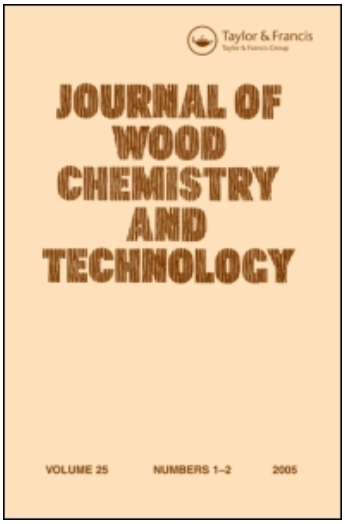

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Guro Elise Fredheim[a]; Svein Magne Braaten[b]; Bjørn E. Christensen[c]
[a] Østfold College, Sarpsborg, Norway [b] Borregaard Lignotech AS, Sarpsborg, Norway [c] Norwegian Biopolymer Laboratory (NOBIPOL), Department of Biotechnology, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

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Comparison of Molecular Weight and Molecular Weight Distributions of Softwood and Hardwood Lignosulfonates

Guro Elise Fredheim,[1] Svein Magne Braaten,[2] and Bjørn E. Christensen[3,*]

[1]Østfold College, Sarpsborg, Norway
[2]Borregaard Lignotech AS, Sarpsborg, Norway
[3]Norwegian Biopolymer Laboratory (NOBIPOL), Department of Biotechnology, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

ABSTRACT

Lignosulfonates obtained from spruce (*Picea abies*), aspen (*Populus* sp.) and two species of Eucalyptus (*E. globulus* and *E. grandis*) were characterized by aqueous size exclusion chromatography (SEC) combined with in-line multi-angle laser light scattering (MALLS). In general, the hardwood lignosulfonates were shifted to lower

*Correspondence: Prof. Bjørn E. Christensen, Norwegian Biopolymer Laboratory (NOBIPOL), Department of Biotechnology, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway; E-mail: b.christensen@chembio.ntnu.no.

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molecular weights ($M_w = 5.700$–12.000 g/mol) as compared to softwood lignosulfonates ($M_w = 36.000$–61.000 g/mol). Lignosulfonates from *E. grandis* were further fractionated to obtain fractions of different molecular weights (3.500–30.000 g/mol). The degree of sulfonation increased with decreasing M_w for the fractions as previously found for fractions of spruce lignosulfonate (Fredheim, G.; Braaten S.M.; Christensen, B.E. Molecular weight determination of lignosulfonates by size exclusion chromatography and multi-angle laser lightscattering. J. Chromatogr. **2002**, *942*, 191–199). The relationship between the intrinsic viscosity (in 0.1 M NaCl) and molecular weight was essentially the same for spruce and *E. grandis* lignosulfonate fractions, with an estimated Mark–Houwink–Sakurada (MHS) exponent of 0.36. This value, combined with the low intrinsic viscosities, confirms that lignosulfonates are compact structures in aqueous solution. Based on the SEC–MALLS results a SEC-method using a UV-detector (SEC–UV) was developed, where lignosulfonate fractions were used as broad molecular weight calibration standards.

Key Words: Lignosulfonate; Hardwood; Softwood; Light scattering; Molecular weight; Molecular weight distribution.

INTRODUCTION

The heterogeneity of lignin is well recognized for numerous plants of different botanical sections. In normal softwood lignin the structural elements are derived principally from coniferyl alcohol (more than 95%), with the remainder consisting mainly of *p*-coumaryl alcohol-type units. Normal hardwood lignins are comprised of coniferyl alcohol- and sinapyl alcohol units in varying ratios, and the methoxyl content per phenylpropanoid unit typically is in the range 1.2–1.5.[2] Aryl ether linkages predominantly join the monomers in softwood lignin, but several types of more resistant C–C bonds are also present.[3,4]

Lignosulfonates are polyelectrolytes derived from lignins during chemical pulping (sulfite process), where the lignins are fragmented and sulfonated, and thereby become water-soluble. The rate of delignification is higher for hardwood as compared to softwood, and is attributed to lower content of lignin and also the presence of syringylpropane units in hardwood.[5–7] Commercial lignosulfonates are known to have broad molecular weight distributions,[1,8] and the degree of sulfonation varies from 0.4 to 0.7 sulfonate groups per phenylpropane residue.[1,9] For lignosulfonate fractions from softwood weight average molecular weights

ranging from 5.000 to 400.000 g/mol have been measured.[1,10,11] It has been reported that the weight average molecular weight is lower for hardwood lignosulfonates than softwood lignosulfonates,[12,13] but no molecular weight values are available.

