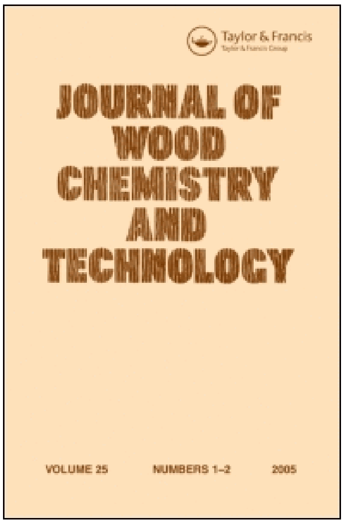

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Charge-Transfer Complexes in Kraft Lignin Part 2: Contribution to Color

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CHARGE-TRANSFER COMPLEXES IN KRAFT LIGNIN
PART 2: CONTRIBUTION TO COLOR

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Dedicated to Prof. Dr. Karl Kratzl

ABSTRACT

Chelation and removal of transition metals from the kraft lignin employed in this study did not reduce the lignin's visible absorbance. Likewise, hydrogenation of carbon-carbon double bonds in this lignin also had no effect on its visible spectrum. This indicated that extended conjugated systems were not a significant contributor to the color of this lignin. Of the structures investigated, quinones were found to be the major visible-light absorbing chromophores. Since a large component of the quinone's absorption results from their participation in charge-transfer complexes (CTC's),[1] CTC's were a significant contributor to the color of this lignin.

INTRODUCTION

In the preceding publication,[1] the existence of charge-transfer complexes (CTC's) in kraft lignin was demonstrated. This paper will

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establish the significance of the CTC's contribution to the color of kraft lignin in comparison to other colored structures which have been proposed or identified in kraft lignin. These structures included quinones, transition metal complexes, and various unsaturated structures (carbon-carbon double bonds and carbonyls), which are thought to form extended conjugated systems.

RESULTS AND DISCUSSION

Transition Metal Complexes

Various transition metals, iron being the most abundant, are found in kraft lignin. In part they originate from the original wood source, and in part they become associated with the lignin during its contact with process waters and machinery. Some metals are able to form colored complexes with phenolic and catecholic structures in the lignin.[2,3] For example, complexes of ferric ions with model lignin catechols[3] have absorption maxima between approximately 550 and 590 nm.

The contribution of metal complexes to the visible absorption spectrum of the present kraft lignin was investigated by the removal of these metals. This was accomplished by their chelation with ethylenediaminetetraacetic acid (EDTA), followed by the extraction of the metal chelates from the lignin *via* electrodialysis.

The average contents of six transition metals found in this lignin are given in Table 1. Iron was the most prevalent metal found, although its content was relatively low when compared to industrially obtained kraft lignins. Also given in Table 1 are the reduced levels of metals found after the lignin was treated with EDTA. The values shown were the lowest levels obtained for each metal, compiled from several different experimental runs.

Table 1. Metal content of kraft lignin.

	Quantity Found (ppm)	
Metal	Original Kraft Lignin[a]	EDTA Chelated Kraft Lignin[b]
Chromium	8.18 ± 1.64	3.2
Manganese	0.55 ± 0.18	< 0.002
Iron	37.67 ± 12.0	9.33
Cobalt	0.70 ± 0.64	< 0.05
Nickel	7.14 ± 1.71	2.0
Copper	8.47 ± 0.81	2.85

[a] Average of three determinations.
[b] Best values.

Spectra of the lignin before and after metal removal are shown in Fig. 1. The particular lignin shown in Fig. 1 was treated with sodium borohydride and diimide (see below) prior to the EDTA treatment. Both of these treatments had no effect on the metal content of the lignin. As is shown in Fig. 1, removal of the metals did not result in a decrease in the lignin's absorbance above 500 nm and, in fact, a slight increase at shorter wavelengths was observed. The absorbance increase at shorter wavelengths was attributed to the reoxidation of some of the borohydride reduced quinones during the lengthy electrodialysis procedure.

For comparison, an industrial kraft lignin (Indulin AT, Westvaco, S.C.) was also investigated. This lignin contained substantially higher levels of metals, as is shown in Table 2. Once again, the EDTA-electrodialysis treatment was able to significantly reduce these levels.

