The polyelectrolyte behavior of randomly branched lignosulfonates

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ABSTRACT: Lignosulfonates are formed by the random breaking of the "infinite" lignin network in wood, resulting in smaller sulfonated fragments. The resulting lignosulfonate molecule might be best described as a randomly branched polyelectrolyte. In this study, the scaling laws for polyelectrolyte expansion for this model are derived, as well as scaling laws for other models for lignosulfonate. The author also compares scaling laws with experimental values.

The polyelectrolyte expansion is in quantitative agreement with the randomly branched polyelectrolyte model, but it disagrees with the microgel models. The temperature dependence of the randomly branched polyelectrolyte model is in qualitative agreement with experimental results.

Application: This newly developed model provides a better description of the observed behavior of lignosulfonate molecules than the earlier microgel model.

Although the sulfite pulping process is used in relatively few pulp mills, the resulting lignosulfonate polymer has many technical applications as a dispersing or binding agent. About half a million tons a year are used as dispersants in concrete. To improve the performance of this renewable raw material, a better understanding of the structure of the lignosulfonate polymer is needed. This study shows that the randomly branched polymer model best accounts for the polyelectrolyte expansion seen in lignosulfonates.

Lignin in wood is a randomly cross-linked sheet-like polymer encrusting the cellulose fibers [1]. The native lignin is broken down during the sulfite pulping process by randomly cutting ether bonds in the lignin. The introduction of sulfonic acid groups makes the fragments water-soluble.

Studies of the resulting lignosulfonate molecules in solution led Rezanowich and Goring [2] to propose that the lignosulfonate molecules form microgels in solution. Their microgel is a compact, highly cross-linked material with charged sulfonate groups on the surface. This model has been elaborated [3–4] and used to explain adsorption phenomena [5–6] and variations in chemistry with molecular weight [7].

Although the spherical microgel model explains the solution behavior of the lignosulfonate, it does not fit with the dimensions of lignosulfonates at interfaces. In this case, a disk-like molecule was proposed instead of a sphere [8]. No attempt has been made to reconcile this disk-like molecule with the known behavior in solution.

Lignosulfonates at air-water interfaces form an 18 Å (1.8 nm)-thick layer [9]. On a carbon surface, a 1.5–2.1 nm layer has been observed [8]. A thickness of 1–3 nm has recently been found at magnesium oxide surfaces [10]. For microgels (whether spherical or disk-like) to form, the molecular weight should be above 10,000 Da, or else the structure will be too strained to form several closed loops. This is a higher molecular weight than that found for a large portion of the lignosulfonates used as dispersants.

The author recently proposed that the resulting lignosulfonate polymer can be better represented as a randomly branched polyelectrolyte [11].

THEORY

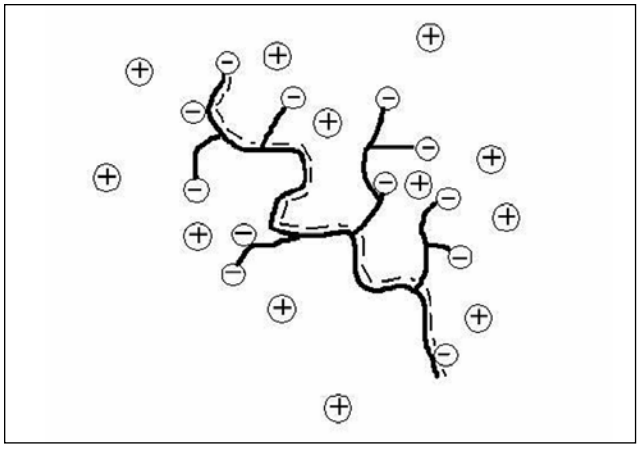
The randomly branched polyelectrolyte model

Figure 1 schematically shows the randomly branched polyelectrolyte model. It consists of a single long continuous chain, with shorter side chains on this backbone. The side chains might also be further branched, or, in rare cases, connect to the backbone again, forming closed loops. The backbone is less sulfonated than the side chains. Because the sulfonation process breaks an ether bond, it is improbable that many sulfonic acid groups could be incorporated into the backbone without breaking it down to a shorter backbone.

For this study, l represents the contour length of the longest continuous chain through the molecule [12], i.e., the backbone. This length will be a function of the molecular weight, and the author suggests that it will scale as follows: $l \sim m^a$, where $m^{0.5} < l < m^1$.

