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Summary

The objective of this work was to determine the effect of various processing operations on the electrophoretic mobility (E.M.) distribution of fiber fines. The variables studied included pulping method, pulp yield, chemical bleaching, and degree of refining. The chemical changes occurring in the long fibers and fiber fines during these operations were measured independently and correlated with electrokinetic properties. The results indicate that a relationship exists between the weak acid content of the fines and their average E.M. Fiber modification processes that increase the weak acid content of the pulp (i.e., bleaching with hydrogen peroxide) produce fines with a more negative E.M. Processes that reduce the weak acid content (i.e., decreasing kraft pulp yield and bleaching of kraft pulp using a CEDED bleaching sequence) produce fines with a less negative E.M. Increasing the level of refining did not appreciably affect the weak acid content or the average E.M. The width of the E.M. distribution was not significantly affected by pulp yield, bleaching, or refining.

Introduction

Wood fibers, like many other particles, acquire a negative surface charge when suspended in water. The origin of the surface charge in wood fibers is generally believed to result from the ionization of surface acidic groups (1, 2). Although it is difficult to measure the surface charge of wood fibers or fiber fragments, the electrokinetic (or zeta) potential produced by charged surfaces can be measured indirectly using streaming current, streaming potential, electroosmosis, or microelectrophoresis techniques (3). With microelectrophoresis, it is possible to obtain the distribution of electrophoretic mobilities within a colloidal system, from which the zeta potential distribution can be calculated. Smith (4) found the distribution of zeta potentials to be more useful than the average zeta potential value for interpreting the electrokinetic effects of fines in a papermaking furnish. The zeta potential of wood fibers and fines has been shown to play a significant role in many colloidal interactions that take place during paper formation, including fiber flocculation, (2) pigment and dye retention, (5, 6) and polymer adsorption (7).

Wood fiber processing operations that change the overall chemical composition of wood fibers, such as pulping, bleaching, and refining, would also be expected to alter their surface chemical composition and electrokinetic properties. McKenzie (8) studied the electrophoretic mobility of fines from a number of different papermaking pulps and found that within the same wood species, different pulping methods produced fines with considerably different electrokinetic potentials. Chemical bleaching was also found to affect the zeta potential of pulp fines. The observed differences in zeta potential were attributed to chemical changes that had occurred during the pulping and bleaching processes, although no chemical analysis results were reported.

The purpose of this work was to investigate the effect of pulping, bleaching, and refining operations on the electrophoretic mobility distribution of wood fiber fragments (called "fines"). Chemical changes occurring in the long fibers and fiber fines during these operations were also measured and correlated with changes in the magnitude and distribution of the electrophoretic mobility of the fines fraction.

The overall objective was to increase our understanding of the development of papermaking fiber electrokinetic properties.

Experimental Design

The experimental design is divided into 1) thermomechanical pulp (TMP) phase, and 2) kraft pulp phase. A schematic of the experimental design is shown in fig. 1. One variable, the effect of bleaching, was studied in the TMP phase. The variables of interest in the kraft pulp phase included pulp yield, bleaching, and degree of refining. Three pulp yields were studied at two levels of bleaching (unbleached and bleached) and two degrees of refining (arbitrarily "low" and "high"). The parameters used to evaluate the electrokinetic properties of fiber fines were the average electrophoretic mobility and the standard deviation of the electrophoretic mobility distribution. Properties relating to the chemical composition of the pulp fibers and fiber fines were also measured.

Materials and methods

Thermomechanical pulp bleaching

The commercially prepared TMP used in this study contained a mixture of black spruce (*Picea mariana*) and white spruce (*Picea glauca*). The quantity of fines, defined as the fraction passing through a 200-mesh screen, was 33.0% by weight. Duplicate bleaching treatments were performed on 30g samples at 5% solids. The bleach liquor contained 2.0% hydrogen peroxide on pulp, 5% of 40°Be' sodium silicate, and 0.20g/L magnesium sulfate. A pH of 11.0 was maintained throughout the 4-hour bleaching period.

Kraft pulping

A sample of spruce chips used in the production of the TMP was also obtained for use in the kraft pulping phase. Kraft cooks were conducted on 800g charges of screened chips using a laboratory scale batch digester. A liquor-to-wood ratio of 3.5:1 was used for all three cooks. The effective alkali concentration was 19%, with a sulfidity of 28%. Pulp yield was varied by cooking at 173°C under identical

conditions to different H-Factors. At the end of a cook the chips were removed, washed with tap water, and defibered using a Williams stirrer. The pulp was screened using a slotted flat vibratory screen with 0.0315mm openings. Unscreened and screened yield results are summarized in table 1.

Table 1. Unscreened and screened yield results for spruce kraft pulps.

Sample	H-Factor	Unscreened Yield (%)	Rejects (%)	Screened Yield (%)
Y1	576	54.35	5.61	48.74
Y2	927	49.92	1.61	48.31
Y3	3300	44.71	0.41	44.30

Kraft pulp bleaching

A 50g sample of each of the three kraft pulps was bleached using the following five-stage sequence: 1) chlorination, 2) caustic extraction, 3) chlorine dioxide, 4) caustic extraction, and 5) chlorine dioxide. The goal was to obtain a high brightness pulp in each sample. Because of the wide range of lignin contents, the amount of chlorine added in the first stage was adjusted for each sample to obtain a similar final brightness. The bleaching conditions are summarized in table 2.

Table 2. Experimental conditions for CEDED bleaching of kraft pulps.

Stage	% Solids	Temp. (C)	Time (hr)	Addition Level (% on o.d. pulp)
Chlorination	3	25	1	$\% \, Cl_2$ = kappa no. $\times$ 0.23
Extraction 1	10	70	1	$\% \, NaOH = \% Cl_2 \times 0.55$
Chlorine dioxide 1	10	70	4	$\% \, ClO_2 = 1.0$; $\% NaOH = 0.50$
Extraction 2	10	70	1	$\% \, NaOH = 0.50$
Chlorine dioxide 2	10	70	4	$\% ClO_2 = 0.60$; $\% NaOH = 0.10$

Kraft pulp refining

Prior to refining, the kraft pulps were fractionated through a 200-mesh screen to remove primary fines. Unbleached and bleached pulps were refined at 10% solids using a PFI Mill with a gap clearance of 0.20mm between beating elements. The two refining levels used in this work were 7,500 and 15,000 revolutions. In general, the

7,500 revolution refining level resulted in pulps with a Canadian Standard Freeness around 500ml. The 15,000 revolution level produced pulps in the 200 - 250ml CSF range.