Visible spectra of the Indulin AT before and after the EDTA treatment are given in Fig. 2. For this lignin, removal of the metals produced a small, but clearly evident decrease in the long wavelength region of the spectrum centered at approximately 520 nm. The results obtained with the Indulin AT agreed well with the

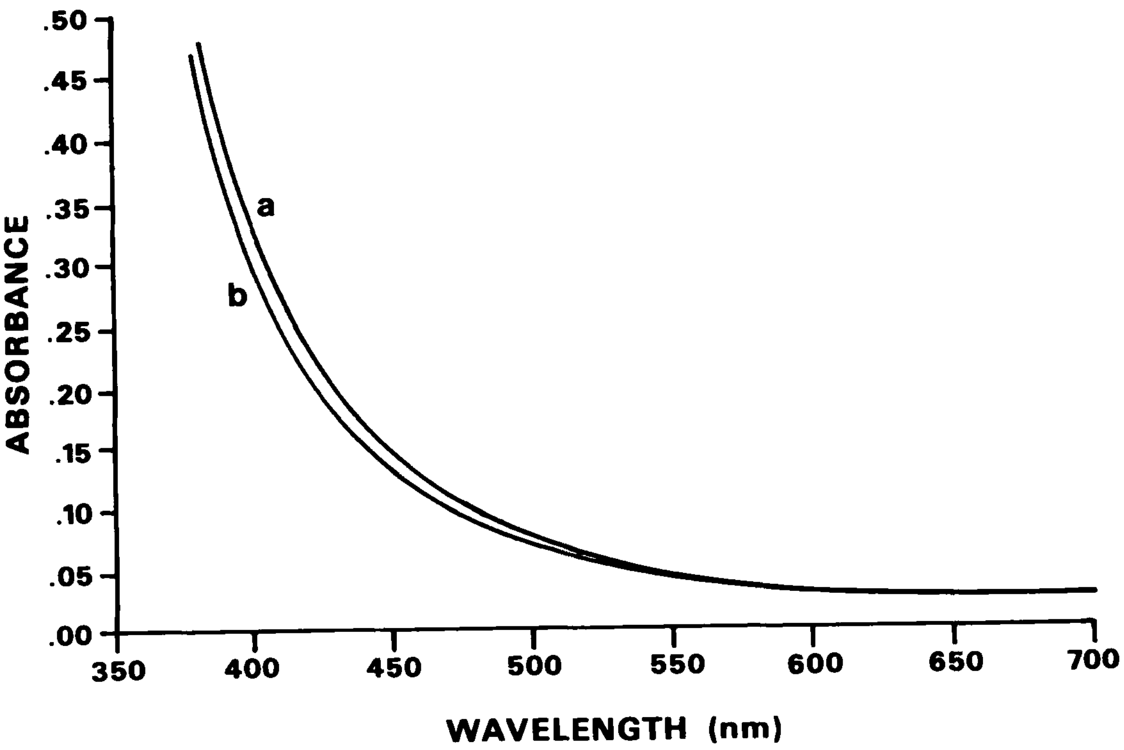

Figure 1. Visible absorption spectra of (a) $NaBH_4$ reduced, N_2H_2 hydrogenated, and EDTA treated kraft lignin (9.33 ppm Fe); and (b) $NaBH_4$ reduced, N_2H_2 hydrogenated kraft lignin; concentration, 7.5 mg/25 mL of 2-methoxyethanol.

Table 2. Metal content of Indulin AT.

	Quantity Found (ppm)	
Metal	Before Removal	After Removal
Chromium	2.34	1.71
Manganese	56.7	0.09
Iron	176	8.28
Cobalt	1.14	0.81
Nickel	2.78	1.56
Copper	1.26	0.72

earlier published data of Meshitsuka and Nakano,[4] who found EDTA treatment of a thiolignin produced a decrease in the lignin's absorbance centered at 500 nm. The present absorbance decrease is also close to the spectral region indicated from studies of ferric complexes with model catechols.[3]

The different behavior of the laboratory and industrial kraft lignins indicated the possibility of a threshold level of iron, below which, removal of additional iron would have no beneficial effect in terms of color reduction. However, addition of iron (400 ppm) to the EDTA-treated laboratory kraft lignin did not result in an increase in its absorbance. It would therefore appear important to consider the types of chelation sites available in each particular lignin preparation. In this respect, chelation sites within the Indulin AT appeared to be the more effective color producers. Another possible source of the difference between these two lignins was the much larger manganese content of the Indulin AT. However, the effects of this metal were not further investigated.

Extended Conjugated Systems

The color contribution from extended conjugated systems, of the type proposed by Marton,[5] was examined by hydrogenating their