$l \sim m^1$ represents linear polymers without branches, so this will be the upper limit. The side chains will by definition be shorter than or equal to the distance between the branching point and the end of the chain. With densely packed side chains each of the maximum possible length along the backbone, the result would be $l \sim m^{0.5}$.

The hydrodynamic radius (r) of the molecule scales with the length of the backbone (l), $r \sim l^b$. For a polyelectrolyte like a lignosulfonate, b will be a function of the ionic strength (μ) of the medium, the spacing between the μ side chains, and the length of the side chains. The ionic strength ($\hat{I}$) is defined



1. Schematic view of the randomly branched polyelectrolyte model. The longest continuous backbone is indicated with the dashed line. The sulfonic acid groups (circles) are introduced where bonds in the original lignin macromolecule are broken and will reside mostly at the ends of the chains. The positively charged counter-ions form a cloud around the lignin macromolecule.

by $Ì = {}^{1}/_{2}(\Sigma c_{+} I_{+}^{2} + \Sigma c_{-} I_{-}^{2})$ [13], where c_{+} and c_{-} are the concentrations of positively and negatively charged ions respectively, I_{+} and I_{-} are the charges of the positive and negative ions, and Σ indicates the sum over all ions present; $Ì = 0$, b=1. In other words, when all the charges are unscreened and electrostatic forces dominate, the backbone will be fully stretched. When the charges from the sulfonic acid (and other) groups are screened, the polymer behaves as an uncharged polymer [13], and the backbone collapses to the minimum value for b. In this case, the result will be $r \sim m^{ab}$.

For uncharged randomly branched polymers, the following relationship between the radius and the molecular weight is given by $r \sim m^{1/df}$, where *df* is the fractal dimension [14–15]. For a three-dimensional structure such as a real polymer, values of 2.0 to 2.5 have been given for *df* [14–15]. Thus, in the case when the electrostatic interactions are screened, 0.4<ab<0.5.

POLYELECTROLYTE EXPANSION

General considerations

A polyelectrolyte is more expanded than an uncharged polymer [13]. Electrostatic repulsion between the charges will cause the polymer to expand. This expansion will depend on the total ion concentration in the solution and occurs through two different effects. The first is the dissociation-association equilibrium. As the concentration of a low-molecular-weight salt with a common ion is increased, the degree of dissociation will decrease, and thus there will be fewer charges on the polymer chain [13,16–17]. This effect has been measured for lignosulfonates [18–19] and will result in a lesser degree of expansion of the polymer. The second effect is that a higher ionic concentration in the solution will also result in a screening of the charges on the polymer chain and a lesser degree of expansion of the polymer chain. The combined effect can be described through the equation:

$$[\eta] = AR + B Ì^{-3}, \quad (1)$$

where [η] is the intrinsic viscosity, Ì is the ionic strength, and R, A, and B are empirical constants [20].

For Ì larger than 0.1 M, the difference between the observed intrinsic viscosity and the intrinsic viscosity for the fully relaxed polymer is less than 10% [21]. It has been observed that lignin behaves as an uncharged polymer in 0.25 M $CaCl_2$ solution [22]. The same behavior has also been observed in 0.75 M LiCl solution [23], which has the same ionic strength (0.75). It can thus safely be assumed that electrostatic charges are fully screened for 1 M NaCl concentration. This result has also been confirmed by the author's experiments.

The polyelectrolyte expansion is defined as $\epsilon = V_{max}/V_{min}$, where V_{max} is the maximum volume a molecule can occupy and V_{min} is the minimum volume of the molecule in the high-salt situation where all charges are screened. $V \sim r^3$, where *r* is the radius of the molecule.

Neither *V* nor *r* is directly observable. However, the intrinsic viscosity is related to the volume by:

$$[\eta]m \sim kr^3, \quad (2)$$

where *m* is the molecular mass and [η] is the intrinsic viscosity [12,24]. Combining the different proportionalities:

$$\varepsilon = V_{max}/V_{min} \sim r_{max}^{3}/r_{high\text{-}salt}^{3} \sim m[\eta]_{max}/m[\eta]_{high\text{-}salt}. \quad (3)$$

Thus the polyelectrolyte expansion is easily obtained from the experimental intrinsic viscosities.

$$[\eta]_{max}/[\eta]_{high\text{-}salt} = \varepsilon. \quad (4)$$

Polyelectrolyte expansion for a randomly branched polyelectrolyte

As before, $\varepsilon = V_{max}/V_{min} \sim r_{max}^{3}/r_{high\text{-}salt}^{3}$, by definition. $r \sim l^b$ in the relaxed state, thus $r_{high\text{-}salt} \sim l^b$, and $r \sim l^1$ in the fully stretched state. This gives $r_{max} \sim l$.

