{2}\right) \tag{5}$$

R_θ is the Rayleigh factor (cm^{-1}); $\bar{R}_\theta$, the excess Rayleigh factor (cm^{-1}) $\bar{R}_\theta = R_\theta \langle \text{solution} \rangle - R_\theta \langle \text{solvent} \rangle$; $\bar{M}_w$, the weight-average molecular weight (mol^{-1}, or g/g-mol); K, the optical constant (cm^2 mol/g); $P(\theta)$, the particle scattering factor; n, the refractive index of the solvent; λ, the wavelength of the incident light (632.8 nm = 6.328×10^{-5} cm); C, the solute concentration (g/mL); R_g, the radius of gyration (cm); dn/dc, the SRII (mL/gm); θ, the angle at which the scattering light is determined; N, Avogadro's constant (6.02×10^{23} mol^{-1}); and A_2, A_3, virial coefficients.

When a low angle is used for measurement and the solute concentration becomes very small, eq. (3) reduces to the following simple form:

$$\frac{KC}{\bar{R}_\theta} = \frac{1}{\bar{M}_w} + 2A_2 C \tag{6}$$

When $KC/\bar{R}_\theta$ is plotted vs. concentration, C, $\bar{M}_w$ can be determined from the reciprocal of the y-in-

tercept and the second virial coefficient, A_2, can be determined from one-half of the slope.

CORRECTION FOR OPTICAL EFFECT

Fluorescence

Molecules existing in the ground state are excited to certain higher states when they absorb light. After excitation, they rapidly revert to the first (lowest) excited state. When the molecules return from the first excited state to the ground state, fluorescence is emitted. Therefore, fluorescent light has lower energy and greater wavelength than those of the incident light. Without correction, the photomultiplier will detect both the scattered and fluorescent light. Hence, the fluorescence effect results in an overestimation of R_θ and $\bar{M}_w$ [eq. (6)]. Lundquist and co-workers[25,26] found that structural elements of the stilbene type dominate the fluorescence spectra of sulfate lignin. Forss and co-workers[19] investigated fluorescence effects at wavelengths of 365, 436, and 546 nm by utilizing the excitation–emission spectrum. They found that the fluorescence of the lignosulfonate solution becomes weaker as the wavelength increases and is very weak at 546 nm. However, Kolpak and co-workers[1] reported that a dramatic change occurs in the LALLS signal (λ = 632.8 nm) when a 632.8 nm filter is placed between the sample of the kraft lignin solution and the photomultiplier, whereas nothing significant is observed on the fluorescence spectrum at an excitation wavelength of 633 nm. They also found that, by placing the filter in the scattered light path to filter out the fluorescent light, the corrected GPC/LALLS chromatogram of the kraft lignin eluted by THF changed dramatically from a bimodal to a monomodel chromatogram. Brice and co-workers[27] developed a lengthy correction method for fluorescence by addition of dye into starch aqueous solution and polystyrene solution in toluene (not lignin).

Errors due to fluorescence in a scattering solution can be minimized by (a) choice of a wavelength for the incident light that does not result in fluorescence; (b) filtering out the fluorescent light in the scattering light path; or (c) correction of the apparent scattering ratio determined in the usual manner.[27] In this report, the second correction method is employed.

Absorption

It is obvious that the effect of absorption reduces the intensity of scattered light. Without correction, this will result in an underestimation of the Rayleigh factor, R_θ, and of $\bar{M}_w$. Usually, the effect of absorption is corrected for by compensation for the lost scattered light. As a general rule,[20,27,28] the correction is dependent on the scattering angle, θ; however, when the measuring cell is cylindrical and the optical density of the solution is sufficiently weak, the correction becomes partially independent of the scattering angle. In this case, the absorption effect can be corrected for simply by dividing the apparent Rayleigh factor by the transmittance of the solution.[1,19,20]

Anisotropy

Scattering theory[17] predicts that an ellipsoid scatters more intensely than does a sphere of the same volume; a sphere comprising an anisotropic medium will scatter more intensely than will an isotropic sphere of the same volume. Hence, the effect of anisotropy may result in an overestimation of the molecular weight if no correction is made. There have been a few reports of different correction methods;[20,29] however, the effect of anisotropy is most frequently corrected for by applying the Cabannes factor.[18] Although a vertical polarized source is employed on the LALLSP, it is still necessary to use the conventional depolarization ratio and the Cabannes factor of unpolarized light[30] for this correction. The proper Cabannes factor that was used in this study is given by eq. (7)[17]:

$$C_u(\theta) = \frac{1 + \rho_u(90) + [1 - \rho_u(90)]\cos^2\theta}{[1 - (7/6)\rho_u(90)][1 + \cos^2\theta]} \quad (7)$$