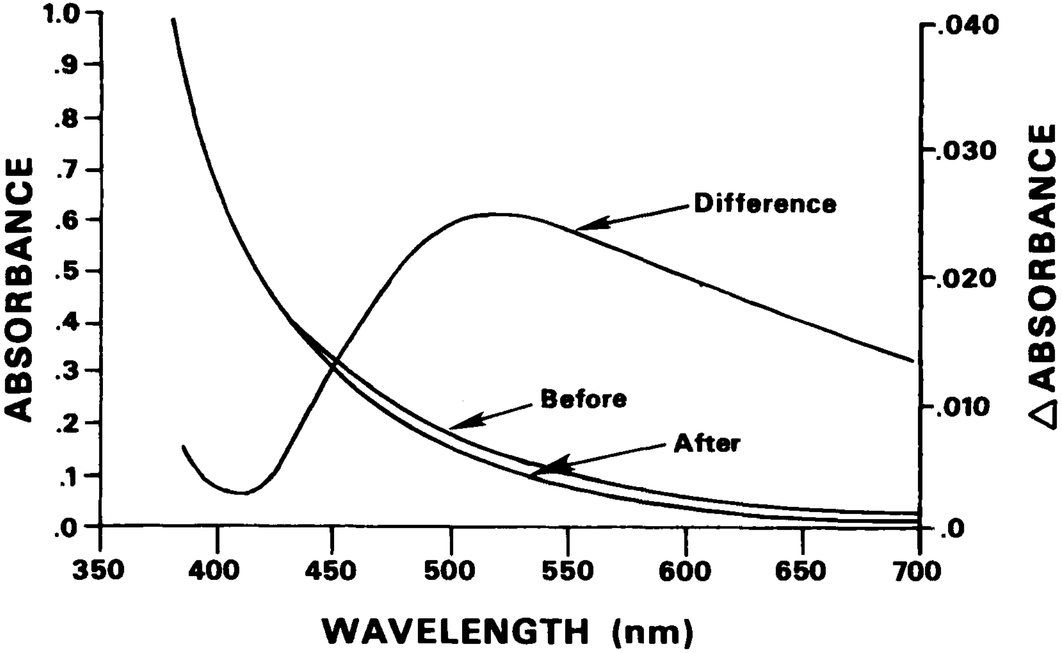

Figure 2. Visible absorption spectra for Indulin AT before and after metal removal, and corresponding difference spectrum (refer to right hand scale); concentration, 7.6 mg/25 mL of 2-methoxyethanol.

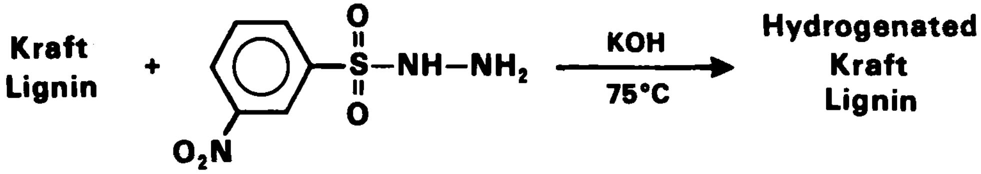

Figure 3. Hydrogenation of kraft lignin.

connecting carbon-carbon double bonds, thereby interrupting the conjugation in these systems. The hydrogenation was accomplished with diimide. Diimide, N_2H_2, was chosen over catalytic agents in order to avoid the problems of catalyst poisoning, steric restrictions involved with approach to the catalyst surface, and nonspecificity of reductions.

The presence of sulfur groups in a molecule does not affect diimide's ability to function as a reducing agent. Being a small molecule, diimide should be able to approach all carbon-carbon double bonds within the lignin macromolecule. Finally, diimide reduces only nonpolar C-C and N-N multiple bonds; polar functional groups, including carbonyls, are inert. Reviews of diimide and its mechanism of hydrogenation have been published by Miller[6] and by Hünig and coworkers.[7]

For the hydrogenation of kraft lignin, diimide was generated _in situ_ from the cleavage of _meta_-nitrobenzenesulfonyl hydrazide. This cleavage was catalyzed thermally and by the addition of a small amount of base, as shown in Fig. 3. The solvent used for the hydrogenation was 2-methoxyethanol.

Diimide hydrogenation of the kraft lignin was monitored spectroscopically. Additional charges of _meta_-nitrobenzenesulfonyl hydrazide were added to the lignin solution until no further decreases in the lignin's UV spectrum were detected. This method is illustrated by the difference curves in Fig. 4; the third 4-hour diimide treatment did not produce any further

