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Intrinsic viscosity and the molecular weight of kraft lignin

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This study developed Kuhn–Mark–Houwink–Sakurada (KMHS) equations for kraft lignin, based on the absolute molecular weight characterized with low-angle laser light scattering. The KMHS exponential factors of kraft lignin were found to be 0.11, 0.13 and 0.23 in dimethylformamide (DMF) at 318.2 K, in DMF at 350.7 K and in 0.5 N sodium hydroxide at 303.2 K, respectively. Lignin molecules in solution are approximately spherical particles and slightly solvated with solvent.

(Keywords: kraft lignin; intrinsic viscosity; molecular weight)

INTRODUCTION

Lignin is a macromolecular substance that occurs naturally in close association with cellulose in plants and trees. It may be considered to be a random three-dimensional network polymer comprising phenylpropane units linked in different ways[1,2], and it functions as a cementing matrix, 'nature's glue'[3], which holds the cellulose fibres together[4,5], if one views wood as a composite material.

Although cellulose and lignin are the two most abundant natural polymers in the world and both originate from the same sources, practical applications and theoretical studies of these two polymers are enormously different. While cellulose has been a very important material with many applications and has attracted most of the attention in the development of polymer science of these materials, lignin has been studied much less and its primary use has been as a fuel in the pulp and paper industry[6].

Lignin is extracted from wood during pulping operations in the paper industry and goes to the by-product stream, black liquor. Approximately 80×10^6 tons of black liquor solids[6] are produced annually in the USA and Canada, about 40% of which is lignin. A great deal of effort has been made to develop potential non-fuel applications for lignin since the 1970s, such as lignin-based carbon fibres, lignin-based plastics, lignin-based surfactants, lignin-based elastomer-reinforcing agents, lignin-depolymerized low-molecular-weight chemicals, etc. Characterization of lignin would be of fundamental importance in these applications.

Our previous paper[7] reported studies of the optical effects of lignin solutions in the determination of the weight-average molecular weight of kraft lignin and a reliable method for determination of molecular weight has been established.

The objective of this study was to develop the Kuhn–Mark–Houwink–Sakurada (KMHS) equation and provide the KMHS constants for kraft lignin.

EXPERIMENTAL

Preparation of lignin sample

The starting material was black liquor prepared by pilot-scale experimental kraft pulping of slash pine. Detailed cooking conditions can be found elsewhere[8]. About 450 ml of black liquor at 10% total solids and a pH of about 13 was filtered through a glass-fibre filter to exclude fibril or particulate impurities and then titrated under stirring with 1.0 N sulfuric acid at a titration rate of $2.0 \pm 0.5\,\mathrm{ml\,min^{-1}}$ to a final pH of about 2.0. The subsequent slurry was centrifuged and the supernate decanted; the lignin was washed with 700 ml deionized water, centrifuged and the supernate decanted. This precipitated lignin was redissolved in 0.1 N sodium hydroxide and the solution pH was adjusted to about 13. It was then filtered through a filter paper to separate an insoluble substance. The subsequent filtrate was retitrated with 1.0 N sulfuric acid at a rate of $2.5 \pm 0.5\,\mathrm{ml\,min^{-1}}$ to a final pH of 2.0, the slurry was centrifuged and the supernate decanted. The reprecipitated lignin was washed, centrifuged and the supernate decanted with deionized water once, 0.01 N sulfuric acid twice and deionized water three more times (about 700 ml deionized water or 0.01 N sulfuric acid was used for each wash). Then, the washed lignin was freeze dried. Finally, the dried lignin was extracted with hexane to remove organic impurities and freeze dried again.

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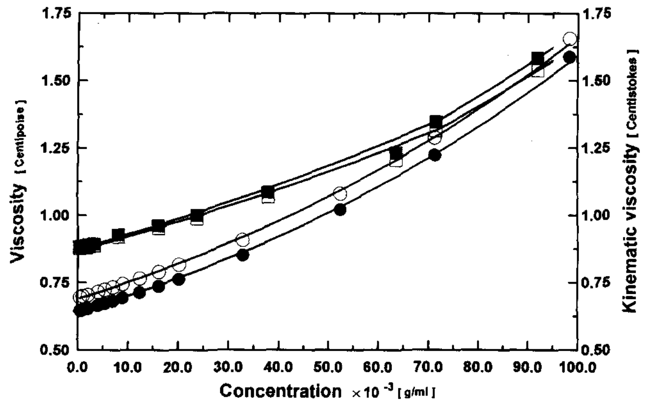