where

$$\rho_u(90) = \frac{2\rho_v(\theta)}{1 + \rho_v(\theta)} \quad (8)$$

where $C_u(\theta)$ is the Cabannes factor of unpolarized light at an angle, θ, $\rho_u(90)$ is the depolarization ratio of unpolarized light at 90°, and $\rho_v(\theta)$ is the depolarization ratio of the vertically polarized light at an angle, θ. On the LALLSP, one actually measures

$$\rho = \frac{G_\theta^H}{G_\theta^V} \quad (9)$$

and a relation between ρ and $\rho_v(\theta)$ is given by eq. (10), because the full cone of scattered light is collected:

$$\rho_v(\theta) = \frac{\rho[1 + \cos^2\theta]}{[2 - \rho + \rho\cos^2\theta]} \quad (10)$$

where G_θ^H and G_θ^V are the radiant powers measured with the polarizer oriented with its plane of polarization crossed (horizontal) and parallel (vertical) with respect to the plane of polarization of the incident light beam.

EXPERIMENTAL

Sample Preparation

Three experimental kraft black liquors were prepared by pulping slash pine in a pilot scale digester (3.5 ft^3) with liquor circulation. The detailed digester information and pulping conditions were reported elsewhere.[31] One mill black liquor from kraft pulping of sugar maple was obtained from industry sources. The pulping conditions for the black liquors are summarized in Table I. The lignin samples were carefully isolated from the black liquors using the following procedure: The black liquor was adjusted to about 10% total solids and a pH of about 13, filtered through a glass fiber filter, precipitated by 1.0*N* H_2SO_4 to a pH of about 2.0, and washed with deionized water; the precipitate was redissolved in 0.1*N* NaOH and filtered through a filter paper; this solution was retitrated with 1.0*N* H_2SO_4 to a pH of 2.0 to precipitate the lignin; the slurry was centrifuged to separate the lignin and the liquor decanted; the precipitated lignin was washed once with deionized water, twice with 0.01*N* H_2SO_4, three more times with deionized water, and then freeze-dried; and, finally, the lignin was extracted with hexane and freeze-dried again. These purified lignins were used for analysis.

The organic solvents used were ACS-grade pyridine and DMF filtered through a Millipore Teflon membrane with a pore size of 0.45 μ. HPLC-grade Optima® water was used to make the 0.1*N* NaOH solution, which was filtered through a Gelman Nylaflo® nylon filter membrane of pore size 0.45 μ before use. Lignin solutions at a concentration of about 8.0×10^{-3} (g/mL) were prepared and filtered with a syringe filter having a pore size of 0.45 μ before dilution.

Determination of Specific Refractive Index Increment (SRII)

It is critical to determine SRII accurately, because the optical constant is directly proportional to its square [eq. (4)]. The LDRM was calibrated with a NaCl solution prepared with Optima water, and an instrument constant of 1.2692×10^{-7} was obtained. When the lignin solutions were measured, some difficulties were encountered because of absorption and high viscosity when organic solvents were used and even higher absorption when aqueous solutions such as 0.1*N* NaOH were used. This may result in either less sensitivity or a loss of signal, especially when the concentration is higher than 2.0×10^{-3} (g/mL). In this case, the power of the light source must be compensated for with the cell in position and filled with both solvent and the sample solution.

The refractive index of the solvent appears as the square in eq. (4) and also affects the instrument optical parameters, such as θ, σ, and l of the LALLSP. The values of the refractive index of the solvents obtained from reference sources are listed in Table II. For 0.1*N* NaOH, the refractive index increment was measured against water and then added to the refractive index of water. The scattering angles calculated with a field stop 0.2 and a 6°–7° annulus are also summarized in Table II.

Determination of Rayleigh Factor and Depolarization Ratio

A stainless-steel cylindrical cell with a thickness of 0.493 cm was used for determinations of R_θ. An online filter membrane with a diameter of 13 mm and pore size 0.2 μ was always used. When an organic

Table I Pulping Conditions of Kraft Black Liquors

No.	Type	Wood	*EA* (%)	*S* (%)	*t* (min)	*T* (°C)	*K #*	*H*	Y (%)
#1	Kraft	Slash pine	13.0	20.0	40	166	106.8	556	69.6
#2	Kraft	Slash pine	16.0	35.0	40	166	53.6	631	52.0
#3	Kraft	Slash pine	14.5	27.5	60	171	51.1	1270	53.2
#4	Kraft	Sugar maple	13.5	30.0	45 Ramp 120 Cook	170	15.0	1414	

EA, effective alkali; *S*, sulfidity; *t*, cooking time; *T*, cooking temperature; *K#*, KAPPA number; *H*, *H* factor; *Y*, yield. #1, #2, and #3 are experimental liquors; #4 is a mill liquor.