Determination of absolute molecular weight of lignosulfonates by gel filtration and SEC (HPLC) have been restricted by the lack of commercial absolute molecular weight standards, and calibration has been performed with polymers like poly(styrene sulfonate) (PSS),[14,15] pullulans[16] or proteins.[17] Lewis et al.[11,18] and Buchholz et al.,[9] introduced lignosulfonate fractions with molecular weights determined independently by analytical ultracentrifuge for calibration. A major improvement in the field of molecular weight determination is the on-line combination of SEC and light scattering. In light scattering the observed zero-angle ($\theta = 0$) Rayleigh factor (R_θ) is related to the weight-average molecular weight through the standard equations:

$$Kc/R_\theta = 1/M_w + 2A_2c, \tag{1}$$

$$K = 4\pi^2 n_0^2 (dn/dc)^2 N_A^{-1} \lambda_0^{-4} \tag{2}$$

dn/dc is the refractive index increment (which has to be known from independent measurements), n_0 is the refractive index of the solvent, N_A is Avogadro's number, λ_0 is the wavelength of the incident light (in vacuo), and A_2 is the second viral coefficient. For each elution slice (i) in SEC the concentration (c_i) is obtained from a concentration sensitive detector, usually a refractive index detector or UV detector, and R_0 is obtained from the MALLS (after extrapolation to zero angle). $M_{w,i}$ is then calculated according to equation 1. A_2 must be known from independent (batch) light scattering measurements, unless the sample concentration is kept so low that $A_2c \ll 1/M_w$.

In a previous article a size exclusion chromatography and multi-angle laser light scattering method (SEC–MALLS) for determination of the absolute molecular weights (M_n, M_w, M_z) and molecular weight distribution was developed, and the method was further applied to softwood (spruce) lignosulfonate fractions.[1] In the present article the SEC–MALLS method is used to characterize eight different lignosulfonate samples with different botanical origin and process conditions. A hardwood lignosulfonate sample from *E. grandis* is further fractionated into fractions with narrower molecular weight distributions and varying degrees of sulfonation, and each fraction is studied to investigate possible heterogeneities in the sample. Since SEC–MALLS is not always available in some laboratories a simpler SEC–UV method (calibrating with lignosulfonate standards) is evaluated.

MATERIALS AND METHODS

Materials

Eight industrial lignosulfonate samples (assigned LS1-LS8) produced by the sulfite process were obtained from Borregaard LignoTech, Norway. The wood type and the process of the eight samples are presented in Table 1. Polydisperse poly(styrene sulfonate) was obtained from Polysciences. Six lignosulfonate fractions (F-40–F-70, prepared from LS1) that had been characterized earlier[1] were included in this study.

Size Exclusion Chromatography–Multi Angle Laser Light Scattering (SEC–MALLS)

SEC–MALLS was performed as described earlier.[1] The instrument set-up consisted of a SEC-column (Jordi Glucose–DVB, 10^4 Å pore size, 500×10 mm, 60°C) combined with a DAWN-F MALLS detector followed by a RI detector (Shimadzu RID-10A). Data acquisition and

Table 1. Wood type, cation, and process for eight lignosulfonate samples.

Sample	Wood type	Cation	Process
LS1	Spruce	Na	–Ion exchanged –Ultrafiltered
LS2	Spruce	Na	–Ion exchanged –Filtered
LS3	Spruce	Na	–Ion exchanged –Ultrafiltered –pH adjusted to 12–13 –Heat treated
LS4	Spruce	Na	–From filtered black liquor –Ultrafiltered –Desulfonated –Oxidized
LS5	80% Spruce 20% Birch	Na	–Ion exchanged –Centrifugated
LS6	Aspen	Ca	–No treatment
LS7	*E. globulus*	Na	–Ion exchanged –pH adjusted to 9–10
LS8	*E. grandis*	Ca	–Heat treated

molecular weight calculations were performed using the ASTRA software, Version 4.70.07 (Wyatt Technologies). The mobile phase used was a phosphate/DMSO/SDS buffer, pH 10.5.

Fractionation of Lignosulfonates from *E. grandis*

Lignosulfonate from *E. grandis* (LS8) was fractionated into 16 fractions according to their solubility in ethanol/water.[1,19]

Sulfur-Analysis

The sulphur analyses were performed on a NCS element analyser (Thermo Quest) as previously described.[1]

Intrinsic Viscosity (Batch Measurements)

Measurements were performed at 20.0°C in an Ubbelohde capillary viscometer (Schott–Geräte capillaries nos. 53610/I and 53101/0a) equipped with an AVS 310 control unit. The solvent (0.1 NaCl) flow--through times were 100.1 s and 200.2 s for the two capillaries, respectively.

Size Exclusion Chromatography–UV Detection (SEC–UV)

In an alternative series of molecular weight determinations the samples (LS1–LS8) were analyzed with the same SEC-column and eluent using an UV-detector only. Data acquisition and analysis was performed with the Millennium software (Waters). The column was calibrated (broad standard, linear calibration method) with four softwood lignosulfonate standards[1] with known number average (M_n) and weight average (M_w) molecular weights (determined by SEC–MALLS).