Figure 1 Viscosity of lignin solution as a function of concentration: (●) viscosity, DMF at 318.2 K; (○) kinematic viscosity, DMF at 318.2 K; (■) viscosity, 0.5 N NaOH at 303.2 K; (□) kinematic viscosity, 0.5 N NaOH at 303.2 K

Solvents and density

Lignin density was measured with an AccuPyc 1330 Pycnometer[R] (Micrometrics, Norcross, Georgia) at 303 K. Since the density of purified lignins fluctuates very little from sample to sample, an averaged value of $1.350\,\mathrm{g\,cm^{-3}}$ was used for all lignin samples in this study. Dimethylformamide (DMF) used in this study was ACS grade obtained from Fisher Scientific with a density of $0.943\,\mathrm{g\,cm^{-3}}$ at 298 K. A density increment of $\Delta\rho/\Delta T = -7.4\times10^{-4}\,\mathrm{g\,cm^{-3}\,K^{-1}}$ was used to correct the density to the temperatures at which the viscosity was measured. Densities of water ($0.99567\,\mathrm{g\,cm^{-3}}$ at 303.2 K) and pure sodium hydroxide ($2.130\,\mathrm{g\,cm^{-3}}$ at 298 K) were obtained from ref. 9. Subsequently, the density of 0.5 N sodium hydroxide was calculated to be $1.0063\,\mathrm{g\,cm^{-3}}$ at 303.2 K.

Viscosity

Kinematic viscosities of lignin solutions were measured with a Cannon No. 25 Ubbelohde capillary viscometer (Cannon Instruments Co.) immersed in a 15 gallon water bath. Temperature fluctuation was well controlled within ±0.1 K or less during measurement. The viscometer used is suitable for kinematic viscosities from 0.5 to 2.0 cSt (centistokes).

Lignin solution was made at a concentration of about $0.1\,\mathrm{g\,ml^{-1}}$. The original solution was sonicated for 2 h and allowed to stand for 24 h. Then, it was filtered through a 0.45 μm Glass Acrodisc[R] syringe filter (Gelman Sciences, Ann Arbor, Michigan) to exclude any particles in the solution. Subsequent lower concentrations were obtained by volumetric dilution in the viscometer.

The weight-average molecular weight of lignin

The weight-average molecular weight of kraft lignin was determined with low-angle laser light scattering (l.a.l.l.s.). The optical effects (fluorescence, absorption and optical anisotropy) of lignin solution were corrected, and the fully corrected molecular weight was used to develop KMHS equations for kraft lignin. The detailed l.a.l.l.s. methodology and the correction procedure have been described elsewhere[7].

RESULTS AND DISCUSSION

Figure 1 shows the dependence of solution viscosity on the lignin concentration in DMF and in 0.5 N sodium hydroxide. In a broad concentration range of 0.001 to $0.1\,\mathrm{g\,ml^{-1}}$, the viscosity of kraft lignin solution can be fitted by exponential equations. For example, the following equations were obtained for lignin ABAFX1516 in DMF at 318.2 K with a linear correlation coefficient ($\log\eta$ *versus* C) of 0.9994 or higher:

$$\log\eta = 9.1432C - 0.44806 \tag{1}$$

$$\log\nu = 8.81359C - 0.37375 \tag{2}$$

where η and ν are the viscosity in centipoise (cP) and the kinematic viscosity in centistokes (cSt), respectively, and C is the lignin concentration in $\mathrm{g\,ml^{-1}}$. Since the lignin solutions in 0.5 N sodium hydroxide have densities slightly higher than $1.0\,\mathrm{g\,cm^{-3}}$, their viscosities are slightly higher than the kinematic viscosities at the same concentration. On the other hand, a lignin solution in DMF has a density less than $1.0\,\mathrm{g\,cm^{-3}}$, and its viscosity curve is lower than the kinematic viscosity curve. In this study, viscosity (instead of kinematic viscosity) data were always used to avoid any error that might be caused by the density.

Figures 2 and *3* show the reduced viscosity of kraft lignin solution as a function of concentration. *Figure 2* indicates that, as the lignin concentration is increased from 0 to about $0.005\,\mathrm{g\,ml^{-1}}$, the reduced viscosity of lignin solution in 0.5 N sodium hydroxide increases