Table II Solvent Index of Refraction and the Scattering Angle

Solvent	Temp (°C)	Refractive Index n	Reference	θ (Degree)	$1 + \cos^2\theta$
0.1*N* NaON	23.0	1.3335		4.870	1.9928
DMF	80.0	1.4020	21	4.630	1.9934
Pyridine	50.0	1.4907	21	4.357	1.9942
Water	25.4	1.3324	32		

solvent was used, the Millipore Teflon filter membrane was chosen and preconditioned on-line at least 24 h with the pure solvent at the experimental temperature before use for measurement. For an inorganic solvent, a Gelman Nylaflo nylon filter membrane with a pore size 0.2 μ was used on-line; a new filter membrane was used for each lignin sample (five solutions), and the filter was set up just before the measurement with the casting (glossy) surface facing the down-flow direction. All experiments were conducted at a stable filtration flow rate of about 0.1 mL/min.

The LALLSP was checked with pure toluene with a 0.05 μ Millipore mixed cellulose ester membrane filter on-line, and a Rayleigh factor of $R_{\theta\text{toluene}} = 13.85 \times 10^{-6}$ and a depolarization ratio of $\rho_u(90) = 0.498$ at ambient temperature were determined. The Rayleigh factor corrected for fluorescence, $R_{\theta f}$, was directly measured on LALLSP with a sharply defined 632.8 nm narrow-band filter, which blocks out the fluorescent light, inserted in between the sample volume and the photomultiplier detector. The polarized radiant power G_θ^H and G_θ^V (as defined previously) were measured with both the filter and the polarizer placed in between the sample volume and the photomultiplier.

Transmittance of the Lignin Solution

The transmittances of the lignin solutions were measured against the solvent on the dual-beam UV-visible photometer at a wavelength of 632.8 nm. The cells used have a thickness of 0.500 cm. A water bath and circulation system was used to maintain a constant temperature at which R_θ was measured.

Correction Procedure

The Rayleigh factors R_θ and $R_{\theta f}$ were directly measured, and $R_{\theta fp}$ and $R_{\theta fpa}$ were calculated by eq. (11) and (12), respectively:

$$R_{\theta fp} = \frac{R_{\theta f}}{C_u(\theta)} \tag{11}$$

$$R_{\theta fpa} = \frac{R_{\theta fp}}{T} \tag{12}$$

The corresponding excess Rayleigh factors were calculated and substituted into eq. (6) to obtain the molecular weights of $\bar{M}_w$, $\bar{M}_{wf}$, $\bar{M}_{wfp}$, and $\bar{M}_{wfpa}$. Notice that the subscripts f, p, and a denote "corrected for fluorescence, anisotropy, and absorption," respectively; no subscript means "apparent or uncorrected"; and the T in eq. (12) denotes the transmittance of the lignin solution determined at 632.8 nm.

RESULTS AND DISCUSSION

As shown in Figure 1, the refractive index increment vs. lignin concentration exhibits a perfectly linear relation (the correlation coefficient $r = 1.00$). Therefore, the SRII (dn/dc) values can be accurately determined from the slopes. The SRII results and the optical constants calculated from eq. (4) are listed in Table III. The data of Table III indicate that the SRII of the same lignin sample determined in different solvents varies substantially, and the SRII increases as the refractive index of the solvent

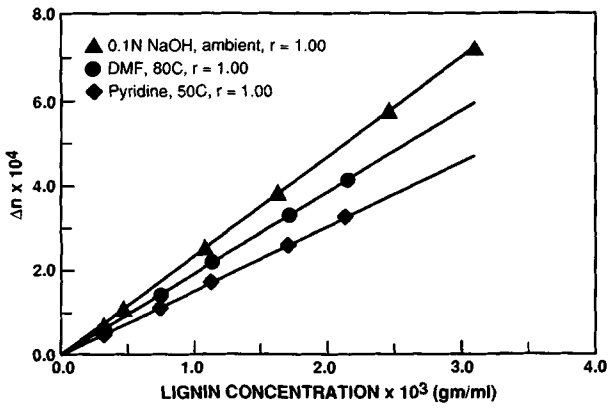

Figure 1 Refractive index increment vs. lignin concentration for determination of SRII (dn/dc) (lignin #1, slope = dn/dc).

