Determination of fiber charge components of Lo-Solids unbleached kraft pulps

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Abstract

Four different titration methods for measurement of fiber charge were used in this study. Each method gave different fiber charge values depending on the acidity of the end point and the interaction between the fiber chemical components and the titrant. Also, the interactions between the ionizable groups on the fiber had significant effects on the interpretation of these results. The conductometric titrations showed trends similar to the results obtained from the potentiometric titration. The conductometric titrations with NaOH produced higher fiber charge values, higher than the titrations with NaHCO₃. The differences between the results obtained from the potentiometric and polyelectrolyte titrations, which were associated with the dissolved fiber components during the delignification, were linearly related to the kappa number of pulps. The positive intercept of this linear relationship indicated that the kraft pulping process not only removed the ionizable groups associated with the dissolved components, but at the same time provided conditions to form new ionizable groups in the fibers. The polyelectrolyte titration results indicated that the lignin content in the fibers did not affect the fiber surface charge. Data extracted from the FTIR spectra of protonated fibers were highly correlated with the fiber charge values obtained from the conductometric titration with NaOH.

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1. Introduction

Wood pulp fibers carry a charge when suspended in water due to the ionization of acidic groups in the hemicelluloses and lignin. These ionizable groups are mainly carboxylic acid, sulfonic acid, and alcoholic, phenolic, and hydroxyl groups [1]. The fiber charge density depends on the origin of the fiber, chemical treatment (pulping and bleaching), and mechanical treatment (refining or beating). The carboxylic and sulfonic acid groups are the major contributors to the fiber charge. Kraft pulps have higher carboxyl content than sulfite pulps. In both softwoods and hardwoods the majority of carboxyl groups can be found in gluconurxoxyans. The rest can be found in pectic substances, which are located in the middle lamella region of the wood. The sulfonic acid groups are mainly found in sulfite pulps.

The charge density on cellulotic fibers depends not only on the mechanical and chemical treatment applied to the wood but also on pH and the electrolyte concentration in the surrounding water.

During alkaline pulping the carboxyl content of the fibers is successively decreased because of the dissolution of acidic polysaccharides, particularly xylans [1,2], at the same time carboxyl groups can be formed through oxidation reactions (O₂) in an alkaline environment by so-called disproportionation reactions of the Cannizzaro-type [3].

During typical kraft pulping up to 20% of the phenyl propane units can be oxidized in this way [3].

Bleached pulps have a lower acid content of ionized acidic groups primarily because lignin and hemicelluloses are dissolved during bleaching.

The fiber charge is an important factor in papermaking processes because many of the interactions between soluble and particulate fractions of papermaking furnish are charge-induced. The effects of fiber charge on retention of additives at the wet end of paper machines are the main subject in many studies [4,5].

The charge density of the fibers is also a major factor in formulation of hydrogen bonding between fibers. Pulp properties such as hydrophilicity (wettability) and fiber swelling
have also been shown to be influenced by fiber surface charge [6]. Measurements of fiber charge are therefore important parts of optimization of stock preparation prior to the sheet formation stage [7].

Few methods have been used for determining fiber charge [8–11]. Titration techniques such as potentiometric [12,13], conductometric [14], and colloidal [15] have been developed. Polyelectrolyte titration, which determines the amount of a charged polymer that is adsorbed on the fiber surface, has proved to be a popular method for the control of the wet-end chemistry [16].

The fiber charge is related not only to the carboxylic groups of the carbohydrate but also on the phenolic groups of lignin in the fibers. It is evident that pulping and bleaching conditions, which are directly related to the destruction and formation of these groups, have significant effects on the electrokinetic properties of fibers [17–22].

In this paper, the fiber charges of high-yield kraft pulps of different Kappa number were determined using the potentiometric, conductometric, and polyelectrolyte titrations. The results were then compared to identify the fiber components that are associated with the measurements. The relationship between the fiber charge and data on IR spectra of the pulps were also studied.