Analysis of pulps

Lignin Analysis

Various pulp properties were used as a measure of the lignin content. These included hypochlorite number (9), kappa number (10), pulp brightness (11), and Klason lignin analysis (12). Selected pulp samples were also analyzed using diffuse reflectance Fourier-transform infrared (FTIR) spectrometry (13). A linear relationship has been shown to exist between the peak area at 1510cm^{-1} and various measures of lignin content, including kappa number and Klason lignin. An advantage of this method is that sample sizes of a few milligrams are used, allowing the lignin content of fiber fines to be determined and compared to long fibers from the same sample.

Carbohydrate analysis

Selected pulp samples were analyzed to determine the carbohydrate composition. The analysis was conducted using a gas chromatographic technique (14). Measurements of araban, xylan, mannan, galactan, and glucan contents were performed on both long fiber and fines fractions.

Weak acid content analysis

The methylene blue dye adsorption method (15) was used to measure the weak acid content of the pulp. This technique was chosen because it is suitable for small sample sizes, and therefore can be used for both the long fiber and fines fraction.

Measurement of electrophoretic mobility

Electrokinetic measurements were performed using the Zetasizer IIc Particle Electrophoresis Analyzer (Malvern Instruments). The Zetasizer IIc uses laser Doppler anemometry to measure the velocity of suspended particles moving under the influence of an applied electric field. This technique allows the distribution of electrophoretic mobilities to be determined for colloidal samples.

Measurements were conducted on the fines fraction (<400-mesh) suspended in aqueous electrolytes of 0.0002$\underline{M}$, 0.002$\underline{M}$, and 0.01$\underline{M}$ NaCl (corresponding to specific conductances of approximately 30, 250, 1,180 μmhos/cm, respectively). Prior to performing a measurement, the pulp was soaked in 0.10$\underline{M}$ HCl for 45 minutes (twice) to remove metal ions, and washed thoroughly with distilled, deionized water to a constant conductance. The pulp was redispersed in the appropriate electrolyte and fractionated through a 200-mesh screen. The filtrate was collected and fractionated through a 400-mesh screen. The filtrate from the 400-mesh fractionation, containing the fines, was diluted with electrolyte solution and the pH adjusted to 6.00 ($\pm$0.05) using dilute HCl or NaOH.

Ten electrophoretic mobility measurements were performed on every sample, two measurements each on five consecutive loadings of the instrument. The average electrophoretic mobility and standard deviation of the electrophoretic mobility distribution were determined for each measurement. Examples of electrophoretic mobility distributions for TMP and kraft fiber fines are shown in figures 2 and 3.

Results and Discussion

Thermomechanical pulp

Bleaching of pulp with alkaline hydrogen peroxide solutions results in the conversion of conjugated chromophoric groups present on the lignin to carboxylic acids and other degradation products (16, 17). Decomposition of hydrogen peroxide to oxygen or hydroxy and hydroperoxy radicals can also result in a certain degree of color reversion and lignin degradation (17). To prevent lignin degradation,

Table 4. Results of TMP long fiber and fiber fines chemical analysis.

Sample	W.A.C. (meq/100g)	Araban (%)	Xylan (%)	Mannan (%)	Galactan (%)	Glucan (%)	Klason Lignin(%)
U-L. Fiber	8.24	1.2	6.2	12.9	2.4	50.8	22.8
U-Fines	13.88	2.0	6.4	9.2	3.7	34.2	36.8
B1-L. Fiber	17.37	1.2	6.3	13.2	2.6	56.6	23.1
B1-Fines	35.88	1.9	6.5	10.2	3.8	37.1	36.1
B2-L. Fiber	17.51	---	---	---	---	---	---
B2-Fines	35.33	---	---	---	---	---	---

Selected samples of TMP long fibers and fiber fines were examined under a scanning electron microscope. An analysis of the long fiber fraction revealed two distinct fiber types: fibers with the primary wall still intact or partially intact; and fibers with the primary wall removed and the secondary wall beginning to show severe damage. Similarly, two distinct fines fractions were observed: flake-like fines originating from middle lamella and primary wall fragments; and ribbon-like fines derived from the secondary wall. Complete details of the scanning electron photomicrographs are given in reference (19). The two distinct fractions in both the long fiber and fiber fines would be expected to have very different surface chemistries.

The average electrophoretic mobility and standard deviation of the electrophoretic mobility distribution data for the TMP fines are shown in table 5.

Table 5. Average electrophoretic mobility results for TMP fines.

Sample	0.0002M NaCl		0.002M NaCl		0.01M NaCl	
	E. Mobility*	St. Dev.**	E. Mobility	St. Dev.	E. Mobility	St. Dev.
TMP-U	-2.39	0.39	-1.30	0.27	-0.74	0.21
TMP-B1	-2.59	0.43	-1.81	0.27	-1.22	0.22
TMP-B2	-2.52	0.39	-1.84	0.23	-1.18	0.21

* Electrophoretic Mobility (μm cm/volt sec).
**Standard deviation of electrophoretic mobility distribution.

The average electrophoretic mobility values for both the unbleached and bleached TMP fines are plotted versus the logarithm of the suspending electrolyte (NaCl) concentration in fig. 4. The error bars represent one standard deviation on either side of the mean of ten measurements. The lines represent linear regressions of the average electrophoretic mobility data. The results indicate that bleaching with hydrogen peroxide produces fines with a more negative electrophoretic mobility. A linear relationship between zeta potential and log_{10} [electrolyte] over the concentration range in this work has also been reported (20) for bacteria and glass particles in dilute KCl solutions.

The standard deviation of the electrophoretic mobility distribution is plotted versus the logarithm of the electrolyte concentration in fig. 5. The data points in each grouping have been separated for clarification. Each data point in fig. 5 corresponds to the indicated value along the x-axis. For both the unbleached and bleached fines, the distribution becomes narrower with increasing electrolyte concentration; however, no significant difference exists between the three samples. This implies that although the average electrophoretic mobility of TMP fines becomes more negative with hydrogen peroxide bleaching, the shape of the electrophoretic mobility distribution does not change.

