Electrokinetic study of kraft lignin

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ABSTRACT

The authors studied the zeta potential of kraft lignin with or without various metal ions over a wide range of pH. They also investigated the salt effect on surface adsorption. Kraft lignin has a negatively charged surface and its isoelectric point (IEP) is approximately 1.0. The authors propose that the negative charges originate mainly from ionization of hydroxyl groups on the kraft lignin surface. Monovalent and divalent ions generally adsorb indifferently on kraft lignin, but trivalent ions of aluminum do exhibit specific adsorption and shift the IEP of lignin to a higher pH.

ELECTROKINETIC STUDY OF KRAFT lignin is an unexplored area. Searching *Chemical Abstracts* electronically up to 1993 under broad key word combinations such as "lignin/zeta potential" produced three entries. McKenzie's work *(1)* mainly focused on the cellulosic fines in a pulping process. The work only reported a single value of zeta potential for milled wood lignin and for Klason lignin without specifying the pH. Nyman, Rose, and Ralston *(2)* reported the coagulation of kraft lignin or lignosulfonates with some salts. The publication of Rusetskaya *et al. (3)* was an application of zeta potential in the air flotation of sulfate slurry waste water. Further searching of the literature produced an examination of the zeta potential of lignosulfonate to monitor oil drilling muds.

All the studies only reported or used some zeta potential values of lignin in their applications. There was no report on the dependence of lignin zeta potential on pH and no isoelectric point (IEP) information of lignin.

Lignin is a polar macromolecular material. It is usually present or has use in a system that accounts for a large interfacial effect. A surface interaction will significantly contribute to the properties of lignin or of the lignin containing system. This is because the interfacial region normally has a very strong electric field of approximately 10^6 V/cm or higher *(4–6)*. A knowledge of the electrokinetic properties of kraft lignin is therefore clearly of fundamental and practical importance.

The aim of this work was to obtain electrokinetic data for purified kraft lignins with or without various metal salts as a function of pH using microelectrophoretic techniques. We also investigated surface interactions of kraft lignin in aqueous medium using monovalent, divalent, and trivalent ions at different concentrations.

EXPERIMENTAL

Materials

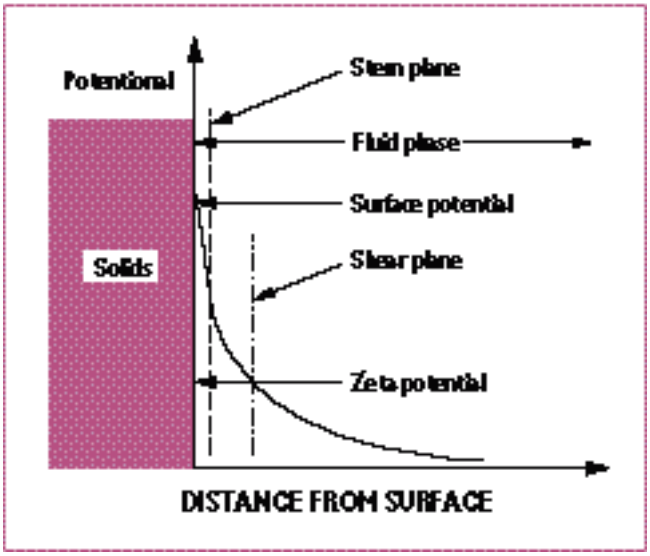
All the experimental liquors in this study came from cooking of slash pine in a 3.5 ft^3 vertical batch digester using forced liquor circulation. Detailed pulping conditions and liquor handling information are available elsewhere *(7–9)*.

We prepared purified lignin samples from the skimmed black liquors and characterized lignin molecular weight by light-scattering techniques *(10, 11)*. Black liquor samples at 10% solids with a pH of approximately 13 underwent filtration through a glass fiber filter to exclude fibril or particulate impurities before titration with 1.0*N* sulfuric acid slowly to a final pH of approximately 2.0 using stirring. We centrifuged the subsequent slurry and decanted the supernate. The lignin underwent washing with deionized water, centrifuging, and decanting of the supernate. We redissolved this precipitated lignin in 0.1*N* sodium hydroxide and adjusted the solution pH to approximately 13. Then there was filtration through paper to separate any insoluble substance. The subsequent filtrate underwent another titration with 1.0*N* sulfuric acid. Next we washed and centrifuged the reprecipitated lignin and decanted the supernate decanted with deionized water once, with 0.01*N* sulfuric acid twice, and with deionized water three additional times. We then freeze dried the washed lignin. Finally, we extracted the dried lignin with hexane to reduce the organic impurities and freeze dried again.