### 2. Materials and methods

#### 2.1. Chemicals

The analytical grades of NaOH, HCl, NaCl, and NaHCO3 were used in the conductometric titrations. Polydiallyldimethyl ammonium chloride (Poly-Dadmac) and sodium polyethylene sulfate (PES-Na), which were used in the polyelectrolyte titration, were obtained from ACA Scientific Pty. Ltd. These chemicals were diluted with deionized water with a conductivity of 8.4 mS/cm to the desired concentration with deionized water before use. Nitrogen was used to prevent the absorption of carbon dioxide into the test samples during the potentiometric and conductometric titrations.

#### 2.2. Sources and preparation of pulps

The unbleached kraft pulps were produced from *Pinus Radiata* using flow-through reactors. The cooking conditions were designed to simulate a commercial Lo-Solids kraft pulping method, which included three stages: impregnation at 110 °C for 30 min; first stage of cooking at 139 °C for 50 min; second stage of cooking at 143 °C for different time periods to obtain the target Kappa number. All cooking stages were operated using a cooking liquor of 0.5 M of effective alkali as Na2O and at a sulfidity of 30%.

These pulps were kept in never-dried condition prior to the charge measurement. All the pulp samples were stored in a refrigerator at 4 °C in the form of wet fiber pad at dry content of about 30 ± 2%.

Before the charge measurements were undertaken, the pulp samples were converted to their fully protonated form by soaking the redispersed pulp pad at 1% consistency in 0.01 M hydrochloric acid for 16 h as suggested by Lloyd and Horne [19]. The pulp pH after 16 h of soaking was close to 2.2. The pulps were then vacuum-filtered using a Buchner funnel and washed several times with deionized water until the pH of the water filtrate was close to 6.0. The vacuum was maintained until no more water could be extracted from the pulp mat. After each titration, the amount of fiber in each sample was determined gravimetrically by (1) filtering the pulp on preweighed filter paper and (2) drying in an oven at 105 °C until the constant weight was obtained.

#### 2.3. Determination of Kappa number in pulps

Tappi test method T 236 om-99 was used in this study.

#### 2.4. Determination of charge

##### 2.4.1. Conductometric titrations

Approximately 0.5 g of the protonated pulp was dispersed in 1 mM sodium chloride (100 ml) and addition of 0.5 ml of 0.05 M HCl was made before the start of titration. The titration was performed with two kinds of titrant; one was 0.05 M NaOH and the other was 0.05 M NaHCO3, in a constant-temperature water bath set at 25 °C. The 718 STAT Titrino autotitrator from Metrohm and the LC-81 conductivity meter from TPS Pty. Ltd. were used for the titration. Conductivity measurements were made every minute after each addition of 0.1 ml of alkali solution, except near the point of inflection where readings were taken after every 0.05 ml of alkali. The conductometric titration is based on changes in conductance of the suspension. The conductance is related to the concentration of the most highly conducting ions, i.e., the hydrogen and hydroxyl ions in the suspension. The addition of HCl is made before the start of titration. The conductance decreases due to a neutralization reaction between strong acid and added alkali. Further additions of alkali react with the weak acid groups bound to the pulp, causing a buffering effect, and do not change the conductance. Excess alkali again raises the conductance. The resultant conductivity of the suspension was plotted against the volume of alkali added. The fiber charge was calculated using the volume of alkali required to reach the second inflection point from the first inflection point of the plot.

##### 2.4.2. Potentiometric titration

The potentiometric titrations were performed using a high-precision, microprocessor-controlled autotitrator (Metrohm-718 STAT Titrino). The pH of the slurry was determined using a combined pH glass electrode. The electrode was calibrated using buffer solutions of pH 4.0, 7.0, and 9.2. During the titrations, a magnetic stirrer with a Teflon rod was used to mix the pulp suspension. The rate of titrant addition was controlled at 0.3 ml/min. The data were recorded...
every 30 s by a data logger. All the potentiometric titrations were performed with a pulp suspension at 0.5% consistency in 0.005 M HCl in 1 mM NaCl and at 25 °C. A 100-ml blank solution of 0.005 M HCl in 1 mM NaCl was used and titrations were performed with 0.05 M NaOH in 1 mM NaCl to determine the blank titration curve. The fiber charge was calculated using the formula

\[ Z_p = \frac{1000V_c}{w} \]

where \( Z_p \) is fiber charge (mmol/kg), \( V \) is titer difference (ml), \( c \) is titrant concentration (mol/l), and \( w \) is weight of dry pulp (gm).