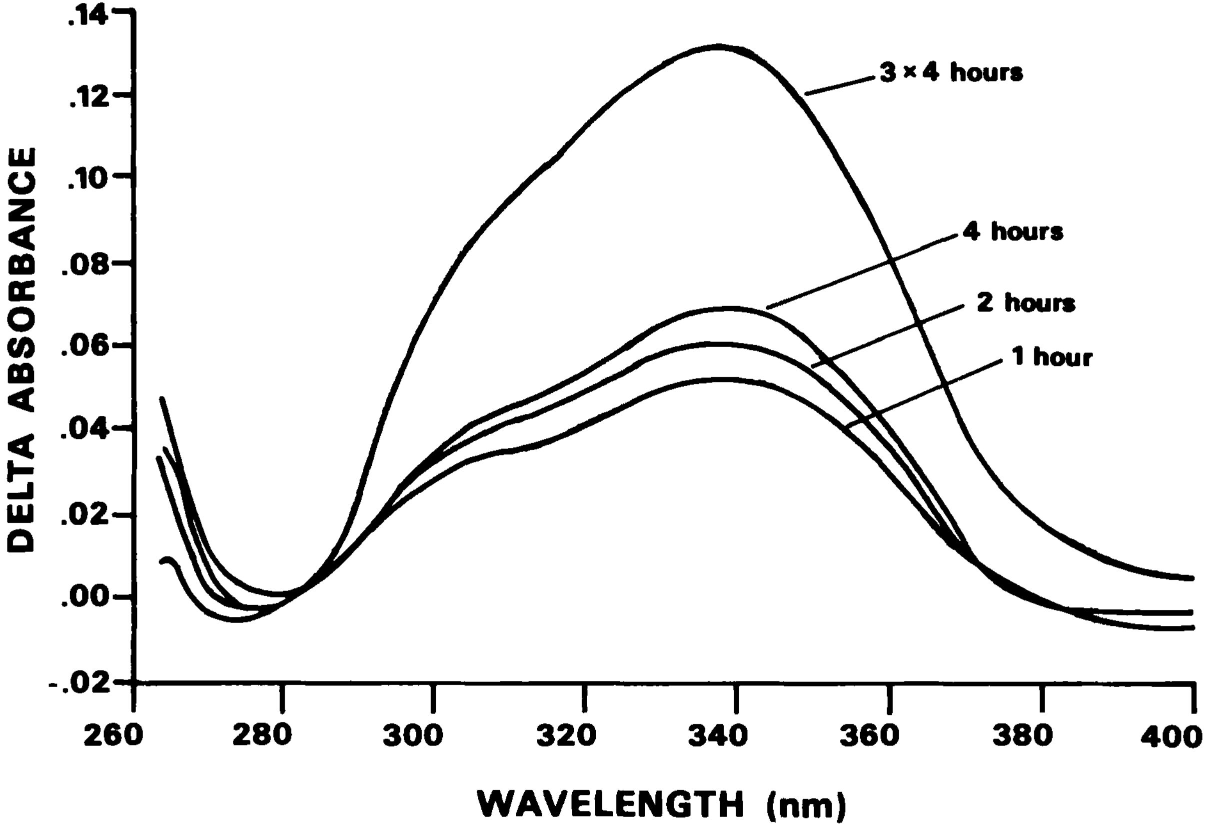

Figure 4. Difference spectra, for the times shown, between the original and hydrogenated kraft lignins.

reduction in absorbance over the second treatment. The maximum reduction in absorbance occurred at approximately 340 nm.

The shapes of the curves in Fig. 4 suggested more than one carbon-carbon double bond type was hydrogenated. Of the double bonds found in lignin,[8] those conjugated with an aromatic ring absorb near 300 nm, phenylcoumarones absorb near 310 nm, and stilbenes near 330 nm. Evidence was obtained from difference spectra of ionized lignins which indicated stilbene bond types were the most numerous of those removed. Subtraction of an ionized, sodium borohydride reduced, and diimide hydrogenated lignin from an ionized, sodium borohydride reduced lignin yielded a difference spectrum having a maximum at approximately 366 nm. The absorption bands of ionized hydroxy stilbenes[8] have been reported to occur between 370 and 380 nm.

Although the diimide hydrogenation resulted in the large decrease in absorbance centered at 340 nm, no decrease in absorbance was detected in the visible range of the spectrum. This result is shown by the spectra in Fig. 5. These spectra indicated extended conjugated systems do not contribute to the color of kraft lignin. In fact, such extended conjugated systems are probably not present in kraft lignin.

In some hydrogenations, the kraft lignin was first reduced with sodium borohydride prior to treatment with diimide. The results from these hydrogenations were similar to those just described.

The combined effect of borohydride reduction and diimide hydrogenation on the lignin's UV spectrum is shown in Fig. 6 and 7. As can be seen, hydrogenation had a substantially greater effect in reducing the lignin's absorbance. Overall, there was little absorbance left in this region of the UV spectrum, except for the 280 nm phenolic maximum. The difference spectrum between the original and the borohydride reduced and diimide hydrogenated kraft lignins (Fig. 7) had a maximum at 328 nm. In the visible