It is known that $l \sim m^a$ in both cases, as the branching will not change. The above expression can therefore be rearranged to give:

$$\varepsilon \sim r_{max}^{3}/r_{high\text{-}salt}^{3} \sim l^{3}/l^{3b} \sim m^{3a}/m^{3ab} = m^{3a(1-b)}. \quad (5)$$

In other words, the polyelectrolyte expansion will have a strong molecular weight dependence if b is sufficiently different from 1. For a linear polymer, a will be equal to 1. The expansion will then have the following molecular weight dependence:

$$\varepsilon \sim m^{3(1-b)}. \quad (6)$$

Generally, this experiment cannot distinguish between a linear model for lignosulfonates and the randomly branched

polyelectrolyte model, because they both show a molecular weight dependence.

Polyelectrolyte expansion for the microgel models

The microgel model is structured as a system with many chain segments between branching points [16]. All have approximately the same length and can expand by the same amount. The length of these chain segments is independent of the molecular weight. However, a higher-molecular-weight material will contain a greater number of chain segments that can expand. The total expansion will be proportional to the expansion for each segment and to the number of segments. The number of segments is directly proportional to the molecular weight of the material. Thus for the microgel, the expected relationship is:

$$\varepsilon \sim r_{max}^3 / r_{high\text{-}salt}^3 \sim N\lambda_{max} / N\lambda_{high\text{-}salt} = \lambda_{max} / \lambda_{high\text{-}salt}, \quad (7)$$

where N is the number of branching points in the gel, λ is the average chain length between branching points, λ_{max} is the length of the fully stretched chains, and $\lambda_{high\text{-}salt}$ is the length of the relaxed chains in the high-salt situation. The chain lengths between branching points are assumed to be independent of the molecular weight; the number of branching points then depends on the molecular weight as $N \sim m$. It is apparent that for the microgels, there should be no molecular weight dependence in the polyelectrolyte expansion, ε, irrespective of the shape of the microgel.

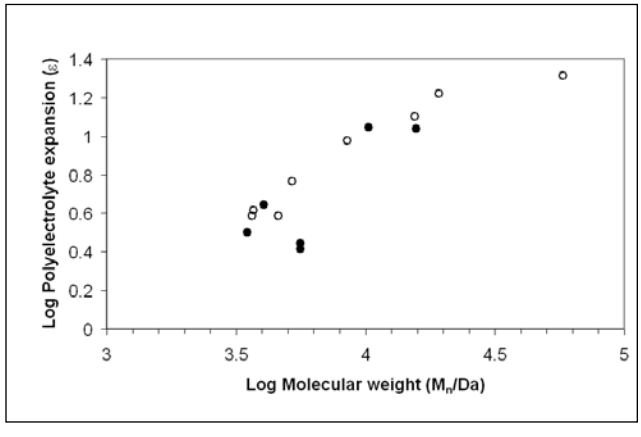
Temperature dependence of intrinsic viscosity

Electrostatic repulsion will tend to stretch the polymer chains as far as possible [13,16–17]. On the other hand, a fully stretched polymer will have little conformational freedom and therefore low entropy. The average conformation, and thus the average size, of the polyelectrolytes will therefore be obtained by minimizing the free energy:

$$\Delta G = \Delta H - T\Delta S \,. \quad (8)$$

ΔH is governed by electrostatic interactions. Except for small changes in the dielectric constant and dissociation constant, this term will be temperature-independent. In very dilute solutions, such as that used to determine intrinsic viscosity, the electrolytes will be nearly completely dissociated, and therefore changes in the dissociation constant will be unimportant. The dielectric constant of water is 82.0 at 15°C and 72.5 at 42°C. [25]

The entropy term will become more important as the temperature increases, because more conformations will become available. These conformations will be less stretched on average. The average size of the polyelectrolyte will thus decrease as the temperature increases. It should be noted that the microgel models also show this temperature dependence.