2.4.3. Polyelectrolyte titrations

A 0.5-g protonated pulp sample was diluted with 100 g of 0.001 N Poly-Dadmac polymer and stirred by a magnetic stirrer for 2 h. The molecular weight of Poly-Dadmac was between 150,000 and 200,000 g/mol. During this time the cationic polyelectrolyte completely neutralized the anionic charge in the pulp. The solid content of the pulp was then removed by filtration using a nylon sieve (100 mesh), and 10 ml of the filtrate were pipetted into the cell of PCD-02 (MUTEK) for titration. The polyelectrolyte titration reagent used was 0.001 N sodium polyethylene sulfate (PES-Na).

The polyelectrolyte titration was performed to the end point when the streaming potential reached 0 mV. The particle charge detector comprised a cylindrical plastic vessel in which the required liquid flow was produced by a vertically reciprocating displacer piston fitted inside. To retain the charge carrier within the flowing medium, solid particles and dissociated polymer from the filtrate were adsorbed at the cylinder and piston surfaces. Depending on the piston movement, the charge cloud was distorted upward or downward. Two electrodes in the upper and lower sections of the test vessel take off the induced streaming potential. The rate of titration was controlled at 0.3 ml/min. In addition 10 ml of Poly-Dadmac solution was titrated with PES-Na to the neutral point to determine the blank value. In this investigation all charge determinations were made at an electrolyte strength of 0.01 M NaCl. The specific charge density of the sample was calculated by the formula

\[ q = \frac{(V_p - V_b)c \times 1000}{w} \]

where \( q \) is specific charge density (mmol/kg), \( V_p \) is volume of titrant used for pulp (ml), \( V_b \) is volume of titrant used for blank (ml), \( c \) is concentration of titrant (mol/l), and \( w \) is solid content of pulp (g).

2.4.4. Measurements using FTIR-ATR

Fourteen protonated pulps with different Kappa numbers in the range 40–128 were used in this exercise. Infrared spectra of paper handsheets made from these pulps were obtained using a Perkin–Elmer FTIR spectrometer (GX model) equipped with a horizontal attenuated total reflectance (HATR) cell. The spectra were recorded in absorbance units. Each sample was scanned four times at 4 cm\(^{-1}\) resolution and scan interval of 1 cm\(^{-1}\) and the average spectrum was accounted. The spectra were normalized using the characteristic band for cellulose at 1030 cm\(^{-1}\). The calibration was performed using the Spectrum Quant+ program, which employs the partial least squares (PLS) method. The spectral data were correlated with the fiber charge values obtained from the conductometric NaOH titration. The IR absorption region 1700–1030 cm\(^{-1}\) was selected for the analysis. Seven samples were used for the calibration and the resultant model was validated using the other seven samples.

3. Results and discussion

3.1. Comparison of charge measurement methods

The shapes of typical titration curves for conductometric, potentiometric and polyelectrolyte titrations using PCD02 are shown in Figs. 1, 2, and 3, respectively.

During the first potentiometric titration the holding time required for the pH of the pulp suspension to reach the equilibrium was investigated. The results as shown in Fig. 4 indicated that the variation of pH within the holding time of about 5 min at pH < 7.0 was less than 0.05 unit and at pH > 10 was about 0.03 units. These insignificant variations
suggested that 5 min of holding time was adequate for the potentiometric titration.

The average fiber charge values, which were obtained from at least three tests on each sample, are summarized in Table 1. It should be noted that the potentiometric and polyelectrolyte titrations have been respectively established for determining the total and surface charge of fibers [20–22]. Laine et al. [20] attempted to interpret the potentiometric titration curve using a model taking into account the existence of two ionized acidic groups on fiber surface. Their results proved that the interactions between the ionized groups on the fiber surface were in fact much more complicated than their assumptions. The conductometric titration methods, which were less time-consuming, were also developed for fiber charge measurements [19].

In this study it is our interest to compare the results obtained from these titrations applied to Lo-Solids kraft pulps of different Kappa number and to use the differences between these measurements to identify the contribution of fiber chemical components on the fiber charge.