RESULTS AND DISCUSSION

Sample Characteristics

Eight lignosulfonate samples are presented in Table 1. LS1 to LS4 are lignosulfonates from spruce. They all come from the same mill, but have

been treated differently. LS1 has been ultrafiltered to remove low molecular weight components such as sugar and gypsum. LS3 has been adjusted to pH 12–13 and heat-treated, which give some desulfonation and a more surface active lignosulfonate. LS4 is made from vanillin black liquor (the waste liquor after the vanillin process), and has been desulfonated and oxidized. LS5 consist of a mixture of 80% spruce and 20% birch. LS6 to LS8 are lignosulfonates from hardwood. LS6 is a sample from aspen and LS7 and LS8 are from *E. globulus* and *E. grandis*, respectively. All samples except LS6 and LS8 have been ion exchanged from Ca- to Na-lignosulfonate.

The degree of sulfonation of each lignosulfonate sample was measured on the basis of C- and S-analyses. The results are reported in Table 2 as the number of sulfonate groups per C_9 unit. The degree of sulfonation was calculated assuming 95% coniferyl alcohol ($C_{9.95}$) for softwood lignosulfonates, and 50% coniferyl and 50% sinapyl alcohol ($C_{10.5}$) for hardwood lignosulfonates. Possible inorganic sulfur and organic carbon from sugars were neglected in the calculations, and the different isolation procedures will therefore have effect on these sulfonation results. For five fractions of *E. grandis* lignosulfonate (the fractionation is described below) the degree of sulfonation was found to decrease with decreasing solubility in ethanol and increasing molecular weight (Table 3). Similar results have been obtained for fractions of spruce lignosulfonate.[1]

Table 2. Molecular weight averages (from SEC–MALLS and SEC–UV) and degrees of sulfonation obtained for eight lignosulfonate samples (LS1–LS8).

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_w/M_n	M_w[a] (g/mol)	$SO_3/C_{9.95-10.5}$[b]
LS1	5.000	61.000		12.3	57.000	0.52
LS2	3.200	36.000	233.000	11.2	37.000	0.59
LS3	5.100	41.000	178.000	8.2	35.000	0.53
LS4		4.400			6.100	0.20
LS5	4.300	36.000	173.000	8.8	36.000	0.52
LS6	2.200	12.000		5.3	11.000	0.54
LS7	2.200	6.300	15.000	3.0	7.200	0.54
LS8	1.900	5.700	14.000	3.0	7.500	0.46

[a]Determined with SEC–UV, calibrated with lignosulfonate standards from LS1.
[b]Calculated for $C_{9.95}$ for LS1–LS5 and $C_{10.5}$ for LS6–LS8.

Table 3. (dn/dc) Values, molecular weight averages (from SEC–MALLS), degrees of sulfonation and intrinsic viscosities [η] for fractions of LS8 (hardwood) and LS1 (softwood).

Fraction	dn/dc (mL/g)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	(η) (0.1 M NaCl, 20°C) (mL/g)	$SO_3/C_{10.5}$
LS8						
F-80	0.174		3.500			0.74
F-67.5			5.100			0.70
F-65			5.600		2.6	
F-62.5			6.400		3.3	
F-57.5			12.000		3.8	
F-55		9.600	13.000	1.4		0.59
F-45	0.188	5.700	17.000	3.0		0.48
F-30		11.000	30.000	2.7		0.45
LS1						$SO_3/C_{9.95}$[a]
F-70			4.600[a]	1.5[a]	1.8	0.64
F-60			8.000[a]	1.3[a]	3.0	0.53
F-55			15.000[a]	1.5[a]	3.8	0.49
F-50			34.000[a]	1.9[a]	5.2	0.44
F-45			68.000[a]	2.3[a]	6.6	0.41
F-40			398.000[a]	3.5[a]	12.1	0.39

[a]Data taken from Fredheim et al. (2001).

SEC–MALLS

Figure 1(a) shows the elution profiles obtained for the five softwood lignosulfonates. By comparing LS1 and LS2, which differ only in an ultrafiltration step during production, a reduction in the low molecular weight area is clearly seen for LS1. LS2, LS3, and LS5 have almost the same broad elution profiles, reflecting considerable polydispersity. Sample LS4 has a more narrow and symmetrical elution profile, which is shifted towards higher elution volumes, indicating both lower molecular weight and lower polydispersity than the other samples. This sample has been exposed to harsh processing conditions, and a reduction in molecular weight was therefore expected.