2. Polyelectrolyte expansion as a function of molecular weight. The ratio between pure water and 1M NaCl is shown as a function of molecular weight. Filled circles are data for various standard and experimental products. Open circles are recalculated data from [20] for samples with a narrow molecular weight distribution.

EXPERIMENTAL

Measurements and sample preparation

Several different lignosulfonates were dissolved in deionized water. The solutions were filtered through a 0.22 µm Millipore filter. A Schott Geräte AVS 310 automatic Ubbelohde capillary viscometer with Schott CT 52 temperature controller was used for the experimental work. The temperature was 25.00 +/-0.01°C for all the measurements, unless stated otherwise.

Runout times were measured for solutions starting at a 1% concentration and progressively decreasing the concentration to the lowest value that could be reliably measured. The cutoff point was chosen as $t_c - t_0 > 0.2$ s, which gives a 10% relative uncertainty in the measurements. The runout times for pure water were 94–164 s, while the lignosulfonate solutions varied in runout time between 95 s and 175 s. No kinematic corrections were made. The maximum error was determined to be 4% at 25°C and 8% at 42°C.

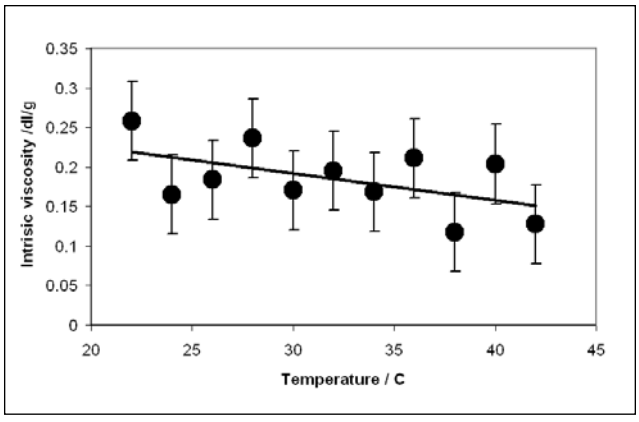
For the measurements at high salt concentrations, the lignosulfonates were dissolved in 1 M NaCl solution. The same 1 M NaCl solution was also used for dilution. For the salt-free systems, deionized water was used.

For the experiments with Al^{3+}, Ca^{2+}, and K^+ ions, the appropriate chlorides were dissolved in deionized water. Ultrazine NA was dissolved in about 100 mL of these solutions, and the same salt solution was used for dilution. For these experiments, a capillary with a runout time of 180 seconds for pure water was used. For this setup, no kinematic corrections were needed.

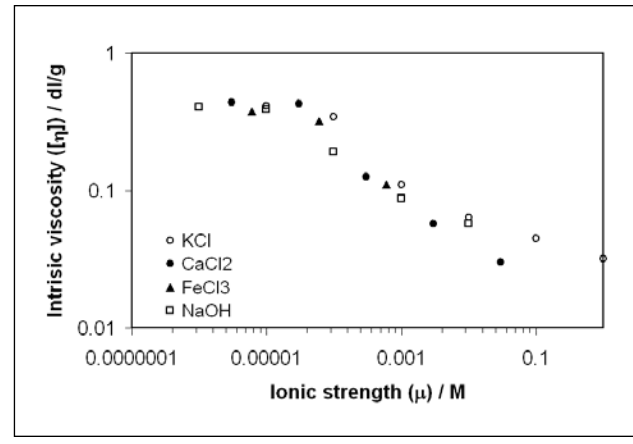
For the experiments with varying pH, NaOH in deionized water was used both as a solvent for Ultrazine NA and to dilute the solutions further. All solutions were filtered through a 0.22 µm Millipore filter before measurements were made.

Determination of intrinsic viscosity

Let $\eta_{rel} = \eta/\eta_0$, where η_{rel} is the relative viscosity, η the viscosity of the solution, and η_0 the viscosity of the solvent. The specific viscosity (η_{sp}) is defined by $\eta_{sp} = \eta_{rel}\eta - 1$. The intrinsic viscosity



3. Temperature dependence of the intrinsic viscosity in deionized water for a high-molecular-weight sodium lignosulfonate.



4. Effect of ionic strength on the intrinsic viscosity of the lignosulfonate Ultrazine NA.

$[\eta]$ is defined by $[\eta_{sp}/c]_{c=0} = [\eta]$. The density component due to dissolved lignosulfonate will not vary for these dilute solutions, so $\eta = kt$ can be used. The specific viscosity is calculated by $\{(t_c/t_0)-1\}/c$, where t_c is the runout time at concentration c and t_0 the runout time for pure water. This gives $[\eta] = [\{(t_c/t_0)-1\}/c,]_{C=0}$.