Kraft pulp

The unrefined kraft pulp chemical analysis results are presented in table 6. The results indicate a wide range of lignin contents within the unbleached pulps. Bleaching the pulp using a CEDED sequence resulted in a considerable decrease in pulp weak acid content. The weak acid content decreased with decreasing yield for both the unbleached and bleached samples.

Table 6. Results of unrefined kraft pulp analysis.

Sample	Hypo. No.	Kappa No.	Klason* Lignin(%)	TAPPI Brightness	Weak Acid Content (meq/100g)
U1	10.5	72.6	12.8	25.8	13.92
B1	—	—	—	89.4	4.72
U2	5.4	36.1	5.6	30.8	9.13
B2	—	—	—	86.6	3.95
U3	2.7	17.8	2.6	35.2	5.41
B3	—	—	—	87.4	3.11

*calculated from diffuse reflectance FTIR analysis.

Selected kraft pulp samples were analyzed for carbohydrate composition to detect changes resulting from decreasing pulp yield and bleaching. The results are shown in table 7. Decreasing the pulp yield decreased the araban, mannan, and galactan content of the pulps. The xylan component was more resistant to removal during pulping than the other sugars. The galactan content was reduced by bleaching and was the only sugar significantly affected by this process.

Table 7. Results of kraft long fiber and fiber fines chemical analysis.

Sample	Araban (%)	Xylan (%)	Mannan (%)	Galactan (%)	Glucan (%)	Klason Lignin (%)	Kappa No.*
U12-Fiber	0.7	6.6	7.2	0.8	75.1	8.7	54.6
U12-Fines	0.7	5.5	7.2	1.1	67.3	15.6*	87.5
U32-Fiber	0.5	7.8	6.6	0.5	78.6	2.3	23.6
U32-Fines	0.4	7.1	6.9	0.4	80.1	3.3*	22.7
B12-Fiber	0.7	7.4	7.3	0.4	81.7	—	—
B12-Fines	0.6	7.4	8.3	0.7	80.8	—	—

*calculated from diffuse reflectance FTIR analysis.

In high yield kraft pulp, the fines had a considerably higher calculated lignin content than did long fibers. This indicates a possible enrichment of lignin-rich primary wall material in the fines fraction. Differences in carbohydrate content also exist between the long fibers and fiber fines from the high yield pulp sample. In

general, the long fibers and fines from the low yield pulp are quite similar in carbohydrate and lignin content.

Analysis of the various fractions using the scanning electron microscope revealed that the surface of a substantial percentage of long fibers from the highest yield (Y1) samples had the S1 layer still intact, as evidenced by a high fibril angle with respect to the fiber axis. The fines fraction from the high yield pulp contained many flake-like fines composed of a network of fibrils. The intermediate yield pulp (Y2) also showed evidence of high fibril angle on the surface of some fibers. In contrast, the surface of long fibers derived from Y3 pulp appeared to originate within the S2 layer, based on the angle of the exposed fibrils. Fines from these pulps were somewhat more fibrillar in nature.

Table 8 summarizes the weak acid content analysis results for the kraft long fibers and fiber fines. With the exception of the high yield samples (U11 and U12), the fines fraction had a considerably lower weak acid content than the long fibers. This is most likely due to differences in hemicellulose content between the two fractions. Some researchers have reported that lignin possesses base-exchange (i.e., acidic) properties (21, 22, 23), and therefore differences in the weak acid content may also result from differences in lignin content. In general, pulps refined at the high level had a slightly lower weak acid content than pulps refined at the low level.

Table 8. Results of kraft long fiber and fiber fines weak acid content analysis.

Sample	Weak acid content (meq/100g)	Sample	Weak acid content (meq/100g)
U11-Fiber	13.10	B11-Fiber	4.50
U11-Fines	13.83	B11-Fines	2.78
U12-Fiber	13.60	B12-Fiber	4.46
U12-Fines	13.61	B12-Fines	2.26
U21-Fiber	9.48	B21-Fiber	3.56
U21-Fines	8.95	B21-Fines	2.64
U22-Fiber	9.45	B22-Fiber	3.31
U22-Fines	7.17	B22-Fines	2.33
U31-Fiber	5.53	B31-Fiber	2.80
U31-Fines	3.51	B31-Fines	2.14
U32-Fiber	5.58	B32-Fiber	2.88
U32-Fines	3.17	B32-Fines	2.10

The average electrophoretic mobility and distribution standard deviation data for the unbleached and bleached kraft pulp fines at both levels of refining are presented in table 9. The average electrophoretic mobility of unbleached kraft fines from pulps refined at the low level (7,500 revolutions) is plotted versus the logarithm of the electrolyte concentration (fig. 6). The lines represent a linear regression of the data, while the error bars depict one standard deviation on either side of the mean of ten measurements. For the spruce kraft pulps, decreasing pulp yield resulted in fines with a less negative electrophoretic mobility. A similar trend was observed with fines from the pulps refined at the high level (i.e., 15,000 revolutions).

Table 9. Average electrophoretic mobility results for kraft fines.

Sample	0.0002M NaCl		0.002M NaCl		0.01M NaCl	
	E. Mobility*	St. Dev.**	E. Mobility	St. Dev.	E. Mobility	St. Dev.
Kraft-U11	-2.40	0.32	-1.68	0.22	-1.12	0.18
Kraft-U12	-2.38	0.30	-1.68	0.23	-1.13	0.20
Kraft-U21	-2.29	0.31	-1.54	0.23	-0.99	0.18
Kraft-U22	-2.39	0.33	-1.59	0.23	-1.05	0.20
Kraft-U31	-2.16	0.34	-1.34	0.23	-0.80	0.19
Kraft-U32	-2.14	0.33	-1.45	0.25	-0.79	0.19
Kraft-B11	-2.19	0.28	-1.39	0.23	-0.82	0.18
Kraft-B12	-2.19	0.29	-1.41	0.21	-0.84	0.18
Kraft-B21	-2.10	0.36	-1.31	0.25	-0.64	0.18
Kraft-B22	-2.11	0.30	-1.35	0.22	-0.73	0.17
Kraft-B31	-1.95	0.32	-1.19	0.23	-0.64	0.18
Kraft-B32	-2.01	0.29	-1.23	0.23	-0.71	0.18

* Electrophoretic Mobility (μm cm/volt sec).
**Standard deviation of electrophoretic mobility distribution.