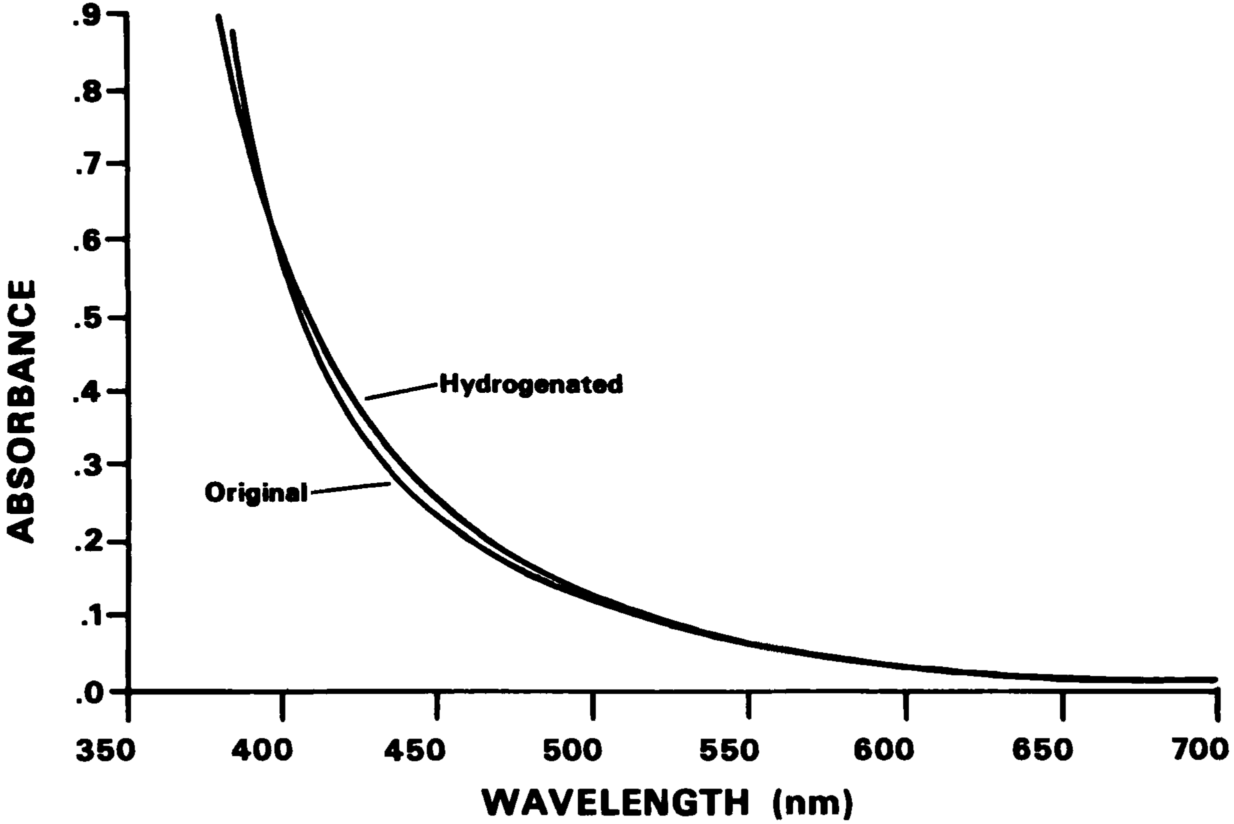

Figure 5. Visible absorption spectra of original and hydrogenated kraft lignins; concentration, 7.5 mg/25 mL DMF.

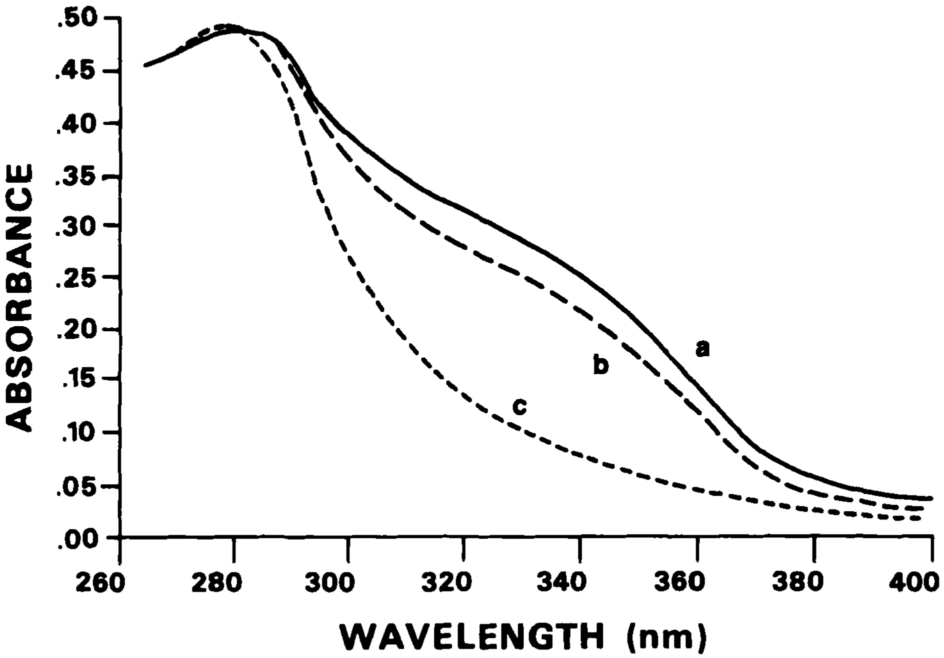

Figure 6. UV spectra of (a) original kraft lignin, (b) $NaBH_4$ reduced kraft lignin, and (c) $NaBH_4$ reduced and N_2H_2 hydrogenated kraft lignin; concentration, 0.375 mg/25 mL 2-methoxyethanol.

region of the spectrum, sodium borohydride had a much greater effect than diimide hydrogenation in reducing the lignin's absorbance. These results are discussed below.