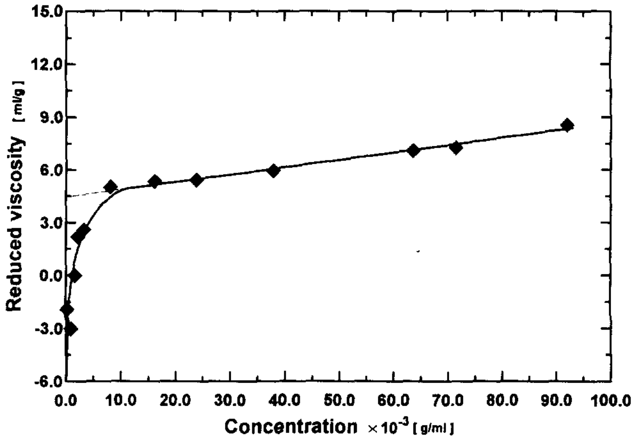

Figure 2 Reduced viscosity *versus* concentration of kraft lignin in 0.5 N sodium hydroxide at 303.2 K

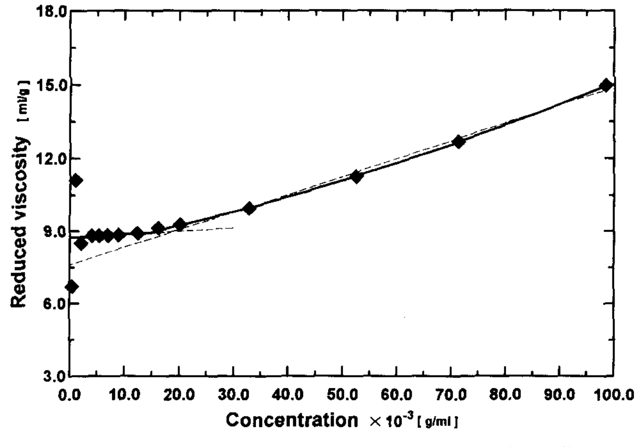

Figure 3 Reduced viscosity *versus* concentration of kraft lignin in DMF at 318.2 K

sharply, then a transition region appears from 0.005 to 0.01 g ml^{-1}. After that, a good linear relationship ($r=0.987$) between the reduced viscosity and concentration exists in the region of 0.01 to about 0.1 g ml^{-1}. Notice that, in the very low concentration region, negative values of reduced viscosity were observed owing to the unsuitability of the viscometer in this region, since very small uncertainty in the viscosity measurement can result in a substantial error in the reduced viscosity.

Figure 3 indicates that the lignin dissolved in DMF behaves differently from lignin dissolved in sodium hydroxide solution. The entire curve can be fitted by two straight lines. In the concentration region below 0.015 g ml^{-1}, the reduced viscosity increases very slowly as the concentration is increased; in the region of 0.02 to 0.1 g ml^{-1}, the data can be fitted by a straight line ($r=0.997$).

Figures 2 and *3* raise a question as to how the intrinsic viscosity should be determined. Normally, a concentration region is best chosen such that[10] the relative viscosity lies between about 1.2 and 2.0. The upper limit results from the fact that the relationship between the reduced viscosity and concentration becomes increasingly non-linear with increasing concentration. The lower limit arises from the fact that anomalies begin to appear at low concentrations. These anomalies are usually considered to be apparatus-dependent and to result from adsorption of macromolecules on the capillary wall[10]. It is obvious that, in the 0.5 N sodium hydroxide solution, the reduced viscosity data in the concentration range below 0.01 g ml^{-1} cannot be used in obtaining the intrinsic viscosity (*Figure 2*). In the solvent DMF, extrapolating the data in different concentration regions will result in two different values of intrinsic viscosity (*Figure 3*).

In this study, intrinsic viscosity was obtained by fitting the data in the concentration region of about 0.02 to 0.1 g ml^{-1}, then extrapolating the fitted line to zero concentration. Generally, there exists a good linear relationship between the reduced viscosity and lignin concentration in this region (see *Figures 4* and *5*). It has to be pointed out that the density of lignin solution depends on the concentration, owing to the density difference between the solvent and the solute lignin. In this study, we calculated the density of lignin solution at each concentration to obtain accurate results.

Figure 4 illustrates the reduced viscosity *versus* concentration plots for three lignins of different molecular weights in DMF at 318.2 K. The intrinsic viscosity of these lignins in DMF at 318.2 K can be obtained from the extrapolated intercepts at zero concentration. These curves are almost parallel and the intrinsic viscosity increases only slightly as the molecular weight of lignin increases.

Figure 5 shows the dependence of reduced viscosity of a lignin (ABAFX2122) upon the concentration measured in different solvents and at different temperatures. It indicates that the reduced viscosity and the intrinsic viscosity of lignin dissolved in 0.5 N sodium hydroxide are much lower than those for lignin dissolved in DMF at a fixed concentration. However, the intrinsic viscosity of a lignin in DMF does not decrease much as temperature is increased from 303.2 to 350.7 K.