Once the pulps have been bleached, the effect of yield on the average electrophoretic mobility becomes slightly less pronounced, as shown in fig. 7. Nevertheless, the trend of decreasing pulp yield resulting in a less negative

electrophoretic mobility is the same as the unbleached data. The results for bleached fines at the 7,500 revolution refining level were similar.

The standard deviation of the electrophoretic mobility distribution for kraft pulp fines was not significantly affected by changes in pulp yield. All of the distributions were unimodal, and resembled a Gaussian distribution. Bleaching the pulp did not have a large effect on the standard deviation of the distribution, but may have reduced it somewhat. The distribution standard deviation results for all kraft fines are plotted in fig. 8. Because of the large number of data points in fig. 8, the error bars have been omitted so individual points can be observed more easily.

Bleaching the kraft pulps using a CEDED sequence resulted in a less negative electrophoretic mobility of the fines. McKenzie (8) reported similar results after bleaching *Pinus radiata* sulfate pulps with hypochlorite. The major constituents removed during CEDED bleaching were lignin and hemicelluloses, specifically galactan. Another result of the bleaching process was a significant decrease in the weak acid content of the pulp. We believe that the decrease in weak acid content is responsible for the change in electrophoretic mobility.

Very little difference in electrophoretic mobility was observed between fines from pulps refined at the two levels used in this study. In some samples, fines from the highest refining level were slightly more negative than those from the low refining level. Nevertheless, the effect was small compared to the effect of pulp yield and bleaching. Jaycock and Pearson (24) have reported that increased refining produces a more negative zeta potential for bleached sulfate pulps. The authors attribute this decrease in zeta potential to either the adsorption of negative species during refining or to an increase in the number of negative sites on the fibers. No experimental evidence was given to support either hypothesis. Strazdins (25) has also reported a more negative zeta potential with increased refining of bleached sulfite pulp. In direct contrast, Anderson and Penniman (26) report no change in the electrophoretic mobility of spruce sulfite fines with increased refining over the freeness range of 800ml CSF to 200ml CSF. Davison and Cates (27) report similar results with bleached kraft fines.

Comparison of Weak Acid Content and Electrophoretic Mobility

If the surface charge of wood fibers originates through ionization of acidic (i.e., carboxyl) groups, it is logical to assume that a relationship exists between weak acid content and electrophoretic mobility. Some researchers have reported that increasing carboxyl content results in a more negative zeta potential (7, 28), while others have found just the opposite trend (29, 30). To examine this relationship, the electrophoretic mobility of kraft fines (<400-mesh) is plotted versus the weak acid content of the fines fraction (<200-mesh) in fig. 9. The data points correspond to the average electrophoretic mobility values for both bleached and unbleached fines at each of the two refining levels. An empirical expression of the Langmuir adsorption isotherm form was used to calculate the curves shown in fig. 9. The equation had the following general form:

$$\text{E.M.} = aBW/(1 + aW) \tag{1}$$

where: E.M. = electrophoretic mobility (μm cm/V s)
   a = empirical constant (100g/meq)
   B = empirical constant (μm cm/V s)
   W = weak acid content (meq/100g)

The constants "a" and "B" were determined from linear plots of 1/E.M. vs. 1/W. The values obtained for each electrolyte concentration are presented in table 9.

Table 9. Values of "a" and "B" for kraft fines in various electrolytes.

Electrolyte	a	B	R^2
0.0002$\underline{M}$ NaCl	2.31	-2.46	0.811
0.002$\underline{M}$ NaCl	1.25	-1.75	0.819
0.01$\underline{M}$ NaCl	0.638	-1.22	0.856

This form of equation satisfies the assumption that the electrophoretic mobility would be "zero" when the weak acid content is "zero," and also predicts some limiting value of electrophoretic mobility (B) as the weak acid content becomes very large. Many other types of equations that also satisfy the two criteria listed above were evaluated; however, this particular form was chosen because it provided the

best fit to the data. As shown in fig. 9, the electrophoretic mobility of kraft fines increases sharply (negatively) with increasing weak acid content at low weak acid content values and levels off at higher values.

A linear relationship was found to exist between the empirical constants "a" and "B" and the logarithm of the molar electrolyte concentration. The linear regression equations are given below:

$$a = (-0.989)\log[NaCl] - 1.37 \quad (R^2 = 0.997) \quad\quad [2]$$

$$B = (0.728)\log[NaCl] + 0.229 \quad (R^2 = 1.000) \quad\quad [3]$$

The ability to calculate "a" and "B" lets us estimate the electrophoretic mobility of spruce kraft fines in any concentration of NaCl, provided that the weak acid content of the fines is known. Substitution of equations [2] and [3] into equation [1] gives equation [4], shown below.

$$E.M.= W\{-0.720(\log[NaCl])^2 - 1.22\log[NaCl] - 0.314\}/\{1 + W(-0.989\log[NaCl] - 1.37)\} \quad [4]$$

Equation [4] was used to calculate the electrophoretic mobility of both unbleached and bleached kraft fines for the specific conditions used in this work. The calculated values are compared with experimental measurements in fig. 10. The results demonstrate the ability of the empirical equation to predict the electrophoretic mobility of spruce kraft fines in sodium chloride solutions at pH 6.0. The applicability of equations [1] - [4] to kraft fines in general, or to spruce kraft fines in other electrolytes, is not known. Future research is warranted to address these and other questions concerning relationships [1] - [4].

When measuring the weak acid content, every acidic site accessible to the methylene blue dye molecule within the particle was theoretically being measured. The electrophoretic mobility, on the other hand, is an indirect measurement of only those (ionized) acid groups on the surface of the particle. Relating the electrophoretic mobility to the total weak acid content is valid for a uniform

distribution of weak acids throughout the particle. It would be desirable to plot the electrophoretic mobility versus the weak acid content of the external surface only; however, a technique for accurately measuring the acidic groups present on the external surface of porous substrates does not now exist.