The fiber-charge values obtained from the conductometric and polyelectrolyte titrations are plotted against the values obtained from the potentiometric titrations in Fig. 5. The results show clearly that the surface fiber charge which is obtained from the polyelectrolyte titration is apparently independent of the total charge, as measured by the potentiometric titration. The average surface charge of the kraft pulps is about 53 mmol/kg.

The results obtained from the conductometric titration with NaOH and the potentiometric titrations are very close and follow similar trends. However, the relationships between these two titrations are not perfectly linear. The differences of these results are most likely due to the different acidity at the point where the titration results are used in the calculation of fiber charge.

It is noticeable that the conductometric titration with NaHCO$_3$ yields the lowest fiber charge values as compared with the results obtained from the potentiometric and NaOH titrations. Perhaps this is because the NaHCO$_3$ titration is dealing with only the carboxylic groups (pK$_a$ 4.0–4.5), while the other titrations involve the ionization of both the carboxylic and phenolic groups (pK$_a$ 9.0–9.5) on the fibers. Pu and Sarkenan [23], who studied the charge of fibers produced from hemlock and cottonwood, found similar results. They postulated that the difference was due to the ionization of some of the phenolic hydroxyls during sodium hydroxide titration, which has a higher end pH. Lloyd and Horne [19] suggested that at pH 8.5 some of the more acidic phenolic hydroxyls in the lignin would have started to dissociate and would be detected as weak acids by the conductometric titration procedure.

### 3.2. Effect of pulp Kappa number on fiber charge

Table 1 and Fig. 6 summarize the results to show the effect of Kappa number on the fiber charge measurements.

The results show that the fiber surface charge as measured by the polyelectrolyte titration varies insignificantly around a mean of 53 mmol/kg suggesting that the lignin content in a well-washed protonated fiber does not affect its surface charge.

In general, the fiber charge values obtained from the potentiometric and conductometric titrations decrease with decreased Kappa number. This trend can be explained by the fact that the losses of ionized groups are related to the dissolution of lignin and hemicelluloses during kraft pulping.

The differences (Δ) between the fiber charge values obtained from the potentiometric and polyelectrolyte titrations are plotted against Kappa number (Fig. 7). These differences represent the contribution to the fiber charge from dissolved lignin and hemicelluloses.

**Table 1**

<table>
<thead>
<tr>
<th>Kappa</th>
<th>Fiber charge, mmol/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potentiometric titrations</td>
<td>Conductometric titrations</td>
</tr>
<tr>
<td>NaOH</td>
<td>NaHCO$_3$</td>
</tr>
<tr>
<td>39.6</td>
<td>75 ± 2</td>
</tr>
<tr>
<td>60.8</td>
<td>78 ± 13</td>
</tr>
<tr>
<td>79.9</td>
<td>94 ± 6</td>
</tr>
<tr>
<td>94.7</td>
<td>109 ± 3</td>
</tr>
<tr>
<td>105.0</td>
<td>97 ± 1</td>
</tr>
</tbody>
</table>

**Fig. 5.** Comparison of fiber-charge values obtained from different methods.

**Fig. 4.** pH variation during a potentiometric titration (Kappa number 103) with a holding time of about 5 min.
Fig. 6. Charge of the kraft pulps of different Kappa numbers as determined by different titration methods.

![Graph showing charge of kraft pulps](image)

Fig. 7. The difference ($\Delta$) in fiber charge against Kappa number as determined by potentiometric and electrolyte titrations.

![Graph showing difference in fiber charge](image)

Fiber components as a result of the delignification. A linear relationship with a regression coefficient, $R^2$, of 0.8 is obtained:

$$\Delta = 0.5(Kappa \ number) + 1.1.$$  

This relationship suggests that the loss of fiber charge is strongly related to the dissolution of lignin from fibers during kraft pulping.

The presence of the positive intercept of the above linear relationship indicates that the delignification not only removes the ionized groups but at the same time creates new ionizable groups in the fibers, as previously suggested [2]. However, this observation should be treated cautiously due to the fact that the intercept is smaller than the error of charge measurements as listed in Table 1.