Table 1 summarizes the intrinsic viscosity results of

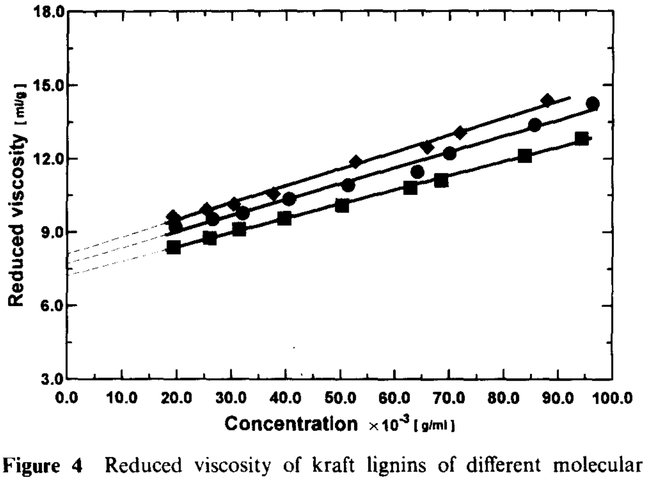

Figure 4 Reduced viscosity of kraft lignins of different molecular weights in DMF at 318.2 K: (■) $M_w=22020$; (●) $M_w=36080$; (◆) $M_w=59530$

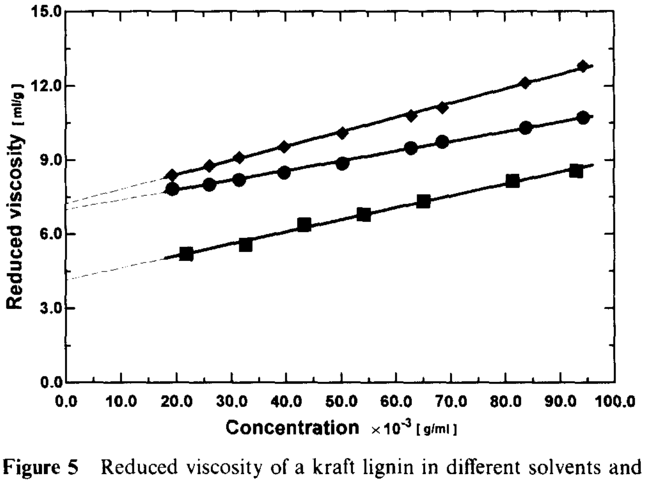

Figure 5 Reduced viscosity of a kraft lignin in different solvents and at different temperatures: (■) in 0.5 N NaOH at 303.2; (●) in DMF at 350.7 K; (◆) in DMF at 318.2 K

Table 1 Intrinsic viscosity (ml g^{-1}) of kraft lignin

		DMF 318.2 K		DMF 350.7 K		0.5 N NaOH 303.2 K	
Lignin	M_w	[η]	r	[η]	r	[η]	r
ABAFX2122	22 017	7.2324	0.999	6.9918	0.998	4.1464	0.997
ABAFX1516	28 620	7.6137	0.997	7.4808	0.991	4.3671	0.981
ABAFX2930	36 078	7.7204	0.993	7.5054	0.999	4.4432	0.986
ABAFX3940	48 442	7.9055	0.999	7.7550	0.999	4.7435	0.989
ABAFX4142	59 528	8.1191	0.996	8.1094	0.989	5.3131	0.994

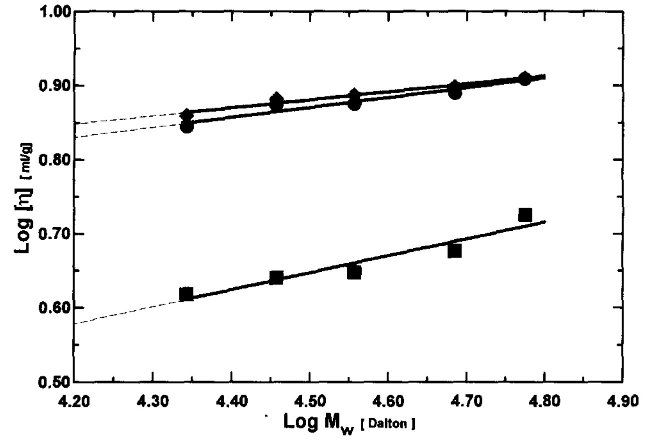

Figure 6 Kuhn–Mark–Houwink–Sakurada plots of kraft lignins in different solvents and at different temperatures: (■) in 0.5 N NaOH at 303.2 K; (●) in DMF at 350.7 K; (◆) in DMF at 318.2 K