In fig. 11, the electrophoretic mobility and weak acid content data from the TMP fines is added to the kraft data from fig. 9. The curves in fig. 11 are extrapolations of those in fig. 9 for the kraft data only. The bleached TMP data points, at approximately 36meq/100g, appear to fit the curves derived for the kraft data. However, the unbleached TMP data points (14meq/100g) do not appear to fit at high electrolyte concentrations. Because of morphological differences between kraft and TMP fines, different relationships would be expected for mobility versus the weak acid content as measured in this study.

The theoretical relationship between the zeta potential (ζ) and the surface charge density (σ_o), derived from Gouy-Chapman theory for 1:1 electrolytes at 25°C, is given in equation [5] (19):

$$\zeta = (102.8)\tanh^{-1}\{e^{-\kappa\delta}\tanh[0.5\sinh^{-1}(30.18\sigma_o c^{-0.5})]\} \qquad [5]$$

where: ζ = zeta potential [$\zeta \cong 12.85(E.M.)$]
      κ = Debye-Huckel parameter
      δ = distance from surface of particle to the shear plane
      σ_o = surface charge density (coulomb/m^2)
      c = molar concentration of electrolyte

Equation [5] has the same general shape as equation [1] (i.e., it passes through the origin and levels off with increasing surface charge density). The application of equation [5] to the data from this study, however, requires assumptions to be made regarding the appropriate values to use for the shear plane distance and the surface charge density. The rough, porous nature of the surface of fiber fines makes determination of the surface charge density difficult. As yet, accurate experimental techniques for measuring the surface charge and external surface area of porous materials do not exist. Until such techniques are developed, application of

electrokinetic theory to systems of wood fiber fines is only possible after making major assumptions regarding the nature of the potential-determining surface.

Conclusions

The following conclusions were drawn on the basis of this work.

1) Hydrogen peroxide bleaching of spruce TMP produces an increase in the weak acid content. The increase in weak acid content results in a more negative electrophoretic mobility of the fines fraction.

2) The standard deviation of the electrophoretic mobility distribution of TMP fines is not affected by bleaching with hydrogen peroxide.

3) For spruce kraft pulps, decreasing the pulp yield decreases the weak acid content, as does bleaching with a CEDED sequence. This is primarily a result of decreasing lignin content and removal or modification of the hemicelluloses during these operations. The decrease in weak acid content results in a less negative electrophoretic mobility of the fines fraction.

4) Increasing the level of refining does not have a significant effect on the weak acid content or electrophoretic mobility over the range studied in this work.

5) No significant change in the electrophoretic mobility distribution occurs with kraft fines as a result of decreasing pulp yield, bleaching, or increased refining. Increasing the electrolyte concentration, however, does reduce the standard deviation of the electrophoretic mobility distribution for both kraft and TMP fines.

6) A relationship exists between the weak acid content and the electrophoretic mobility of wood fiber fines and can be approximated using an expression of the form of the Langmuir adsorption isotherm.

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FIGURE LEGENDS

Fig. 1. Schematic of experimental design.

Fig. 2. Electrophoretic mobility distribution of bleached TMP fines in 0.0002$\underline{M}$ NaCl. (Average electrophoretic mobility = -2.67 μm cm/volt sec, Distribution standard deviation = 0.507)

Fig. 3. Electrophoretic mobility distribution of unbleached kraft fines in 0.0002$\underline{M}$ NaCl. (Average electrophoretic mobility = -2.36 μm cm/volt sec, Distribution standard deviation = 0.314)

Fig. 4. Electrophoretic mobility versus log electrolyte concentration for TMP fines. (■ = unbleached; □ = bleach 1; o = bleach 2)

Fig. 5. Standard deviation of electrophoretic mobility distribution versus log electrolyte concentration for TMP fines.
(■ = unbleached; □ = bleach 1; o = bleach 2)

Fig. 6. Electrophoretic mobility versus log electrolyte concentration for unbleached kraft fines: 7,500 revolutions.
(Δ = 44.7% yield; o = 49.9% yield; □ = 54.4% yield)

Fig. 7. Electrophoretic mobility versus log electrolyte concentration for bleached kraft fines: 15,000 revolutions.
(Δ = 44.7% yield; o = 49.9% yield; □ = 54.4% yield)

Fig. 8. Standard deviation of electrophoretic mobility distribution versus log electrolyte concentration for kraft fines. (■ = unbleached; □ = bleached)

Fig. 9. Electrophoretic mobility versus weak acid content for kraft fines.
(■ = unbleached; □ = bleached)

Fig. 10. Electrophoretic mobility calculated from equation [4] versus measured values.
(■ = unbleached kraft; □ = bleached kraft)