Figure 1(b) shows the elution profiles for the three hardwood lignosulfonates. The elution profiles are all clearly shifted towards higher elution volumes as compared to the samples derived from softwoods, suggesting that the average molecular weight is lower. In these cases distinct low molecular weight molecules appear as individual peaks between

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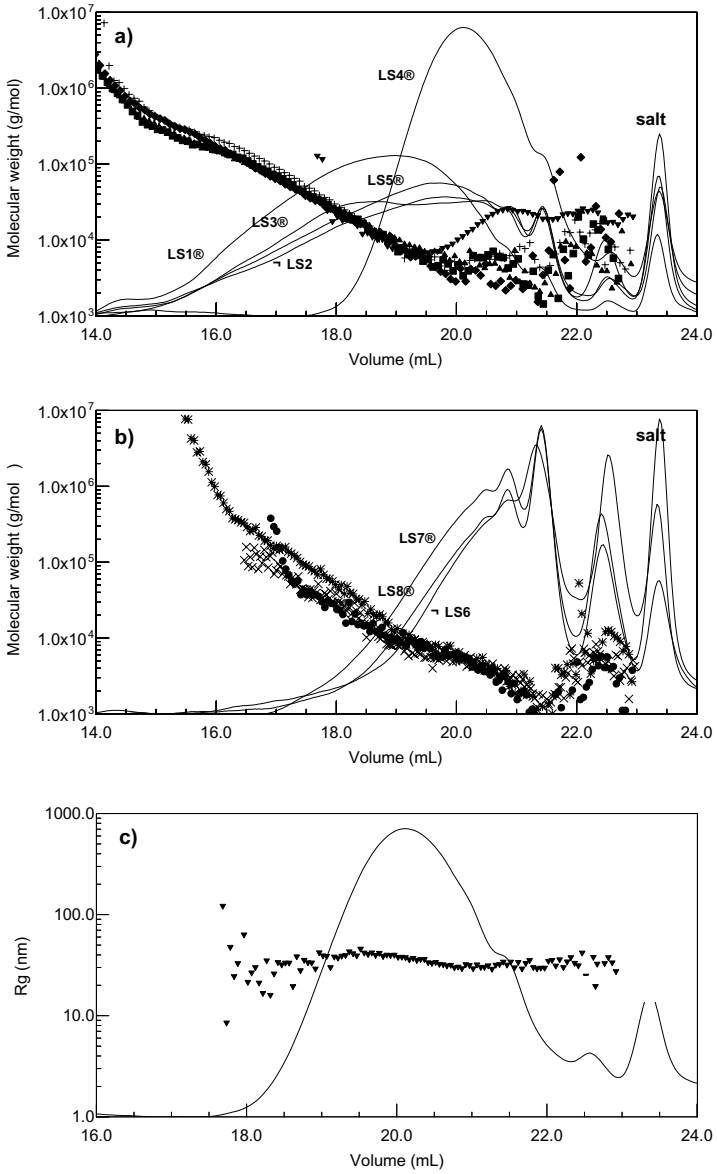

Figure 1. (a) Calibration plots and elution curves for softwood lignosulfonates: LS1 (◆), LS2 (■), LS3 (+), LS4 (▼), and LS5 (▲); (b) Calibration plots and elution curves for hardwood lignosulfonates: LS6 (∗), LS7 (●), and LS8 (×); (c) R_G vs. volume for LS4.

20.5 to 22.0 mL. The calculated plots of log M_w vs. elution volume (hereafter termed calibration curves) are included in Fig. 1(a) and 1(b). We obtain basically the same calibration curve for all the samples except LS4. Provided that non-SEC interactions do not influence the elution behavior these data suggest that both softwood and hardwood lignosulfonates belong to a single polymer family with the same basic conformation, differing primarily in molecular weight.

For LS4 a normal calibration curve was obtained at elution volume below 19.5 mL, whereafter the calculated molecular weight apparently increased with increasing elution volume (Fig. 1(a)). This sample displayed a significant angular dependence of the scattered light (or R_θ). Such dependence is otherwise not observed in lignosulfonates due to their normally small physical dimensions ($R_G < \lambda/20$). For LS4 a radius of gyration of 30–40 nm was calculated across the peak (Fig. 1(c)), almost independent of the molecular weight. We attribute this behavior to the presence of particulate material, which is retained on the column by non-SEC mechanisms.

In Fig. 2 the calculated differential molecular weight distributions for all samples except LS4 are presented. These curves are calculated on the basis of a first order polynomial fit of log M vs. elution volume combined with the concentration data obtained from the RI-detector. The data in Fig. 2 clearly illustrate the high molecular weight and the broad distributions of the softwood lignosulfonates (LS1–LS5) whereas the hardwood lignosulfonates (LS6–LS8) appear to have lower molecular weight averages and more narrow distributions.