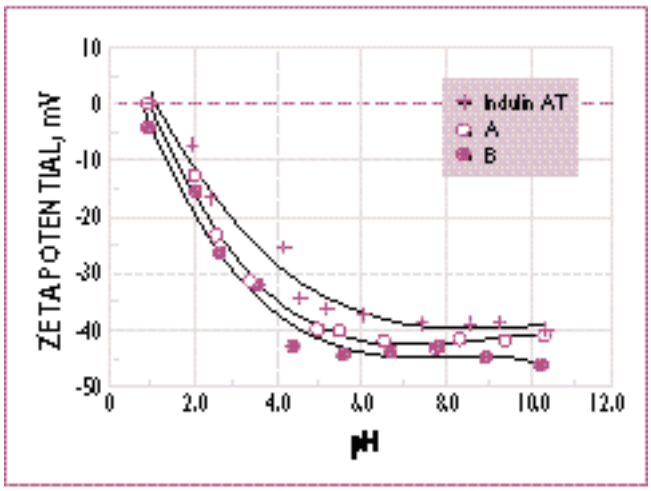
Indulin AT, a commercial softwood kraft lignin from Westvaco, was also in the study for comparison. The reagents used in this study such as sodium hydroxide, hydrochloric acid, sodium chloride, zinc sulfate, calcium chloride, and aluminum chloride were all American Chemical Society grade. The study only used deionized water.

Preparation of lignin suspension

We suspended kraft lignin in deionized water at a mass concentration of 0.05%. Then we sonicated the suspension for 30 min to break loose agglomerates into small particles. We also prepared the suspensions with a known concentration of salt at a lignin mass concentration of 0.05%. We observed that part of the lignin precipitated to the bottom at a mass concentration of 0.05% for both Indulin AT and the experimental lignins. The precipitation resulted in an inconstant lignin concentration during the electrophoresis experiments for the total lignin surface per



1. Schematic of the electric potential in solid-liquid interface region



2. Zeta potential of softwood kraft lignins as a function of pH

unit volume of suspension. This did not affect the results of zeta potential measurement, however, since the surface charge density instead of the summation of charges on total surface area available governs the zeta potential.

Microelectrophoresis measurements

Electrophoresis studies the movement of suspended particles in a fluid influenced by an applied electric field. It is difficult to measure practically the electric potential at a particle surface. Electrophoretic experiments can conveniently determine zeta potential. This is the potential measured at the shearing surface as Fig. 1 shows. When a particle suspended in a liquid moves under the influence of an electric field, a layer of liquid attaches on the particle surface and moves with it. The definition of zeta potential is the electric potential measured at the shearing surface—the interface between the stagnant liquid phase and the moving layer.

Figure 1 shows the schematic of the electric potential in the solid–liquid interface region. It is common belief that the interface region consists of two layers—a Stern layer and a diffuse layer. The former is a layer of ions specifically—chemically—adsorbed at the surface, and the latter is an excess of counter-ions and a deficit of co-ions. When a suspended particle moves in a liquid under the influence of an electric field, a layer of liquid attaches on the particle surface and moves with it.