Quinones and CTC's

The dual role quinones play as chromophores in kraft lignin was pointed out in Part 1 of this paper.[1] As was demonstrated, ortho-quinones acted as acceptor species in charge-transfer complexes with free phenolic groups. The quinones, therefore,

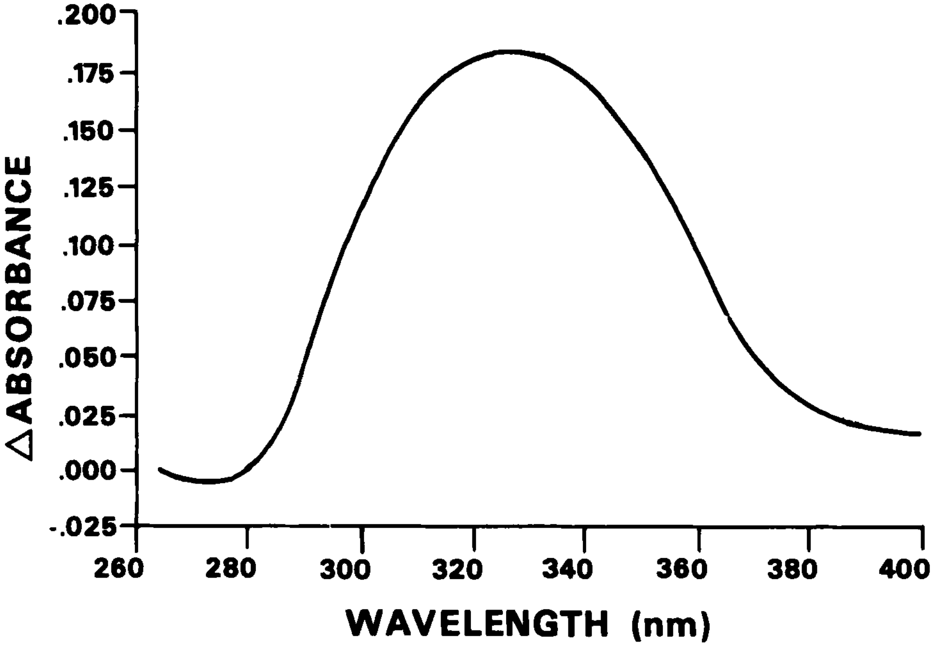

Figure 7. Difference spectrum of original kraft lignin minus $NaBH_4$ reduced and N_2H_2 hydrogenated kraft lignin.

which are colored structures themselves, were also essential to the formation of colored CTC's.

Sodium borohydride reduction of the kraft lignin resulted in decreases of the lignin's absorption spectrum in both the UV and visible regions. The decrease of absorbance in the UV region was shown in Fig. 6. Difference spectroscopy between the original and reduced lignins revealed the maximum decrease occurred at approximately 320 nm. Difference spectra of the ionized original and sodium borohydride reduced lignins revealed a maximum at 353 nm. Both of these results agree with literature values[8,9] for the absorption band of α-carbonyl groups.

In the visible region of the spectrum sodium borohydride reduction produced the decrease in absorbance shown in Fig. 8. This