Fig. 11. Electrophoretic mobility versus weak acid content for kraft and TMP fines. (■ = unbleached (kraft); □ = bleached (kraft); ● = unbleached (TMP); o = bleached (TMP); —— = calculated from [1])
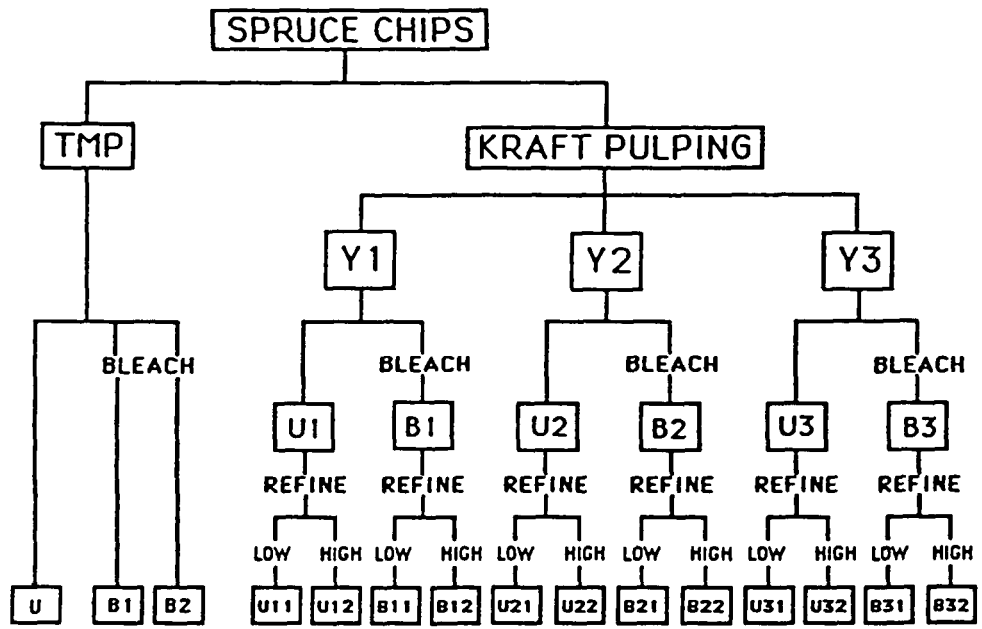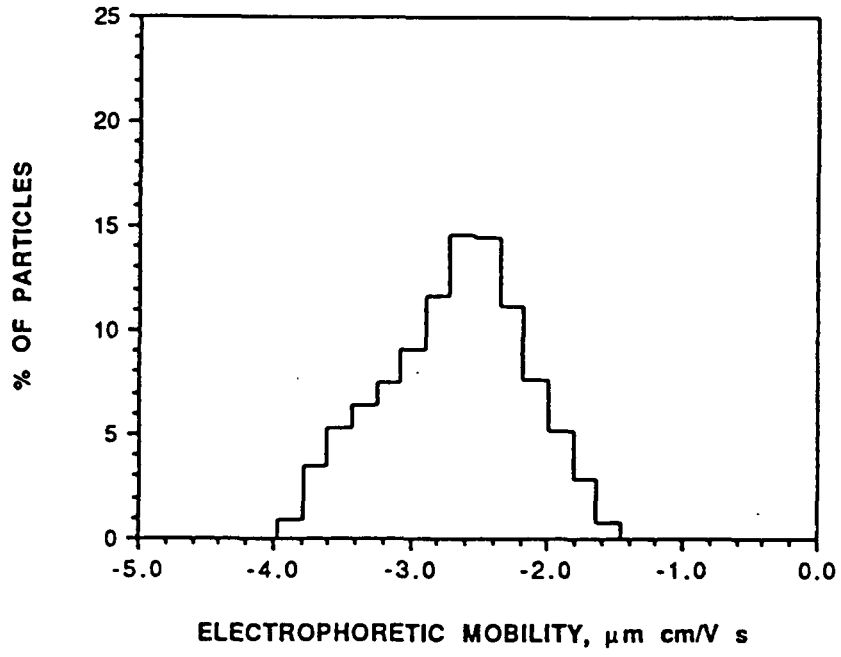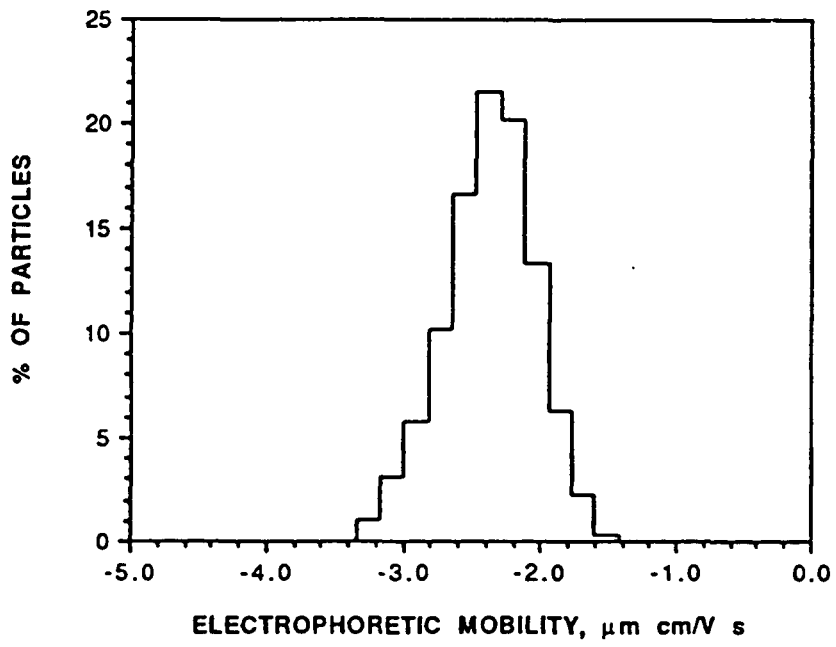
Figure 1.

Figure 2.

ELECTROPHORETIC MOBILITY, μm cm/V s

Figure 3.