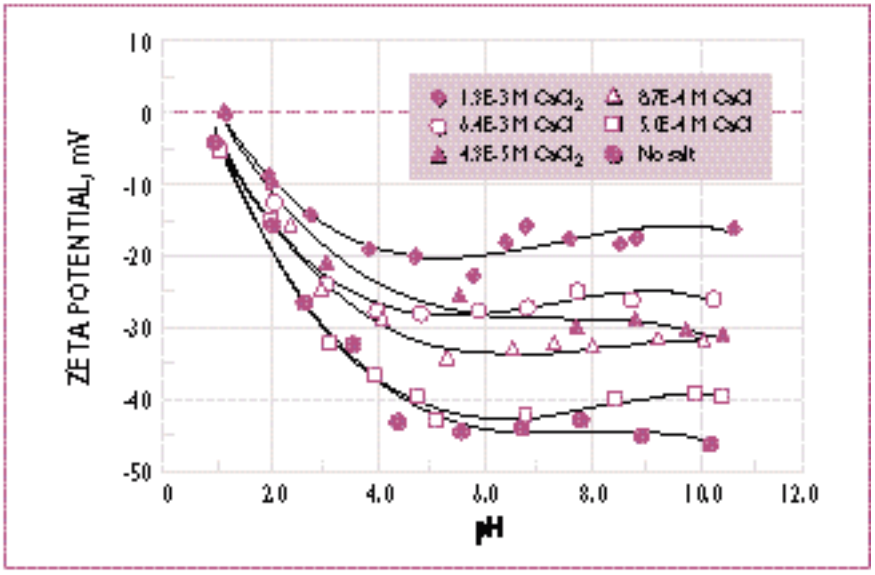
A Model 501 Laser Zee Meter with a 632.8 nm He-Ne laser as light source with a flat cell configuration performed the microelectrophoresis experiments. A System 3000 Automated Electrokinetics Analyzer also examined three lignin samples. Although the dependence of the zeta potential of lignin on the suspension pH measured with two instruments followed the same trend, the magnitude of the zeta potential measured with the System 3000 was consistently higher than the values measured with the Laser Zee 501. This difference might result from the instruments or from normal operator's bias. The difference between the results measured by the two instruments was well within an acceptable range of a few percent, however. For consistency, therefore, all zeta potential data reported in this study used the Laser Zee 501.

Electrophoresis experiments were at ambient temperature with an apparent lignin mass concentration of 0.05%. A Corning 220 pH meter measured the pH values of the lignin suspension. Due to the restriction of the sample cell material used, measurement of zeta potential of lignin suspension used a pH range of approximately 1.0–10.5. The suspension could interact with the sample cell material at a higher pH. We took an aliquot of prepared lignin suspension and adjusted its pH value with either dilute sodium hydroxide or dilute hydrochloric acid immediately before making a measurement of zeta potential. After the measurement, we withdrew the lignin suspension from the sample cell, remeasured the pH, and recorded this pH value with the corresponding zeta potential determined.

RESULTS AND DISCUSSIONS

Zeta potential and IEP

Figure 2 shows the electrokinetic behavior of three kraft lignins as a function of the pH. There was also examination of more experimental kraft lignins produced under different pulping conditions. They had the same electrokinetic behavior shown in Fig. 2. This figure indicates that the



3. Zeta potential of softwood kraft lignin as a function of pH in the presence of sodium chloride or calcium chloride

pH strongly affects the zeta potential of kraft lignin. It also shows that both the technical lignin of Indulin AT and the experimental kraft lignins have the same trends for dependence on pH. As the pH decreased from 10 to 1.0, the zeta potential—absolute value—of kraft lignin decreased monotonically. This indicates that charge density on the lignin surface gradually decreases with reduced pH. The strong dependence of the zeta potential on pH suggests that H^+ and OH^- are the potential determining ions of kraft lignin. A pH of 1.0 is the IEP of kraft lignins.

Since there were no reports of similar work, we compared kraft lignin with some inorganic compounds for the dependence of zeta potential on pH. The zeta potential dependence of kraft lignin on pH is quite similar to that for silica. The zeta potential of both kraft lignin and silica is always negative over a wide range of pH values. IEP of silica is 2.0 *(12)*, however, and the magnitude of its zeta potential is much higher than that for kraft lignin at pH values above 4 *(13)*.

We observed that Indulin AT had a pH value of 5.15 when suspended in water using a nominal mass concentration of 0.05% and a zeta potential of –36.4 mV. Note that this measurement occurred after withdrawing the suspension from the sample cell. The experimental kraft lignins had a pH of about 4.50 and a zeta potential of –38.7 to –43.0 mV. Zeta potentials of –29.4 mV and –31.5 mV for a milled wood lignin and Klason lignin of eucalyptus, respectively, are the only available data reported previously *(1)*. Since there was no specified pH value, a comparison of these data to the results from this work is not valid.