Table III Specific Refractive Index Increment (SRII) of Lignin Solutions and the Optical Constants

Lignin Sample	Solvent	Temp (°C)	*dn/dc* (mL/g)	Optical Constant K (cm mol/g)
#1	0.1*N* NaON	23	0.2327	3.9145×10^{-7}
	DMF	80	0.1911	2.9191×10^{-7}
	Pyridine	50	0.1509	2.0572×10^{-7}
#2	0.1*N* NaOH	23	0.2327	3.9145×10^{-7}
#3	0.1*N* NaOH	23	0.2308	3.8508×10^{-7}
#4	0.1*N* NaOH	23	0.2282	3.7645×10^{-7}

decreases (see Tables II and III). The SRII determined in DMF, about 1.90 (Fig. 2), is comparable to values reported in the literature.[21] The SRII determined in pyridine, about 0.15, falls in the normal range of 0.1–0.2 for most polymers.[33] The SRII of about 0.23 determined in 0.1*N* NaOH is relatively high. Virtually no values of SRII for lignin in pyridine and 0.1*N* NaOH have been reported, but our data are reasonably close to theoretical predictions of the dependence of SRII on solvent refractive index.[33]

Interestingly, the SRII of different lignin samples measured in the same solvent are nearly identical, as shown in Figure 2. This indicates that the molecular weight of these lignin samples is above a certain limit and the SRII is nearly a constant.[33] Also, this is an indication that the preparation used for these lignins produced very uniform samples.

The Cabannes factors of kraft lignin dissolved in different solvents are shown in Figure 3 and 4. The Cabannes factor for the lignin solution in 0.1*N* NaOH is very low and does not depend on the lignin concentration at all; it has a constant value of about 1.075, which is essentially the Cabannes factor of the solvent. However, the Cabannes factors for the lignin dissolved in organic solvents (DMF and pyridine) are much higher and depend strongly on lignin concentration; as the lignin concentration increases, the Cabannes factor decreases rapidly from that for the pure solvent at first, then flattens out gradually, as shown in Figure 3. When the Cabannes factors obtained from three different kraft lignin samples in the same solvent are plotted against lignin concentration, the data points for each solvent fall on the same line (Fig. 4). Also, a very good linear relationship exists between the Cabannes factor and the lignin concentration in an organic solvent up to a concentration of about 2.1×10^{-3} (g/mL); for example, $C_u(\theta)_{DMF} = 1.6733 - 160.1\ C$ (g/mL) (for three lignins) with a correlation coefficient of −.919, and $C_u(\theta)_{pyridine} = 2.2828 - 411.8\ C$ (g/mL) (for lignin #1) with a correlation coefficient of −.960.

Even though the Cabannes factor of lignin solutions in DMF or pyridine is higher (much higher at low concentration) than 1, we think that the an-

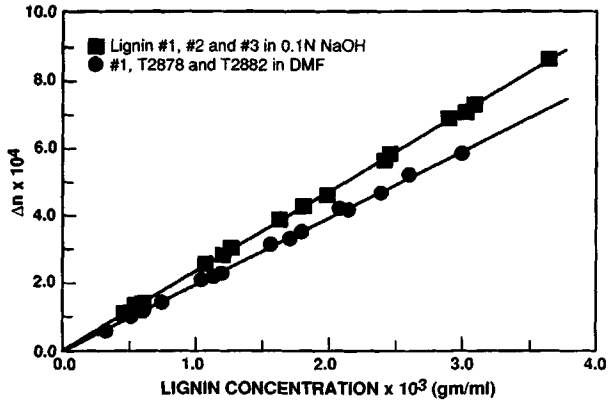

Figure 2 Refractive index increment vs. lignin concentration to show that the SRII of different lignin samples measured in the same solvent are nearly identical.

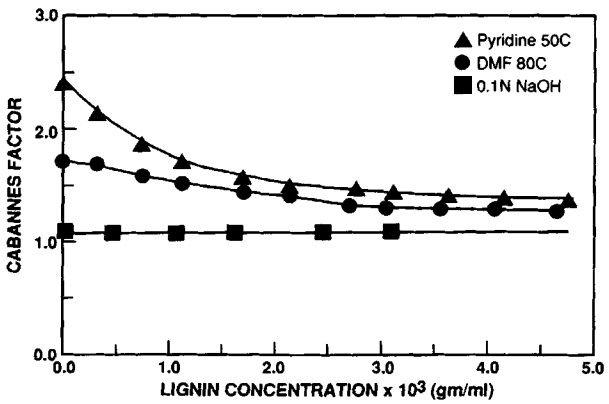

Figure 3 Effect of concentration on the Cabannes factor of lignin solutions (lignin #1 in three different solvents).

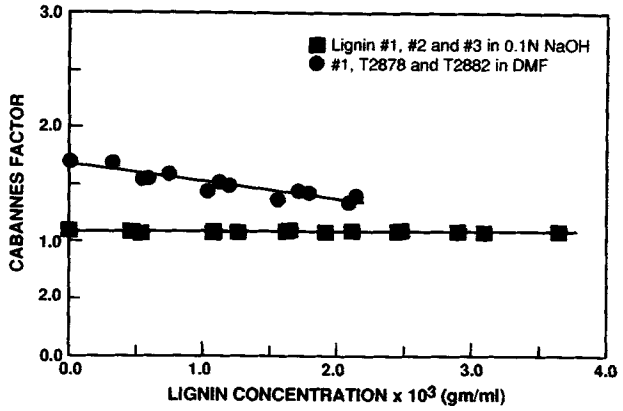

Figure 4 Cabannes factors of different lignin samples in two different solvents.