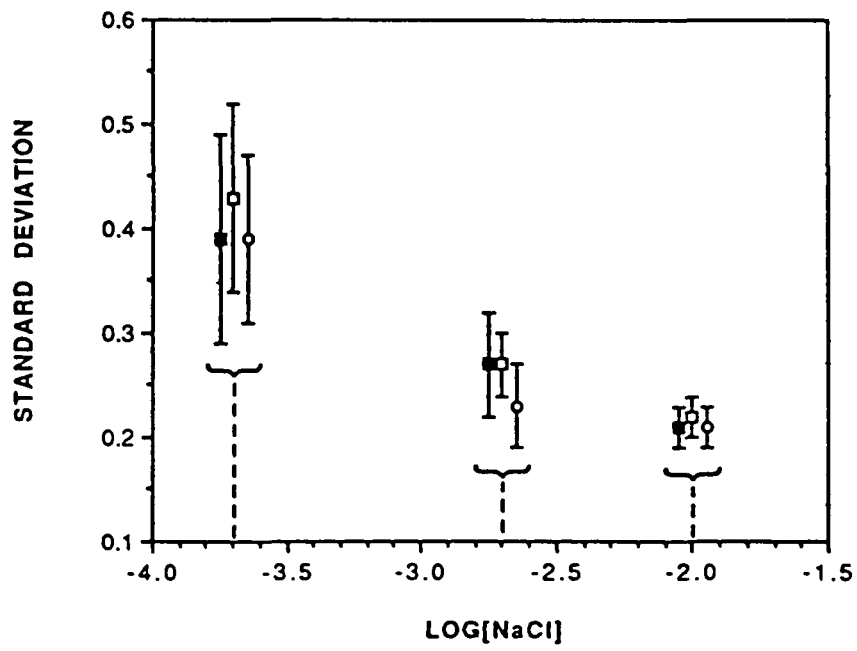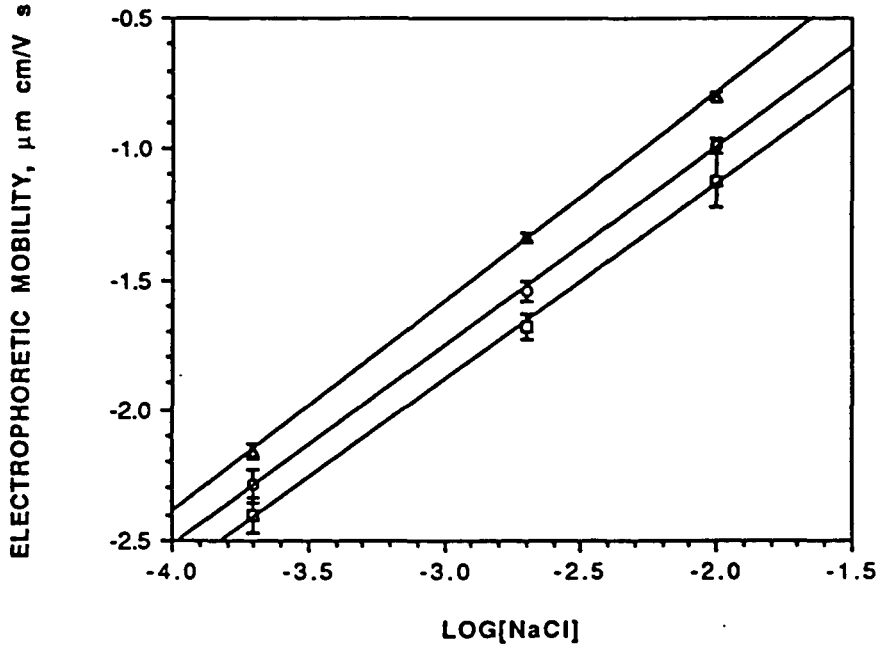

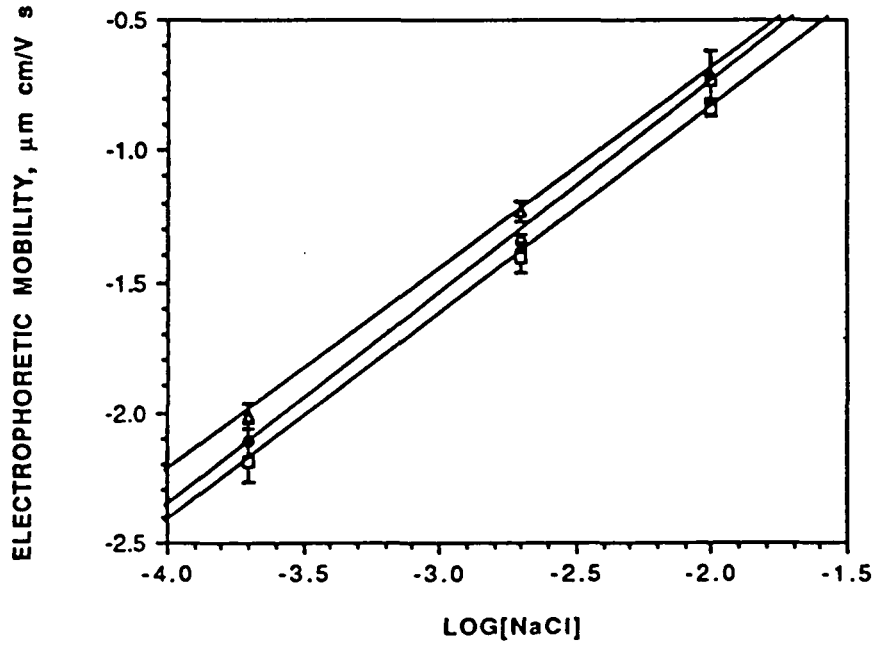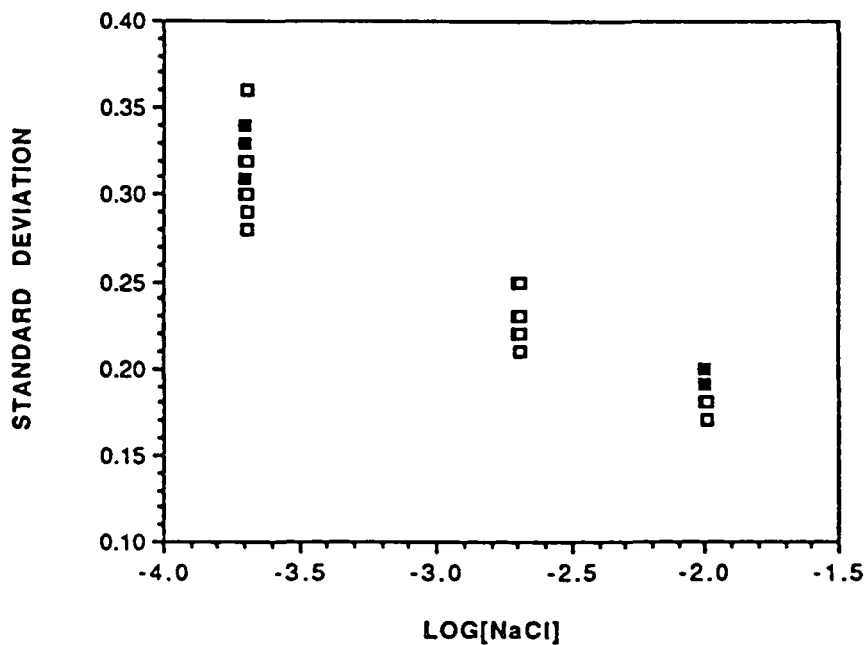ELECTROPHORETIC MOBILITY, μm cm/V s
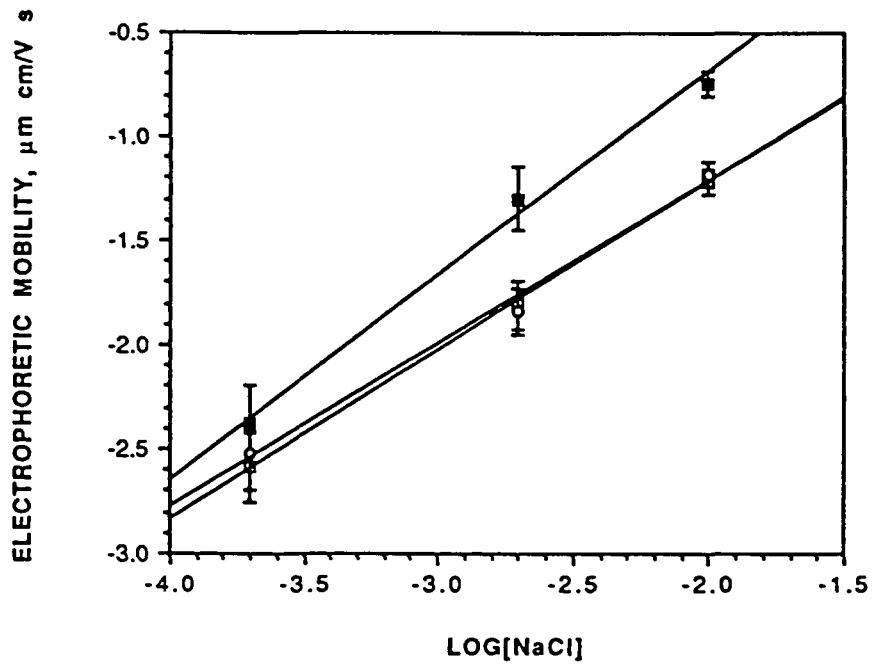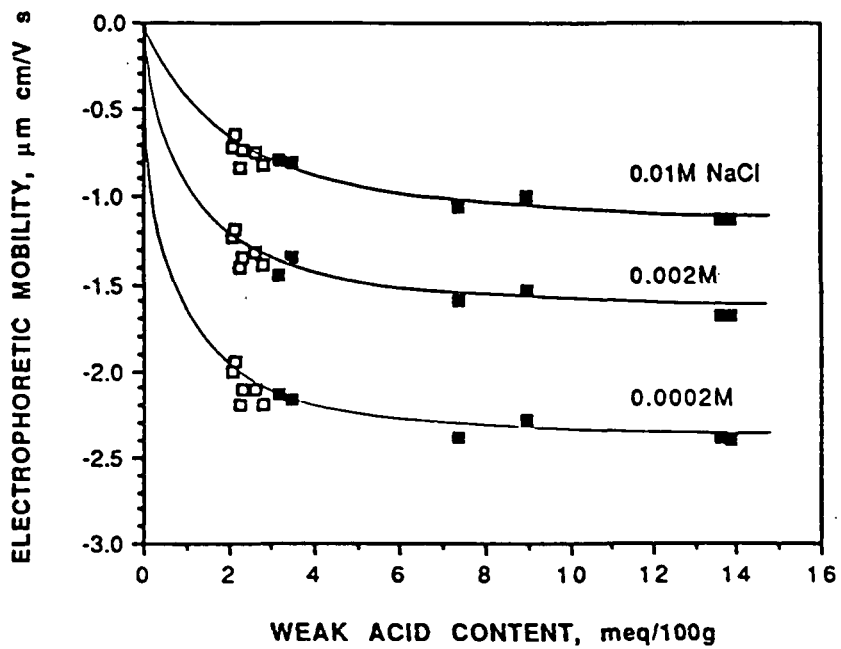