The magnitude of zeta potential of experimental kraft lignins was higher than that of Indulin AT. There are at least two possible reasons for this difference:

- Different separation procedures may result in different functionality or different concentration of functional groups on the surface of lignin.
- Higher impurities of electrolytes associated with the lignin sample may compress the electrical double layer and reduce the magnitude of the zeta potential.

Origination of surface charge

Figure 2 indicates that H^+ and OH^- are the potential determining ions of kraft lignin. Results shown in Fig. 3 support that an addition of sodium chloride or calcium chloride does not affect the IEP of kraft lignin. We therefore propose that ionization shown in Eq. 1 of Table I is the principal mechanism for the origination of surface charges on the kraft lignin surface *(1)*. In the table, R is the three-dimensional backbone of lignin molecule, OH is either an aryl or alkyl hydroxyl group, and n is the total number of OH groups. Using Eq. 1, Eqs. 2 and 3 elucidate the mechanism for the dependence of zeta potential of lignin on pH. As Eq. 1 shows, when a lignin particle contacts water either in liquid or in air many H^+ ions may move away from the surface. This ionization results in a negatively charged lignin surface. In an aqueous medium with pH increasing, Eq. 2 shows that more H^+ ions may dissolute from the lignin surface into water. The surface charge density subsequently increases and results in a higher negative zeta potential. As the pH value decreases, Eq. 3 shows that the H^+ ion moves toward the negatively charged lignin surface. A lower negative zeta potential consequently results. When the concentration of H^+ increases to a point neutralizing all negative charges at the shearing surface, the lignin particle with the attached materials becomes electrically balanced. This pH corresponds to the IEP of kraft lignin.

Table I is an oversimplified model. A polymeric protolignin molecule contains many alkyl and aryl hydroxyl groups. The chemical environment of each hydroxyl group may differ from others due to the heterogeneity of a lignin molecule. Pulping and purification processes may also produce other functional groups such as –COOH, $–SO_3OH$, -SH, etc., on the kraft lignin surface. These pulping generated functional groups for kraft lignins usually occur in small quantities. They depend on the pulping and purification condi-

tions. The acid groups will more easily ionize to give up H^+ ions and produce a negative charge on the lignin surface when contacting water. A higher functionality of acid groups can therefore increase the magnitude of zeta potential of kraft lignin as mentioned previously.

A single hydroxyl group on the lignin surface might not give up a H^+ ion completely. The x, y, and z values in Eqs. 1–3 are the total interactions between the hydroxyl groups on the lignin surface and the H^+ and OH^- ions in water. They are not necessarily integers.

Salt effects and adsorption

Figures 3–5 show the influences of monovalent, divalent, and trivalent salts on the zeta potential of kraft lignin. While sodium chloride or calcium chloride affect only the magnitude of the zeta potential of lignin, zinc sulfate and aluminum chloride cause charge reversals and result in more than one IEP in the pH range studied.

Figure 3 shows the influence of sodium chloride and calcium chloride on the zeta potential of kraft lignin over a wide range of pH values. The presence of sodium chloride reduces the magnitude of the zeta potential. The magnitude of the zeta potential of kraft lignin decreases as the concentration of sodium chloride increases. Calcium chloride affects the zeta potential in the same way as sodium chloride. It reduces the magnitude of the zeta potential of lignin more effectively than sodium chloride. Sodium chloride and calcium chloride do not change the sign of the zeta potential or shift the IEP of kraft lignin.

It is very probable that specific adsorption of Na^+ or Ca^{+2} on the lignin surface does not occur. The sign of the surface charge would reverse, if there were chemical adsorbing. In other words, at least one layer of water molecules must exist between the Ca^{+2} ions and the lignin surface at the equilibrium of both Columbic and thermal interactions.

$$R(OH)_x + xH_2O \rightarrow (O^-)_xR(OH)_{n-x} + x(H^{3+}O) \quad (1)$$

$$(O^-)_xR(OH)_{n-x} + yOH^- \rightarrow (O^-)_{x+y}R(OH)_{n-(x+y)} + y\,H_2O \quad (2)$$

$$(O^-)_x\,R(OH)_{n-x} + zH^+ \rightarrow (O^-)_{x-z}\,R(OH)_{n-(x+z)} \quad (3)$$