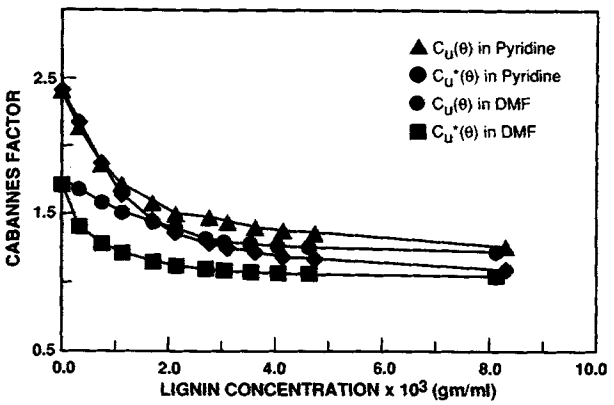

Figure 5 $C_u(\theta)$ and $C_u^*(\theta)$ vs. concentration of lignin illustrates the contribution of lignin to the Cabannes factor.

isotropic effect observed for a lignin solution is contributed mainly by the anisotropy of the solvent itself, rather than by the lignin particles. This point of view is based on experimental observations and arguments. Suppose that the observed Rayleigh factor $R_{\theta\text{obs}}$ can be decomposed into two parts, $R_{\theta\text{iso}}$ and R_θ^*. $R_{\theta\text{iso}}$ is the equivalent Rayleigh factor if the scattering sample were isotropic, and R_θ^* is the excess part due to the anisotropic effect. Then, we have the following equation:

$$R_\theta^* = \frac{C_u(\theta) - 1}{C_u(\theta)} R_{\theta\text{obs}} \tag{13}$$

Furthermore, if the lignin particles suspended in the solvent are perfectly isotropic and there is no experimental error involved, the Cabannes factor of the lignin solution would be equal to $C_u^*(\theta)$, which is defined by eq. (14). Notice that, in order to correct also for the fluorescence effect, the observed Rayleigh factor is $R_{\theta f}$, not R_θ, in the following equation:

$$C_u^*(\theta) = \frac{R_{\theta\text{obs}}\langle\text{solution}\rangle}{R_{\theta\text{obs}}\langle\text{solution}\rangle - R_\theta^*\langle\text{solvent}\rangle} \tag{14}$$

Figure 5 shows $C_u(\theta)$ and $C_u^*(\theta)$ plotted against lignin concentration in the organic solvents. This indicates that a certain difference does exist between $C_u(\theta)$ and $C_u^*(\theta)$, which may be contributed either by the anisotropic characteristic of the lignin particles suspended in the solvent or by the experimental error, or both. In fact, however, this difference is small. For pyridine solutions, the difference is always less than 0.2. For DMF, the difference is less than 0.2 when the lignin concentration is higher than 2.0×10^{-3} (g/mL) and 0.2–0.3 when the concentration is lower than 2.0×10^{-3} (g/mL).

When an approximately isotropic solvent is used, the anisotropic effect of the lignin particles suspended in it disappears. It is obvious (Fig. 4) that the lignin solution in 0.1*N* NaOH is optically isotropic [$C_u(\theta) \to 1.0$, $\rho_u(90) \to 0.0$]. Hence, the lignin particles must have a spherical configuration in the 0.1*N* NaOH solution.

The fluorescence characteristic of the lignin solution does have a dramatic influence on the lignin molecular weight (Fig. 6). In the present study, the effect of fluorescence is treated as follows: Suppose that the observed Rayleigh factor, R_θ, is composed of two parts: one is the contribution of fluorescence, and the other is $R_{\theta f}$. Hence, the effect of fluorescence on the Rayleigh factor can be expressed by $(1 - R_{\theta f}/R_\theta)$ and that on the excess Rayleigh factor $\bar{R}_\theta$ by $(1 - \bar{R}_{\theta f}/\bar{R}_\theta)$. It has been found that about 30% of the observed Rayleigh factor of the lignin solution in 0.1*N* NaOH was due to the fluorescence contribution while fluorescence of the 0.1*N* NaOH solvent is very weak (2%). The fluorescence of the lignin dissolved in an organic solvent is even larger. As the lignin