The FTIR-ATR spectra of the protonated samples are shown in Fig. 8. The Spectrum Quant+ program is used to perform the PLS1 analysis and establish the correlation between the spectral data and charge values of the pulp samples. The PLS1 results are summarized in Table 2. The wavenumber range of 1700–1030 cm$^{-1}$ is selected for this analysis. This range covers the characteristic bands of carboxylic groups (1725–1700 cm$^{-1}$), carboxylate (1610–1550/1420–1300 cm$^{-1}$), and lignin (1505–1600 cm$^{-1}$).

The X-variance shows the cumulative amount of spectral variance as a percentage of the total, and the Y-variance shows the cumulative amount of property variance (fiber charge value) as a percentage of the total. The method for calculation of X-variance and Y-variance is described in the Spectrum Quant+ User’s Reference supplied by Perkin-Elmer. In the range 1700–1030 cm$^{-1}$ two principal components are identified. These components can explain about 95–96% of the variance in the X-matrix and 93–98% of the variance in the Y-matrix. When the wavenumber range...
Table 2
Summary of FTIR-ATR measurement results

<table>
<thead>
<tr>
<th>Particulars</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
<th>Trial 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor compression cutoff point selected at (n = )</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>PC1</td>
<td>PC2</td>
<td>PC1</td>
<td>PC2</td>
<td>PC1</td>
<td>PC2</td>
</tr>
<tr>
<td>X-variance</td>
<td>94.8</td>
<td>96.0</td>
<td>95.0</td>
<td>96.1</td>
<td>96.1</td>
</tr>
<tr>
<td>Y-variance</td>
<td>93.3</td>
<td>98.1</td>
<td>93.3</td>
<td>98.4</td>
<td>93.5</td>
</tr>
<tr>
<td>(R^2) (calibration)</td>
<td>98.1</td>
<td>98.4</td>
<td>98.8</td>
<td>93.4</td>
<td>93.4</td>
</tr>
<tr>
<td>Std. error of estimate (SEE)</td>
<td>4.21</td>
<td>3.86</td>
<td>3.33</td>
<td>6.95</td>
<td>8.42</td>
</tr>
<tr>
<td>(R^2) (actual to predicted charge)</td>
<td>0.973</td>
<td>0.974</td>
<td>0.973</td>
<td>0.963</td>
<td>0.933</td>
</tr>
</tbody>
</table>

Fig. 9. Comparison between fiber charge values obtained from conductometric NaOH titration and predicted values.

is narrowed down to 1650–1050 cm\(^{-1}\), the X-variance increases and the standard error of estimate (SEE) reduces. When the wavenumber range shifts to 1600–1100 cm\(^{-1}\) the PLS model can explain about 96–97% of the variance in the X-matrix and 94–99% of the variance in the Y-matrix, the SEE is further reduced. In the wavenumber range of 1325–1200 cm\(^{-1}\), the number of principal component is reduced to one and the regression coefficient, \(R^2\), of the model is reduced to a lower value (93.4%). It is apparent that the range of 1600–1100 cm\(^{-1}\) is the best for the formulation of the predictive model if \(R^2\) is used as the criterion for model selection. The model is then tested using seven different pulp samples. The comparison of the predicted and the fiber charge values obtained from the conductometric NaOH titrations, as shown in Fig. 9, has a regression coefficient higher than 97%.

4. Conclusions

Four titration methods for fiber charge measurement are used in this study. It is apparent that each method gives a different fiber charge value, depending on the acidity of the endpoint and the interaction between the fibers and the titrants.

The potentiometric and conductometric NaOH titrations yield similar results. Both potentiometric and conductometric titrations with NaOH resulted in higher values of fiber charge in comparison to titrations with NaHCO\(_3\). The differences between the potentiometric and polyelectrolyte titrations, which is approximately linearly related to Kappa number, indicate that the kraft pulping process removes the ionizable groups by dissolving the fiber chemical components. The positive intercept from this linear relationship indicates that the delignification provides conditions to form new ionizable groups within the fibers as well.

The electrolyte titration does not pick up the effect of Kappa number, suggesting that the lignin in the fiber wall has an insignificant effect on the fiber surface charge. This is obviously true only when the fibers are well washed.

The information extracted from FTIR-ATR spectra can be used to identify the wavenumber ranges that are associated with the ionizable groups in fiber. The PLS method can be used to formulate a robust model for predicting the fiber charge based on this finding.

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References