I. The origination of surface charges on kraft lignin and the pH effect on the zeta potential of lignin

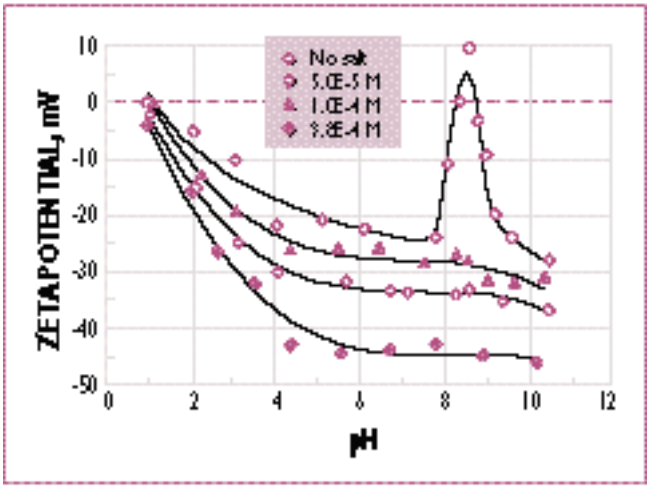
As Fig. 4 shows, the presence of zinc sulfate at low concentrations only reduces the magnitude of the zeta potential of lignin. At a high concentration of approximately $1.0 \times 10^{-3}M$, however, charge reversal occurs at a pH of approximately 8.5. Three IEP values consequently appear on the zeta potential vs. pH curve. The second IEP at pH 8.40 changes the sign of the zeta potential of kraft lignin from negative to positive. The third IEP at pH 8.70 changes the sign from positive to negative. In the region of pH from 6–9, a pH buffering effect occurred when adding dilute sodium hydroxide solution to increase the suspension pH during the experiment.

Interestingly, the IEP of lignin at 1.0 does not change in the presence of zinc sulfate. Comparing the effects of zinc sulfate in Fig. 4 and calcium chloride in Fig. 3, the zinc sulfate reduces the magnitude of the zeta potential of lignin with less effectiveness than the calcium chloride except at the region of charge reversal. The divalent SO_4^{-2} ion having a stronger effect than the monovalent Cl^- as a co-ion in the system may cause this.

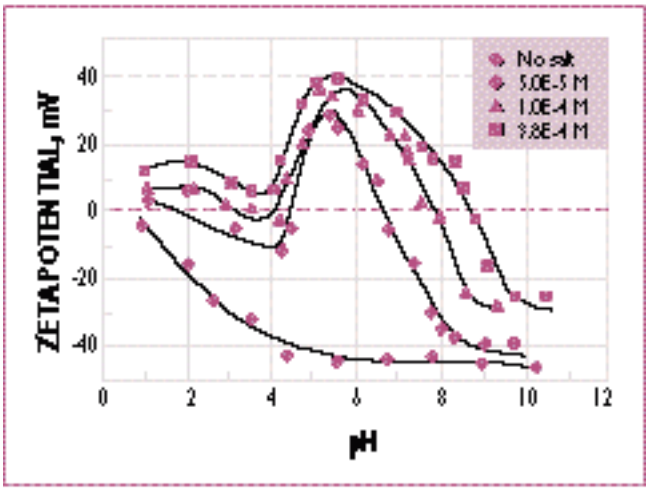
Figure 5 shows the electrophoretic behavior of kraft lignin in the presence of aluminum chloride. Over a wide range of pH, the zeta potential of kraft lignin changes to positive values due to the presence of aluminum chloride. At a low concentration of $5 \times 10^{-5}M$ aluminum chloride, the IEP of lignin shifts from a pH of 1.0 to approximately 2.0. The second IEP and the third IEP exist at pH values of 4.5 and 6.6, respectively. As the concentration of aluminum chloride increases, the second IEP decreases and the third IEP increases giving a broader pH region of positive zeta potential results. With a high concentration of $1.05 \times 10^{-3}M$ aluminum chloride, the first IEP disappears. This is because the zeta potential changes to a positive value in a wide range of pH values below the third IEP.