For the high-salt conditions, the intrinsic viscosity is easily available by extrapolating $(\eta/\eta_0-1)/c$ to $c = 0$. For the salt-free conditions, this extrapolation diverges. As the polymer solution is diluted and the polymer dissociates more and more, it will have more and more negatively charged groups along the polymer chain. In addition, there will be fewer ions available to screen the negative charges. This means that the polymer chain will stretch out. This stretching more than compensates for the dilution, meaning that $[\eta_{sp}/c]$ will increase as c decreases. When, or if, the fully dissociated polymer is obtained, the difference between η and η_0 is so small that it becomes impossible to measure accurately.

Fuoss and Strauss [26] found that the diverging curve for polyelectrolytes could be described by the following equation: $\eta_{sp}/c = A/(1+Bc^{0.5})+D$. Plotting c/η_{sp} versus $c^{0.5}$ should give a straight line. The intercept with $c=0$ allows the determination of $1/[\eta]$. This is not exactly true [17], but the difference is small enough to test the various models.

RESULTS AND DISCUSSION

Figure 2 compares the various models with the experimental data. Gardon and Mason [27] have given intrinsic viscosity values for various lignosulfonate fractions in 2 M NaCl, as well as curves for the reduced viscosity versus concentration for the same fractions in pure water. In this work, the Fuoss extrapolation has been used, which gives a good fit with D=0, to obtain the intrinsic viscosity from these data as well. Then values for ε were calculated for the different fractions and are shown in Fig. 2. From these data, it can be determined that $\varepsilon \sim m_n^{0.70}$. From Gardon and Mason's data in 2 M NaCl, the result a.b = 0.49 can be obtained, which is in excellent agreement with a fractal dimension *df* of 2.0 [14].

It is clear that the microgel models are in disagreement with the observations. They predict a polyelectrolyte expansion independent of molecular weight, whereas this research has found a strong molecular weight dependence. For the fractions of narrow molecular weight distribution, a scaling factor of 0.70 has been obtained. For the samples of broad molecular weight distribution, the scaling factor is almost identical.

Figure 3 shows intrinsic viscosity as a function of temperature for a high-molecular-weight lignosulfonate in pure water. Despite the scattering of the data, the predicted contraction of the molecule at higher temperatures can be clearly seen. The change in intrinsic viscosity corresponds to a 10% decrease in radius between 22°C and 42°C. Some polymers come out of solution and phase-separate as the temperature increases. However, lignosulfonates do not show any phase separation up to 100°C and remain dissolved at even higher temperatures during the sulfite cook.

Figure 4 presents data for the intrinsic viscosity of lignosulfonates in four different salts: $AlCl_3$, $CaCl_2$, KCl, and NaOH. It can be seen that all the data fall more or less on a single line. This indicates that there are no specific interactions at the very low lignosulfonate concentrations encountered here. Above an ionic strength of 0.03 M, no further contraction of the lignosulfonate molecule is observed. This shows that the 1 M NaCl solution is a good approximation of the fully screened system.

CONCLUSIONS

The molecular weight dependence of the polyelectrolyte expansion can be well accounted for with the randomly branched polyelectrolyte model, while the microgel models predict no such dependence.

In dilute solutions with pure water as the solvent, the lignosulfonate will contract as the temperature increases. **TJ**

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INSIGHTS FROM THE AUTHOR

The idea for this research arose when the author encountered some problems with atomic force microscopy measurements which did not agree with existing theories. One possibility in such a case is that maybe the theories are wrong and the experimental results correct. The current research was conducted to investigate this possibility.

Lignosulfonates are generated during the sulfite pulping process by random cutting of ether bonds in the lignin and introduction of sulfonic acid groups. The randomly branched polyelectrolyte model developed here describes lignosulfonate behavior on surfaces better than the previously developed microgel model. It also gives a better description of the polyelectrolyte expansion. The temperature dependence of the randomly branched polyelectrolyte model is also in qualitative agreement with experimental results. However, the new model also gives nearly identical results for situations already described well by the microgel theory.



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Future work will address the behavior of lignosulfonate molecules in concentrated solutions and further investigate behavior at surfaces.

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