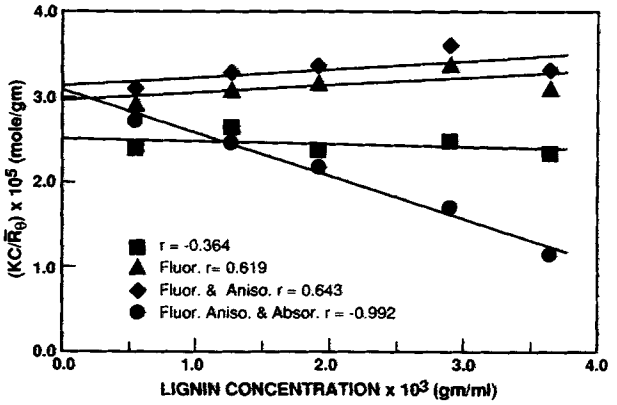

Figure 6 LALLS plots show the correction curves (lignin #2 in 0.1*N* NaOH).

concentration increases, the effect of the fluorescence on the observed Rayleigh factor, R_θ, increases, but flattens out very quickly; the effect of the fluorescence on the excess Rayleigh factor $\bar{R}_\theta$ follows the same trend. The fluorescence of kraft lignin dissolved in DMF contributes about 40–60% and 60–71% to the observed values of R_θ and $\bar{R}_\theta$, respectively. The fluorescence effect of the kraft lignin dissolved in pyridine contributes about 27–52% and 55–80% to the observed values of R_θ and $\bar{R}_\theta$, respectively. It is believed that, because the viscosities of the lignin/DMF and lignin/pyridine solutions are higher than that of the lignin/0.1N NaOH solution, the lignin molecules move less freely in the organic solvents and less energy is dissipated by intermolecular collisions. Therefore, more energy is emitted as fluorescence light from the solution in the organic solvents.

It was observed that lignin solutions do absorb light even at the relatively long wavelength of 632.8 nm. In contrast to the fluorescence effect, the lignin dissolved in 0.1N NaOH absorbs more strongly than when dissolved in the organic solvents. The transmittance was directly measured and used to correct the Rayleigh factor. A very good linear relationship between absorbance and lignin concentration can be obtained (R-squared $\geq$ 99%) from transmittance data by application of Lambert–Beer's law. The absorptivities (optical density) of lignin #1 at 632.8 nm in three different solvents were calculated to be $A_{0.1N\text{NaOH}} = 0.3002$ (1/g cm), $A_{\text{DMF}} = 0.08371$ (1/g cm), and $A_{\text{Pyridine}} = 0.1092$ (1/g cm), respectively. The other slash pine lignins separated from the experimental liquors have absorptivities close to that of lignin #1. However, the sugar maple lignin isolated from a mill liquor has an absorbtivity of $A_{0.1N\text{NaOH}} = 0.4356$ (1/g cm), which is about 45% higher than that for slash pine experimental lignins. As the lignin

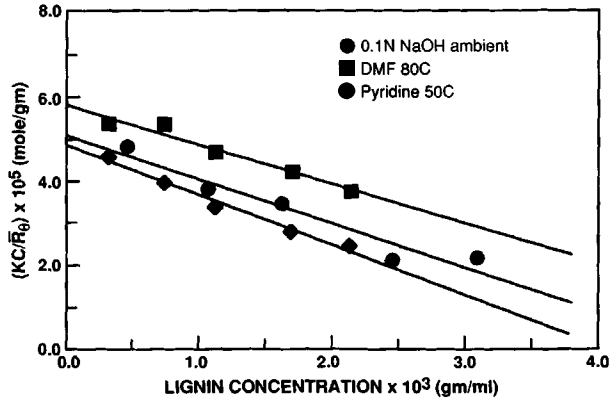

Figure 7 Corrected LALLS curves (lignin #1 in three different solvents).

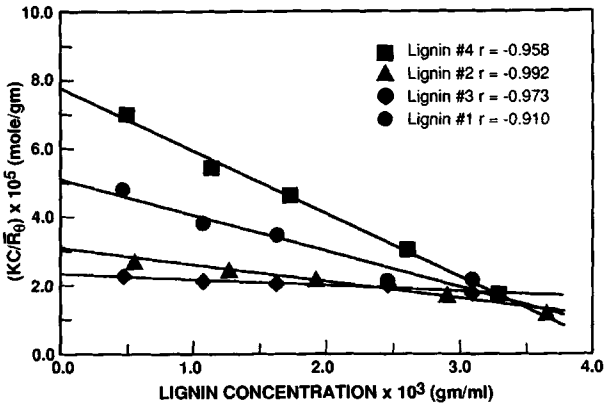

Figure 8 Corrected LALLS curves (four different lignin samples, in 0.1N NaOH).

concentration is increased, the absorption accounts for a larger percentage of the scattering light.