Charge reversal and surface adsorption

Charge reversal of inorganic compounds is common *(14–17)*. James and Healy have studied the general behavior of charge reversal of inorganic substrates caused by hydrolyzable metal ions *(12, 13, 18)*. One work *(18)* reported that a substrate shows an IEP if H^+ and OH^- are the potential determining ions. When they are not, the substrate will have a zeta potential of the same sign over the entire pH range. In the presence of hydrolyzable metal ions, a substrate may have two more charge reversals—a minus to plus reversal at intermediate pH followed by a plus to minus reversal at higher pH. This corresponds to the second and third IEP values, respectively. The first IEP is the characteristic IEP of the substrate *(13, 18)*. The second IEP is from the specific adsorption of charged hydrolysis species—



4. Zeta potential of softwood kraft lignin as a function of pH in the presence of zinc sulfate at different concentrations



5. Zeta potential of softwood kraft lignin as a function of pH in the presence of aluminum chloride at different concentrations

$[Al_8(OH)_{20}]^{+4}$ or $[Zn_3(OH)_3]^{+3}$—at the particle-fluid interface *(19, 20)*. The third IEP is due to the excess hydrolysis that reduces the charged hydrolysis species and increases the neutral hydrolysis species.

The minimum point of zeta potential between the first and second IEP values shown in Fig. 5 occurs at a pH for which the concentrations of the hydrolyzed species are low. The specific adsorption of Al^{+3} ions on the lignin surface causes the charge reversal below this pH. For example, consider the aluminum equilibrium data shown in Table II. At the highest aluminum chloride concentration of 1.05 x 10^{-3}*M* and the corresponding pH of 3.7, the maximum concentrations of Al $(OH)_3$, $Al^{+}(OH)_2$, and $Al_2^{+2}(OH)$ are 2.32 x 10^{-4}*M*, 4.17 x 10^{-4}*M*, and 3.00 x 10^{-4}*M*, respectively, by calculation. The $Al(OH)_3$ is still soluble in the bulk at this condition.

Note that in an aluminum and water system, there are more hydrolyzed aluminum species *(21)* than listed in Table II such as $Al(OH)_4^-$, $Al_9^{+4}(OH)_{20}$, etc. The data calculated here used the approximation that there are only the four species of Al^{+3}, $Al_2^{+2}(OH)$, $Al(OH)_2$, and $Al(OH)_3$ in the system.

Indifferent adsorption of free ions results in only Columbic interaction, however, so that the maximum effect is to reduce the magnitude of zeta potential to zero. This can neither reverse the sign of zeta potential nor shift the IEP of a substrate. Wiese, James, and Healy *(21)* reported that careful streaming potential studies on vitreous silica capillaries indicated a shift of its IEP to a higher pH with the presence of trivalent ions of La(III). The La^{+3} ions adsorb *(21)* specifically at the vitreous silica-water interface. Stryker and Matijevic *(22)* reported that the critical coagulation concentration of aluminum nitride for silver iodide sol remains constant at pH values below 4. Its value is characteristic for counterions of +3 charge for the sol. This indicates that the aluminum ion is present in its unhydrolyzed form below pH 4. As Fig. 5 therefore shows, the Al^{+3} free ion does adsorb specifically at the kraft lignin to water interface. It shifts the IEP of lignin to a higher pH at low concentration. The strong chemical adsorption reverses the zeta potential from negative to positive at higher concentrations in a wide range of pH so that the first IEP disappears.

After passing the minimum point of zeta potential between the first IEP and the second IEP in Fig. 5, the hydrolyzed aluminum species increase as the pH increases. Aluminum ion upon hydrolysis produces one predominant polynuclear hydrolysis product *(19)*. There is general agreement *(16, 19)* that in the intermediate pH region this predominant specie is $[Al_9(OH_{20})]^{+4}$. The specific adsorption of this tetravalent complex octamer on the lignin surface therefore causes an increase of the zeta potential and results in the second IEP of lignin. This process continues to the maximum point between the second and third IEP values. The increased charges on this hydroxylated complex obviously reverse the zeta potential from plus to minus.