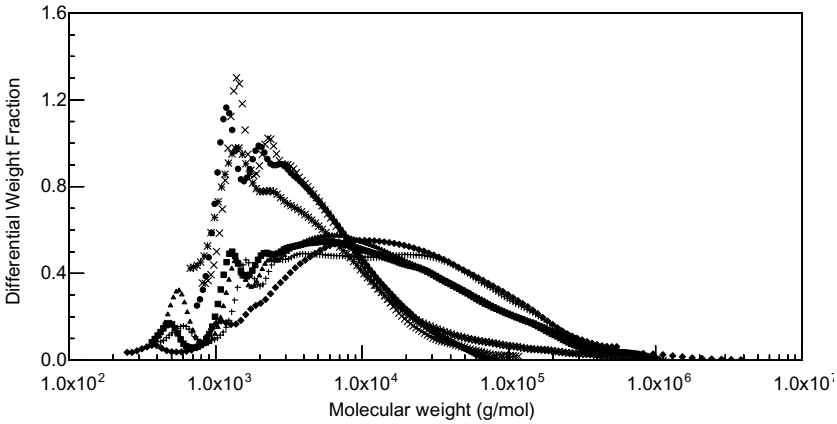

Figure 2. Calculated differential molecular weight distributions: LS1 (◆), LS2 (■), LS3 (+), LS5 (▲), LS6 (∗), LS7 (●), and LS8 (×).

The calculated weight and number average molecular weights (M_w and M_n) and the corresponding polydispersities (M_w/M_n) are summarized in Table 2. In agreement with earlier publications we find the weight average molecular weight of lignosulfonates to be in the range 5.000–60.000 g/mol, and the polydispersity to be high.[1] The softwood lignosulfonate samples (LS1–LS5) have relatively high weight average molecular weights, ranging from 36.000 g/mol to 61.000 g/mol. For LS4 the low M_w (4.400 g/mol) may be attributed to the harsh processing conditions. The hardwood lignosulfonates (LS6–LS8) have generally much lower weight average molecular weights, ranging from 5.700 g/mol to 12.000 g/mol. The estimated polydispersity varies between 3 and 12. In order to obtain correct estimates of the number average molecular weight (M_n) and the polydispersity index (M_w/M_n) it is necessary that a calibration curve be correctly assigned across the entire distribution. For all the samples (except LS4 and LS6) a linear fit was selected. For LS4 a linear fit was assigned below 19.5 mL and extrapolated to cover the entire peak. In order to facilitate the processing of the non-linear calibration curve of LS6 the chromatographic peak was first splitted into two separate regions (below and above 19.3 mL, respectively). Each region was then processed independently by fitting the log M vs. V data to a first order polynom, and a combined molecular weight was finally calculated.

Fractionation of Lignosulfonate from *E. grandis*

The lignosulfonate from *E. grandis* (LS8) was separated into fractions according to their solubilities in ethanol/water.[1,19] The fractions were termed F-90, F-70 etc., according to ethanol concentration at which they eluted from the cellulose column. Two fractions (F-80 and F-45) were selected for analysis of the specific refractive index increment (dn/dc), which is required in the analysis of light scattering data, and which has to be known from independent measurements. Apparently, no such values have so far been determined for hardwood lignosulfonates. The results (0.174 mL/g for F-80 and 0.188 mL/g for F-45) are slightly below those found earlier for softwood lignosulfonates in the same molecular weight range in the same mobile phase. The observed decrease in dn/dc with increasing degree of sulfonation and decrease in molecular weight (Table 3) agrees well with similar observations for softwood samples.[1]

Fraction F-30 was studied by conventional (static) light scattering to obtain M_w and the second viral coefficient A_2, since the latter is

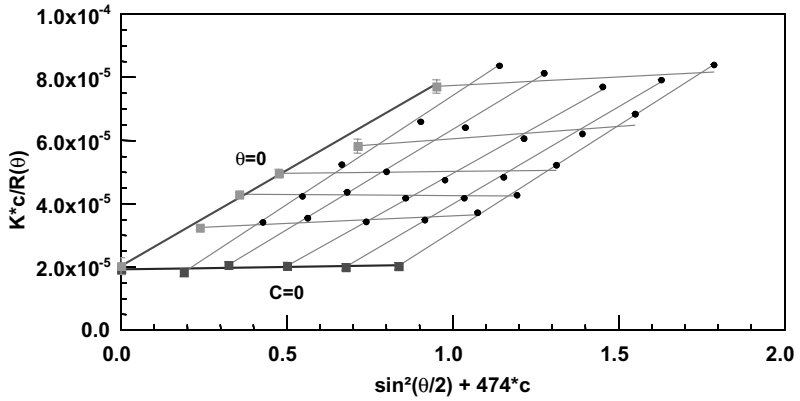

Figure 3. Zimm plot for fraction F-30 from hardwood lignosulfonate (LS8).