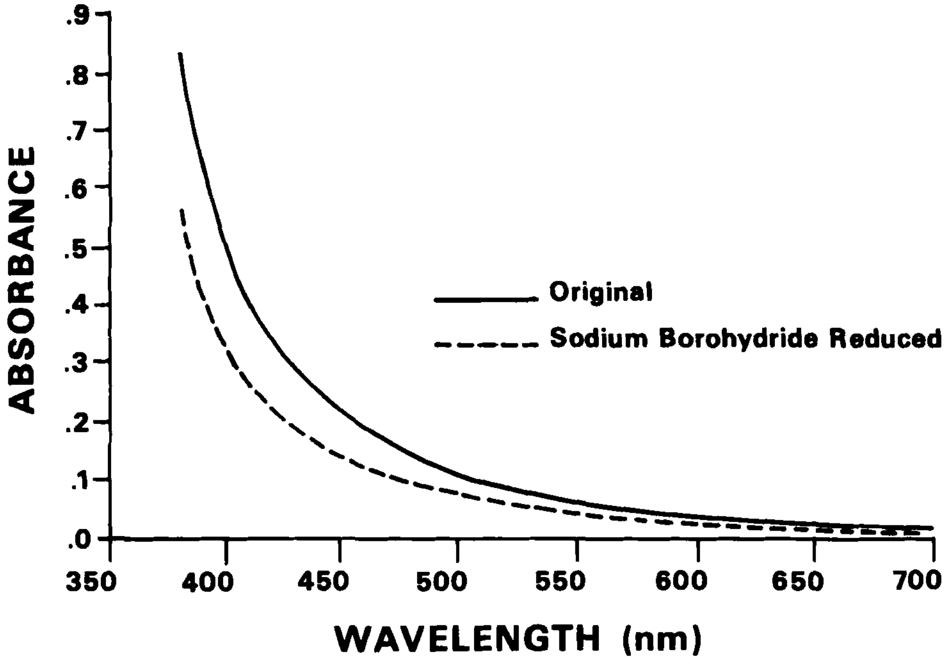

Figure 8. Visible absorption spectra for original and $NaBH_4$ reduced kraft lignins; concentration, 7.6 mg/25 mL 2-methoxyethanol.

decrease was caused by the removal of both the quinone and CTC chromophores. As shown in Part 1, the major portion of this decrease (two-thirds at 430 nm) can be attributed to the CTC's.[1] CTC's, therefore, were a significant contributor to the color of this kraft lignin.

SUMMARY

For the kraft lignin produced in this laboratory, transition metal complexes did not contribute to the lignin's visible absorption spectrum. On the other hand, these complexes were a significant contributor to the visible absorption spectrum of an industrial kraft lignin. This contribution became increasingly more significant at longer wavelengths and accounted for approximately one-half of the industrial lignin's absorbance at 700 nm.

Extended conjugated systems also did not contribute to the visible absorption spectrum of the laboratory-produced kraft lignin. Although hydrogenation of this lignin with diimide produced large decreases in the lignin's UV absorbance, no decrease in the lignin's visible absorbance was detected.

Quinones were the major visible-light absorbing chromophores in the kraft lignin employed in this study. Importantly, the quinones' contribution to the visible spectrum was strongly enhanced by their participation as accepting moieties in CTC's. Removal of these quinones by reduction resulted in a decreased absorbance throughout the visible region. This decrease approached 40% at 400 nm and gradually declined to about 25% at 700 nm. Approximately two-thirds of the absorbance decrease at 430 nm resulted from the disruption of CTC's.

EXPERIMENTAL

The lignin isolation and analysis, $NaBH_4$ reduction, and electronic absorption spectroscopic methods were described in the preceding paper.[1] Indulin AT was obtained from Westvaco, North Charleston, South Carolina.

Metal Ion Removal

In a typical experiment, the kraft lignin (0.78 g) was dissolved in the minimum quantity of 2-methoxyethanol needed to give complete dissolution. This solution was poured into 150 mL of 0.05M EDTA, which precipitated the lignin in a swollen, accessible form. The precipitated lignin mixture was then centrifuged and the supernatant decanted off. The isolated lignin was redispersed in an additional 120 mL of fresh 0.05M EDTA.

This lignin dispersion was loaded into the central compartment of an electrodialysis cell (diagrammed in Fig. 9). The lignin was retained within the cell by two cellulose acetate membranes (Sartorius Filters, Inc.; Hayward, C.A; filter no. SM11739). Impurities in the lignin sample, including EDTA-chelated metals, were electrodialyzed through the membranes and carried out of the cell by the water flowing through the two outer compartments. Additionally, two cation exchange columns (Metex Ionxchanger Model 1; Illinois Water Treatment Co.; Rockford, ILL.) were placed in series in the water line flushing the anodic side of the cell.

A voltage of 40-50 V was applied across the cell during the dialysis. The electrodialysis was continued until the current measured across the cell had decreased to a constant value (3.65 mA, at an applied voltage of 40 V). This required approximately six days. Following completion of the electrodialysis, the lignin-water suspension was removed from the cell and the lignin was recovered by freeze-drying.

Metal analysis was performed by VHG Labs, Inc., 140 Hampstead St., Methuen, MA 01844, using inductively coupled plasma emission spectroscopy.

Diimide Hydrogenation

Diimide hydrogenations were performed on the original kraft lignin and on kraft lignin which had previously been reduced with $NaBH_4$. In each case the procedure was the same. For example, $NaBH_4$ reduced kraft lignin (20.5 g) was dissolved in 700 mL of 2-methoxyethanol (Mallinckrodt AR) and placed in a 2000 mL, 3-neck, round bottom flask. The flask was equipped with a gas inlet tube, a 250 mL dropping funnel, and a magnetic stir bar. The flask was placed in a 75°C oil bath and the lignin solution was adjusted to pH 8 by the addition of 10% KOH.