Beyond the maximum point of zeta potential in Fig. 5, excess hydrolysis reduces the amount of the tetravalent species and increases the amount of neutral aluminum hydroxide species. The anionic charge on the lignin surface simultaneously increases. As the pH further increases, the zeta potential therefore decreases and a dual surface colloidal particle with coated and uncoated lignin surface area pre-

KEYWORDS
Adsorption, alkali lignins, bibliographies, electric charge, electrophoresis, isoelectric point, lignins, sodium chloride, surface properties, zeta potential.

$Al^{+3} + H_2O = Al^{+2}(OH) + H^+$	Log K (25°C) = -4.97
$Al^{+2}(OH) + H_2O = Al^{+}(OH)_2 + H^+$	Log K (25°C) = -4.3
$Al^{+}(OH) + H_2O = Al(OH)_3 + H^+$	LogK (25°C) = -5.7

II. Aluminum equilibria

dominates the electrokinetic behavior of the lignin particles.

It is probably unlikely that a divalent ion of Zn^{+2} specifically adsorbs on the lignin surface in Fig. 4. If so, the IEP of kraft lignin would shift to a higher pH. As discussed above, the second and third IEP values at pH values of 8.40 and 8.70 at a zinc sulfate concentration of 9.8 x 10^{-4}*M* are due to the specific adsorption of the hydrolysis species of $[Zn_3(OH)_3]^{+3}$ on the lignin surface and to a dual colloidal surface of coated and uncoated areas with neutral $Zn(OH)_2$, respectively. Using a zinc hydroxide solubility product of 1.8 x 10^{-14} *(23)*, the critical pH at zinc sulfate concentration of 9.8 x 10^{-4}*M* calculates to 8.63. This critical pH agrees with the third IEP value. It is probable that a low available lignin surface per unit volume of suspension resulted in a lignin surface fully coated with zinc hydroxide. We did not expect the fact that the zeta potential of lignin does not increase much in the pH range of the supposed charge reversal at lower concentrations of zinc sulfate.

In addition, we did not expect that at low pH the specific adsorption of Ca^{+2} in Fig. 3 and Zn^{+2} in Fig. 4 ions would not occur. One possibility is that these divalent ions do not have strong enough Columbic interaction with the lignin surface. Another possibility is that the specific absorptions do occur, but the ions adsorbed are very few and not detected by the zeta potential measurement under the present experimental conditions.

Stability

As Fig. 2 shows, the maximum instability for a kraft lignin and water system occurs at pH 1.0. The lignin in water may coagulate in the pH range 1.0–2.5. In the presence of monovalent or divalent ions as in black liquor, however, the instability range becomes broader depending on the specific situation. If the lignin coagulates from black liquor at a high pH of 7 or 8, the product would be a coprecipitate of lignin with some positively charged species in the system. In the presence of trivalent ions, the system stability is more complicated and very sensitive to pH and the concentration of ions present. The products precipitated under different conditions would also be quite different.

SUMMARY

Kraft lignin has a negatively charged surface. The negative charges originate mainly from an ionization of hydroxyl groups on the lignin surface. When it contacts water, kraft lignin exhibits an IEP at pH 1.0 and a negative zeta potential over a wide range of pH values above 1.0. The H^+ and OH^- ions are the potential determining ions of kraft lignin.

Monovalent ions of Na^+ and divalent ions of Ca^{+2} adsorb indifferently onto kraft lignin. Their presence only reduces the magnitude of the negative zeta potential. They do not shift the IEP or reverse the zeta potential of kraft lignin. Trivalent ions of Al^{+3} adsorb specifically at the kraft lignin to water interface at low pH values and shift its IEP to a higher pH.

The presence of trivalent ion Al^{+3} or divalent ion Zn^{+2} causes charge reversals and three IEP values in the pH range studied. The first IEP at low pH is the intrinsic IEP of kraft lignin. The second IEP at medium pH is due to the specific adsorption of the hydrolyzed species $[Al_8(OH)_{20}]^{+4}$ or $[Zn_3(OH)_3]^{+3}$. The cause of the third IEP at high pH is a dual lignin surface coated or uncoated with neutral metal hydroxide. TJ

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