needed in the processing of SEC–MALLS data. The result is presented as a conventional Zimm-plot in Fig. 3. A M_w of 28 000 g/mol and an A_2 value of 2.6×10^{-2} mL mol/g^2 were obtained with the standard SEC mobile phase (phosphate/SDS/DMSO buffer) as solvent. The M_w value agrees well with the value obtained by SEC–MALLS (Table 3). The very high A_2 value found here reflects a highly charged, low molecular weight polyelectrolyte at low ionic strength. Since the calculated molecular weights depend on A_2 according to the Eq. (1), a high A_2 value will give a significant contribution to the calculated molecular weight, especially at such high concentrations which were used here. To minimize this effect, it is important to keep the injected amount to a minimum. This will again be in conflict with the demand to inject enough sample to get a good light scattering signal for the low molecular weight molecules. When A_2 was set to zero in the calculation of weight average molecular weight for fraction F-55 a 7% reduction in molecular weight was observed.

Eight selected fractions of LS8 (F-80, F-67.5, F-55, F-45, and F-30) were analyzed by SEC–MALLS. The elution profiles and the calibration curves of F-67.5, F-55, and F-45 are presented in Fig. 4. The calculated average molecular weights and the polydispersities for the fractions are presented in Table 3. The weight average molecular weight varied from 3.500 g/mol to 30.000 g/mol. The calculated polydispersities were not much reduced compared to the unfractionated sample, indicating that the solubility in ethanol is not very selective for differences in molecular weight, but rather the degree of sulfonation, in accordance with the data in Table 3.

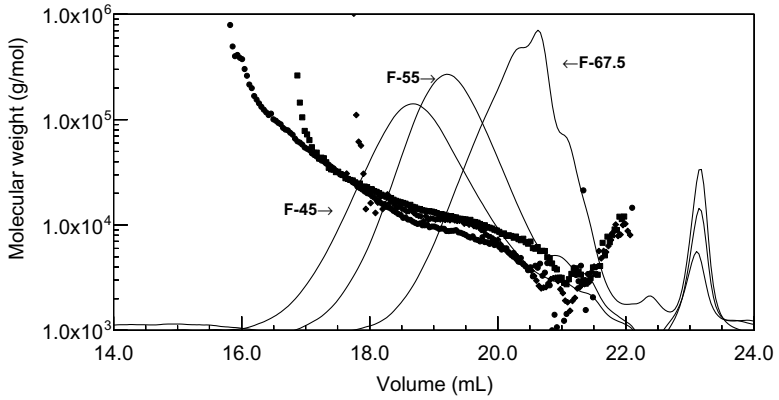

Figure 4. Calibration plots and elution curves for fraction F-45 (●), F-55 (■), and F-67.5 (◆) from hardwood lignosulfonate (LS8).

The DS–M_w Relationship

Figure 5 shows the experimentally obtained values of DS plotted (double logarithmic) as a function of M_w for both spruce and *E. grandis* lignosulfonate fractions. Assuming as a first approximation that the degree of sulfonation per particle (DS_p) is proportional to the available surface area (A) of spherical particles, it follows, since $A = 4\pi R^2$ and $DS_p \propto DS(M$ (assuming a constant specific volume), that $DS \propto M^{-1/3}$. The data in Fig. 5 clearly deviates from that predicted from this simple model (predicted slope of -0.33). For hardwood one obtains $DS \propto M^{-0.24}$, but the value level off for higher molecular weight softwood ($DS \propto M^{-0.12}$). The exponent is somewhat lower than that which may be calculated on the basis of data reported by Buchholz et al. ($DS \propto M^{-18}$) for softwood.[9] These results, and the fact that DS is as high as 0.4–0.6 sulfonate groups per monomer suggests that sulfonate groups may be found also in the interior of each particle.

The [η]–M_w Relationship for Lignosulfonate Fractions

The fractions obtained from *E. grandis* lignosulfonate as well as those obtained earlier for spruce lignosulfonate[1] were used to analyze the relationship between the intrinsic viscosity [η] (in 0.1 M NaCl) and

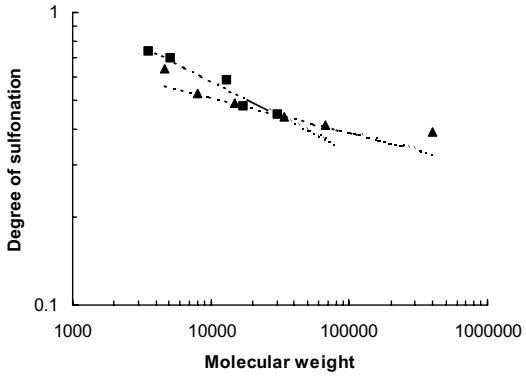

Figure 5. Double logarithmic plot of degree of sulfonation (DS) as a function of M_w for fractions of LS1 (▲) and LS8 (■).