Figure 6 shows the corrected LALLS curves of lignin #2 in 0.1N NaOH (the correction curves in organic solvent were reported elsewhere[2]). Notice that the correction for the effect of fluorescence results in a large increase of the y-intercept while little change is produced by correction for anisotropy and absorption effects. However, corrections for anisotropy and absorption, especially absorption, do affect the slope of the curve (hence, the second virial coefficient) dramatically. The negative second virial coefficient results from correction for the effect of absorption. This is also true for the lignin dissolved in DMF.[2]

The fully corrected LALLS curves ($KC/\bar{R}_\theta$ vs. concentration) of lignin #1 determined in three different solvents are shown in Figure 7. All three curves have negative slopes, and the second virial coefficients are -5.33×10^{-3}, -4.77×10^{-3}, and -6.00×10^{-3} (mL mol/g) for lignin dissolved in 0.1N NaOH, DMF, and pyridine, respectively. As indicated in Figure 8 and Table IV, the absolute values of the second virial coefficients for the three slash pine lignins isolated from experimental liquors decrease as the molecular weight increases. The second virial coefficient for the sugar maple lignin isolated from a mill kraft liquor is larger (absolute value) than that for the slash pine lignins.

As summarized in Table IV, even though the apparent molecular weight of lignin measured in different solvents varies substantially, the fully corrected molecular weights determined in different solvents are very close. The corrected weight-average molecular weight of lignin #1 determined in three different kinds of solvents has a mean of 19,100, and an error range of about ±10%, whereas the apparent molecular weight of this lignin determined in three

Table IV $\bar{M}_w$ Measured in Different Solvents and Corrected for Optical Effects (g/g-mol)

Lignin Sample	Solvent	Temp (°C)	$\bar{M}_w$	$\bar{M}_{wf}$	$\bar{M}_{wfp}$	$\bar{M}_{wfpa}$	$A_2 \times 10^4$
#1	0.1*N* NaOH	23	28,100	19,500	18,100	19,600	−53.3
	DMF	80	86,700	25,800	16,200	17,200	−47.7
	Pyridine	50	80,700	15,200	16,200	20,600	−60.0
	Mean		65,200 ± 57%	20,200 ± 28%	16,800 ± 8%	19,100 ± 10%	
#2	0.1*N* NaOH	23	39,800	33,700	31,900	32,400	−25.5
#3	0.1*N* NaOH	23	51,000	46,600	43,700	42,900	−9.75
#4	0.1*N* NaOH	23	22,900	12,000	11,000	12,900	−92.5

$\bar{M}_w$, apparent molecular weight; $\bar{M}_{wf}$, molecular weight corrected for fluorescence only; $\bar{M}_{wfp}$, molecular weight corrected for fluorescence and anisotropy; $\bar{M}_{wfpa}$, molecular weight corrected for fluorescence, anisotropy, and absorption; A_2, second virial coefficient (mL mol/g).

solvents has an uncertainty of ±57%. Usually, by employing these correction procedures, the corrected lignin molecular weight determined in the same solvent has an uncertainty of ±6% or less.[2] Table IV also indicates that whereas the $\bar{M}_w$ and $\bar{M}_{wfpa}$ differ by 1.43–5.04, $\bar{M}_{wf}$ and $\bar{M}_{wfpa}$ differ by a factor of only 1.01–1.50, depending upon the solvent used. Therefore, the effect of fluorescence accounts for most of the correction to the molecular weight of lignin.

CONCLUSION

In the present study, the optical effects of fluorescence, anisotropy, and absorption of lignin solutions were investigated and corrections for these effects on the measurement of weight-averaged molecular weight of kraft lignin were made. Kraft lignin dissolved in an approximately isotropic solvent 0.1*N* NaOH is essentially isotropic. Even though the lignin dissolved in DMF or pyridine exhibits anisotropic effects that must be corrected for to determine the molecular weight of lignin, the anisotropic effect exhibited by these solutions is contributed mainly by the anisotropic effects of the solvent itself rather than by the lignin. The fluorescence effect is the main source of error in the determination of the molecular weight of lignin if no correction is made. The fluorescence of lignin dissolved in 0.1*N* NaOH accounts for about 30% of the observed Rayleigh factor, and fluorescence contributes about 40–60% and 27–52%, respectively, to the observed Rayleigh factor for lignin dissolved in DMF or pyridine. Corrections for anisotropy and absorption effects, especially the latter, change the second virial coefficient substantially, but affect molecular weight determined for lignin much less than does fluorescence.

The present study shows that the optical effects of the lignin solution may result in large errors on the lignin molecular weight determined by LALLS if no correction is made. Hence, we have proposed a correction procedure. Following this procedure, the corrected molecular weight of lignin determined in three different solvents has an error range of only about ±10%, whereas the apparent molecular weights of the lignin determined in the same solvents without any correction for optical effects differ by ±57%.