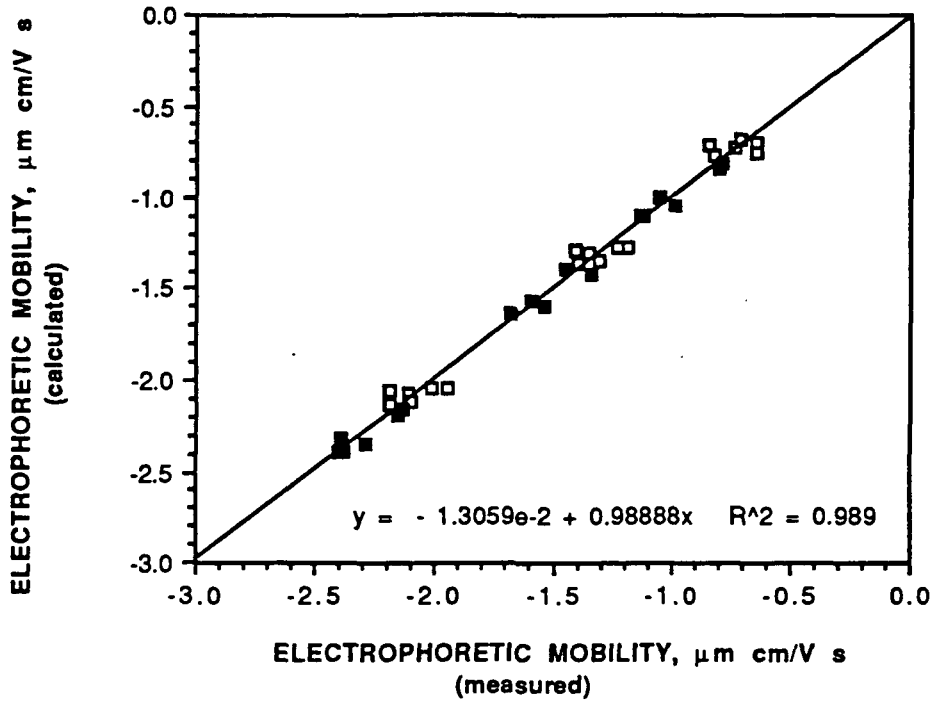
Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

ELECTROPHORETIC MOBILITY, μm cm/V s (measured)

$y = -1.3059e-2 + 0.98888x$ $R^2 = 0.989$

Figure 11.

0.01M NaCl

0.002M

0.0002M

WEAK ACID CONTENT, meq/100g