Table 2 Kuhn–Mark–Houwink–Sakurada parameters of kraft lignin

Solvent	Temp. (K)	α	K	r
DMF	318.2	0.11	2.5100	0.979
DMF	350.7	0.13	1.8895	0.967
0.5 N NaOH	303.2	0.23	0.4165	0.953

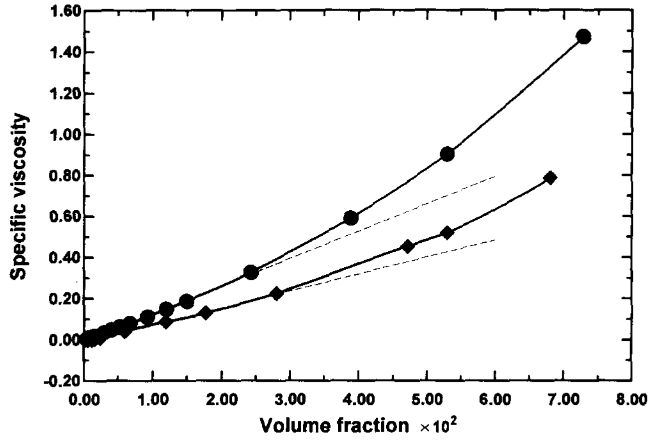

Figure 7 Specific viscosity as a function of the volume fraction of lignin in the solution: (◆) in 0.5 N NaOH at 303.2 K; (●) in DMF at 318.2 K

lignin samples measured in 0.5 N sodium hydroxide at 303.2 K, in DMF at 318.2 K and in DMF at 350.7 K, respectively. The intrinsic viscosity of lignin samples in DMF at 318.2 K varies from 7.23 to 8.12 ml g^{-1}, and that in 0.5 N sodium hydroxide ranges from 4.15 to 5.31 ml g^{-1}. Glasser and coworkers[11] recently reported an intrinsic viscosity of 8.0 ml g^{-1} for acetylated Indulin AT, a commercial lignin of kraft pulping of pine, determined in tetrahydrofuran (THF), and the intrinsic viscosity of 3.7 to 8.0 ml g^{-1} for experimental lignins. Their data were obtained by using a differential viscosity detector (d.v.) in the process of g.p.c. measurement of the molecular-weight distribution of lignin. No intrinsic viscosity data for lignin solution in 0.5 N sodium hydroxide have been reported.

Figure 6 shows the log[η] *versus* log M_w plots (the KMHS plots) for kraft lignin in different solvents and at different temperatures. With the five data points available at each condition, the linear correlation coefficients of these curves are 0.953, 0.967 and 0.979, respectively. The KMHS constants were calculated and summarized in *Table 2*.

Surprisingly, the KMHS exponential factors of kraft lignin measured in DMF are so small, 0.11 at 318.2 K and 0.13 at 350.7 K, that the molecular weight of lignin affects the reduced viscosity only slightly. These results suggest that the lignin molecules in DMF have a compact spherical structure and almost approach the limit of an Einstein sphere, a constant-density sphere[10]. In 0.5 N sodium hydroxide at 303.2 K, kraft lignin has a KMHS exponential factor of 0.23. Therefore, the hydrodynamic volume of the kraft lignin in 0.5 N sodium hydroxide is also not strongly dependent upon the molecular weight. This is in agreement with our light scattering results[7] that lignin dissolved in sodium hydroxide solution is optically isotropic and the anisotropic effect of lignin solution in DMF is mainly contributed by the anisotropic solvent rather than the lignin molecules in the solution.

In 1960, Gupta and Goring[12] reported an exponential factor of 0.32 for alkali lignins. Most recently, Glasser and colleagues[11] found that commercially available lignins and the lignins produced in pilot-scale cooking have KMHS exponential factors from 0.17 to 0.35.

In the light of very low values of the KMHS exponential factor of kraft lignin, we plotted the specific viscosity of a lignin solution with respect to the volume fraction of lignin as shown in *Figure 7*. From the curves in *Figure 7*, we obtained the initial slopes of 13.33 and 8.22 for the lignin solution in DMF at 318.2 K and for the lignin solution in 0.5 N sodium hydroxide at 303.2 K, respectively. In the case of an Einstein sphere (a constant-density, unsolvated sphere) the slope would be 2.5. With respect to an Einstein sphere, therefore, the diameter of lignin molecules in solution is increased only by 75% in DMF and 50% in 0.5 N sodium hydroxide, respectively; and the particle volume is expanded by 4.3 and 2.3 times, respectively. Based on these results, one may consider that the lignin molecules in solution are approximately spherical particles and only slightly solvated with solvent.

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