The authors gratefully acknowledge the stimulating discussions with Professor Ioannis A. Bitsanis of the Chemical Engineering Department and the fruitful suggestions from Professor Andrew W. Cumming of the Physics Department at the University of Florida. The financial support from the U.S. Department of Energy is also acknowledged.

REFERENCES

1. F. J. Kolpak, D. J. Cietek, W. Fookes, and J. J. Cael, *J. Appl. Polym. Sci. Appl. Polym. Symp.* **37,** 491 (1983).
2. S. G. Wolfgang, D. J. Dong, and A. L. Fricke, in *Material Interaction Relevant to the Pulp Paper and Wood Industries,* D. F. Caulfield et al. Ed., MRS Symposium Proceedings, Vol. 197, 1990, p. 21.
3. W. J. Connors, S. Sarkanen, and J. L. McCarthy, *Holzforschung,* **34,** 80 (1980).
4. J. G. McNaughton, W. Q. Yean, and D. A. I. Goring, *TAPPI,* **50**(11), 548 (1967).
5. O. Faix, W. Lange, and E. C. Salud, *Holzforschung,* **35,** 3 (1981).
6. A. L. Fricke, *Physical Properties of Kraft Liquor (Summary Report—Phases 1 and 2),* DOE Report, #DOE/CE/40606-T5(DE88002991), 1987, Chap. 6.
7. W. I. Kaye and A. J. Havlik, *Appl. Opt.* **12**(3), 541 (1973).
8. W. I. Kaye, A. J. Havlik, and J. B. McDaniel, *Polym. Lett.,* **9,** 695 (1971).

9. A. J. Havlik and W. I. Kaye, *Measurement of Scattered Laser Light at Small Angles from Macromolecules in Solution,* Rayleigh Symposium, ACS, Washington, DC, Sept. 1971.
10. J. Marton and T. Marton, *TAPPI,* **47**(8), 471 (1964).
11. H. G. Arlt, Jr. and C. Schuerch, *TAPPI,* **41**(9), 481 (1958).
12. P. R. Gupta and D. A. I. Goring, *Can. J. Chem.,* **38,** 270 (1960).
13. P. R. Gupta and D. A. I. Goring, *Can. J. Chem.,* **38,** 248 (1960).
14. A. L. Fricke, unpublished.
15. T. M. Garver, Jr. and S. Sarkason, in *Renewable-Resource Material: New Polymer Source,* C. E. Carraher, Jr. and L. H. Sperling, Eds., Plenum, New York, 1986, p. 287.
16. P. J. Flory, *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, NY, 1953.
17. M. Kerker, *The Light Scattering and Other Electromagnetic Radiation,* Academic Press, New York, 1969.
18. K. A. Stacey, *Light-Scattering in Physical Chemistry,* Butterworths, London, 1956.
19. K. Forss, O. Schott, and B. Stenlund, *Paperi ja Puu,* **8,** 525 (1967).
20. F. Pla, P. Froment, R. Capitini, and M. Tistchenko, *Cellulose Chem. Technol.,* **11,** 711 (1977).
21. H.-K. Kim, PhD Thesis, University of Maine, 1985.
22. D. J. Dong and A. L. Fricke, to appear.
23. W. Kaye and J. B. McDaniel, *Appl. Opt.,* **13**(8), 1934 (1974).
24. W. Kaye, *Anal. Chem.,* **45**(2), 221A (1973).
25. K. Lundquist, I. Egyed, B. Josefsson, and G. Nyquist, *Cellulose Chem. Technol.,* **15,** 669 (1981).
26. K. Lundquist, B. Josefsson, and G. Nyquist, *Holzforschung,* **32**(1), 27 (1978).
27. B. A. Brice, G. C. Nutting, and M. Halwer, *J. Am. Chem. Soc.,* **75,** 824 (1953).
28. J. L. Lauer, *J. Opt. Soc. Am.,* **41,** 482 (1951).
29. H. Utiyama and M. Kurata, *Bull. Inst. Chem. Res. Kyoto Univ.,* **42,** 128 (1964).
30. LDC Analytical, *Measurement of Molecular Weight by Low Angle Light Scattering Methods,* Application Note LS1, P.O. Box 10235, Riviera Beach, FL 33404.
31. A. A. Zamam, D.-J. Dong, and A. L. Fricke, *Kraft Pulping of Slash Pine,* AICHE 1991 Forest Products Symposium Proceedings, D. W. Bousfield, Ed., Nov. 1991, pp. 49–57.
32. B. Mahn, private communication, LDC Analytical, P.O. Box 10235, Riviera Beach, FL 33404.
33. M. B. Huglin, *Light Scattering from Polymer Solutions,* Academic Press, London, New York, 1972, Chap. 6.

Received October 28, 1992
Accepted March 14, 1993