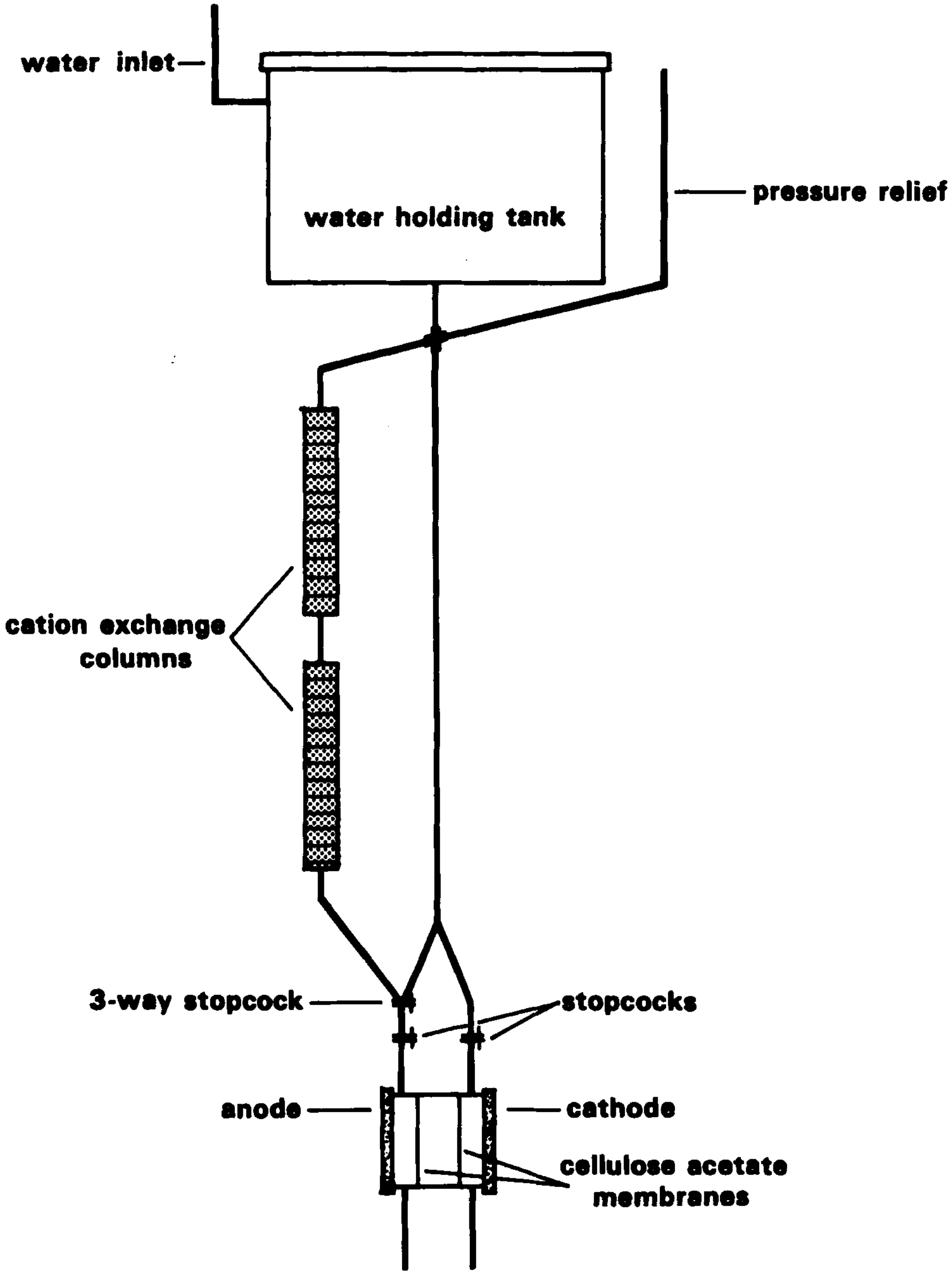

Figure 9. Electrodialysis cell with water supply.

meta-Nitrobenzenesulfonyl hydrazide (12.32 g), dissolved in 100 mL of 2-methoxyethanol, was then added slowly through the dropping funnel over a period of approximately 30 minutes. After completion of this addition, the dropping funnel was replaced with an air condenser fitted with a $CaCl_2$ tube. Gas evolution became evident after approximately 15 minutes. A slight stream of N_2 was left flowing over the lignin solution during the reaction.

After 4 and 8 hours, new charges of meta-nitrobenzenesulfonyl hydrazide (12.32 g in 100 mL of 2-methoxyethanol) were again slowly added to the reaction mixture. Throughout the course of the reaction, the pH of the lignin solution was kept slightly alkaline by the occasional addition of 10% KOH.

After 12 hours, the reaction flask was removed from the oil bath and cooled to room temperature. In portions, the reaction solution was transferred to a 2000 mL beaker. The beaker was placed in an ice bath, and the solution was then acidified (pH 2-3) by the dropwise addition of 1N HCl. The hydrogenated lignin was precipitated by the addition of distilled water. The precipitate was collected by centrifugation and washed twice with distilled water. The isolated hydrogenated lignin was then dried and ground to a uniform powder.

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