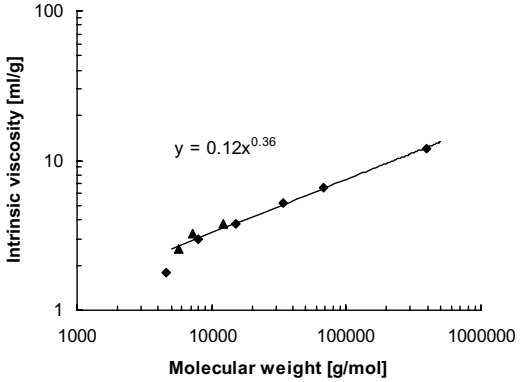

Figure 6. Double logarithmic plot of intrinsic viscosity [η] vs. molecular weight (M_w) for fractions of LS1 (◆) and LS8 (▲).

the molecular weight. The [η] was determined by conventional capillary viscometry at 20°C. The data are included in Table 3, and are presented in Fig. 6 (double logarithmic plot). Both the hardwood and the softwood samples give data which fall on a single line. The linear part of the curve corresponds to a Mark–Houwink–Sakurada (Eq. (4)) exponent of $a = 0.36$, which is close to the value of 0.32 reported by Yean et al.[20] This behavior corresponds to a shape between that of Einstein spheres for which a equals 0 and that of non-free draining coils in a poor or theta solvent where $a = 0.5$. The compactness of the molecules is further corroborated by the low intrinsic viscosities (1.8–12.1 mL/g).

Comparison of SEC–MALLS Results for Lignosulfonates and PSS

PSS have been commonly used in SEC as molecular weight calibration standards.[14,15] In the case of lignosulfonates this practise is questionable due to the obvious differences in chain flexibilities between PSS and lignosulfonate. This could be clearly demonstrated by comparing PSS and lignosulfonate using SEC–MALLS. In Fig. 7, the SEC–MALLS results of softwood lignosulfonate sample from spruce (LS1) and fraction F-45 of the hardwood lignosulfonate of *E. grandis* (LS8) are compared to a poly(styrene sulfonate) (PSS) sample. According to the universal calibration principle,[21] which operates in the absence of non-SEC phenomena, the product between the molecular weight M and the intrinsic viscosity $[\eta]$ is a unique function of the elution volume (V):

$$\log(M[\eta]) = AV + B \tag{3}$$

Here A and B are constants for a particular chromatographic system. The intrinsic viscosity is again related to the molecular weight through the Mark–Houvink–Sakurada equation:

$$[\eta] = KM^a \tag{4}$$

Here, the factor K and the exponent a are constants for a given polymer. By combining the two equations one obtains the following equation, which corresponds to the calibration curve:

$$\log M = \left(\frac{A}{a+1}\right)V + \left(\frac{1}{a+1}\right)(B - \log K) \tag{5}$$

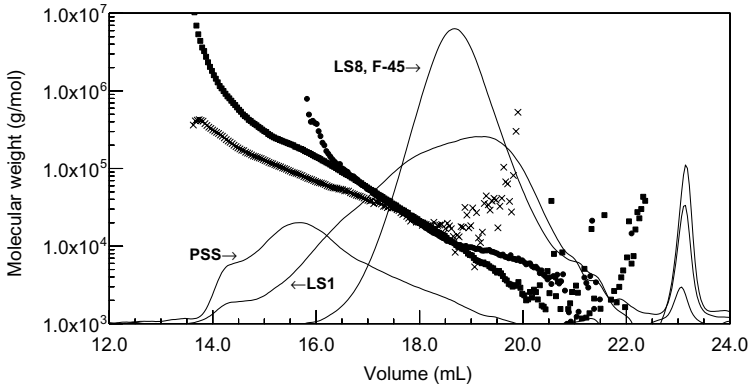

Figure 7. Calibration plots of fraction F-45 from LS8 (●), LS1 (■), and PSS (×).

Thus, the slope of the calibration curve depends on the exponent a. As shown in Fig. 6 $a = 0.36$ for lignosulfonates, whereas for PSS (a randomly coiled polymer) $a = 0.815$.[9] Hence, the higher slope of lignosulfonate as compared to PSS (Fig. 7) may be attributed to a more compact conformation (lower MHS exponent) of the former. These results clearly demonstrate the pitfalls when using PSS as SEC standards without compensating for different chain shapes.

SEC–UV

The lack of general access to lignosulfonate standards has unfortunately led to a restriction in the determination of absolute molecular weight values by conventional SEC. Since we now have softwood (LS1) fractions with known molecular weight available a SEC–UV method could be developed. In SEC–UV the very stable and sensitive UV detector gives a particularly strong signal for lignosulfonates, and very low concentrations may, in contrast to SEC–MALLS, therefore be used. A prerequisite for using SEC–UV for molecular weight determinations is that the extinction coefficient of the solute is independent of the elution volume (or molecular weight). By combining a UV- and a RI-detector we found that the ratio between UV-absorbance and the refractive index (which is proportional to the concentration) was constant across the chromatographic peak, thereby confirming that the UV-detector safely can be used to monitor the lignosulfonate concentration in SEC.

Six lignosulfonate standards obtained from LS1 (spruce)[1] were analysed with SEC–UV. The elution profiles (UV absorbance) are given in Fig. 8. The four fractions (F-45, F-50, F-55, F-60) were employed as broad molecular weight standards (linear calibration method). Since the two fractions F-40 and F-70 had bimodal distributions these were excluded in the calibration process. All the lignosulfonate samples (LS1–LS8) were subsequently analyzed by SEC–UV. The elution profiles in Fig. 9 may be directly compared to the RI-profiles given in Fig. 2. Weight average molecular weights were calculated from the calibrations curve and the results are presented in Table 2. The results obtained with the SEC–UV method are approximately the same as those obtained for SEC–MALLS. If the two fractions F-40 and F-70 were included in the calibration curve less accurate molecular weights were obtained for LS1–LS8. This reflects the difficulties in the determination of molecular weight in the high and low end of the distribution.

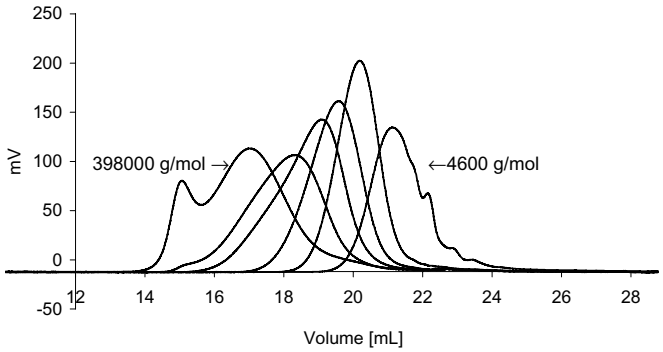

Figure 8. Elution profiles from SEC–UV of six lignosulfonate fractions of LS1 with known molecular weights: 398,000, 68,000, 34,000, 15,000, 8000, and 4600 g/mol.

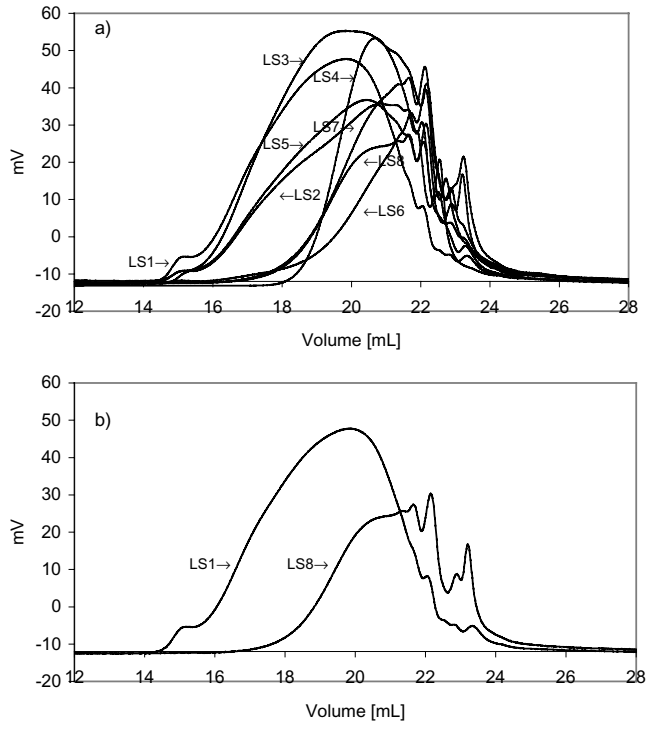

Figure 9. (a) Elution profiles of lignosulfonate samples (LS1–LS8) obtained with SEC–UV; (b) Comparison of elution profiles for LS1 and LS8.

GENERAL CONCLUSIONS

An HPLC-based SEC–MALLS method has been used for molecular weight determination for lignosulfonates. Hardwood lignosulfonates were found to have significantly lower molecular weights than softwood lignosulfonates. Nevertheless, analysis of fractions with different molecular weights demonstrated that both the intrinsic viscosity and the degree of sulfonation of lignosulfonates depend primarily on the molecular weight, and not on the wood type. The overlapping calibration curves obtained in SEC for different lignosulfonates further suggest that despite different origin and preparation, the molecules have essentially the same shape in aqueous solution. A SEC–UV method for molecular weight determination was investigated, and the method gave satisfactory results when compared to SEC–MALLS results.

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