Appropriate Conditions for Polyelectrolyte Titration to Determine the Charge of Cellulosic Fibers

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**Appropriate Conditions for Polyelectrolyte Titration to Determine the Charge of Cellulosic Fibers**

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**Abstract**

The polyelectrolyte titration method has been developed over the years in order to determine the surface charge of cellulosic fibers. The conditions have been varied depending on the author. This work has been aimed at resolving the appropriate conditions for measuring the charge, such as electrolyte concentration and molecular mass of the polyelectrolyte. The charge ratio of variously treated pulps was also investigated.

The polyelectrolyte titration technique is based on a 1:1 adsorption stoichiometry between fiber and polyelectrolyte charges. Adsorption of polydiallyldimethylammonium chloride (poly-DADMAC) was first performed at various electrolyte concentrations and then with various molecular masses. ESCA (Electron Spectroscopy for Chemical Analysis) was used to independently validate the polyelectrolyte titration method.

Results showed that stoichiometry prevails at low electrolyte concentrations. Increasing the electrolyte concentration screens the fiber charges, initially enhancing the adsorption and causing a deviation from stoichiometry. Further increases in electrolyte concentration eventually decrease the adsorption. Deviation from stoichiometry occurred at higher electrolyte concentrations for higher charge density pulps. ESCA-measurements showed that high and low molecular mass cationic polyelectrolyte adsorb to the same extent on the fiber surface, confirming stoichiometry. There was a good agreement between the two techniques, hence, the polyelectrolyte titration technique is a good method to measure surface charges. Comparing the charge ratio between different kind of pulps and treatments, it was found that mechanical pulps have a higher surface charge than chemical pulps. The charge ratio of chemical pulps was, however, practically unchanged when comparing different types of wood and bleaching sequences.

**KEYWORDS:** Adsorption, electrolyte, polyelectrolyte, polyelectrolyte titration, charge stoichiometry, charge ratio, diffuse electric double layer, Debye length, poly-DADMAC, cellulosic fibers, ESCA.
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1 The origin of charge

Wood mainly consists of three substances that are physically or chemically attached to each other: cellulose, hemicellulose and lignin. Cellulose and hemicellulose are polysaccharides that are built of simple sugar monomers, called carbohydrates. Lignin consists of aromatic units. Besides these three substances, wood also contains extractives and other materials in smaller amounts. The relative composition of wood depends on the tree species.

In order to vary the properties of the paper, it is important to be able to control fiber properties such as fibrous structure, optical quality and chemical composition. Generally, long fibers improve strength properties of the paper if the sheet can be formed with small variations in the grammage. Fiber dimensions are changed depending on the type of method used to separate the fibers. Wood tends to delaminate and swell when components are removed by conventional pulping chemicals and when the fibers are subjected to mechanical action, such as beating and refining (Kerr and Goring, 1975).

Ionizable functional groups are an important factor in various unit operations and on paper properties in papermaking (Scallan, 1983; Lindström, 1989, 1992; Eklund and Lindström, 1991). Only the carboxylic acid groups are ionized during normal papermaking conditions (neutral and weakly acidic). A rather high pH is required to ionize phenolic hydroxyl groups and strong alkali is needed for such weak acids as alcoholic hydroxyl groups (Sjöström, 1989).

The carboxyl groups give native wood and mechanical pulp fibers their negative charge, the majority of these carboxyl groups are uronic acid type and mainly attached to xylan. However, native wood only carries a few charges since the carboxyl groups are esterified to various degrees depending on the wood species. The esters are then hydrolyzed during bleaching of mechanical pulp, giving rise to an increased amount of carboxyl groups. The rest of the carboxyl groups are located on minor polysaccharide constituents such as pectic substances (Sjöström, 1989; Lindström, 1992).

Wood chips of chemi-mechanical (CTMP) and chemi-sulfite pulps are treated with sulfite to introduce sulfonic acid groups. The extent of sulfonation, which depends on the pulping and impregnation conditions, is higher for softwood pulps than for hardwood pulps. The ion-exchange capacity decreases during delignification of sulfite pulp as both the residual lignin, where the sulfonic acid groups are introduced, and the hemicellulose content decrease (Lindström, 1992), see Figure 1(a).
During kraft pulping, the carboxyl content decreases because of the dissolution of acidic polysaccharides, particularly xylan (Sjöström, 1989). The major part of the carboxyl groups present in xylan originates from hexenuronic acids (Buchert et al., 1995). Hardwood has a higher charge content than softwood due to a higher xylan and uronic acid content (Laine et al., 1996). Two types of acidic groups were found in unbleached kraft pulp by Laine et al. (1996). The lower pK-value corresponds to uronic acid, while the weaker pK-value corresponds to carboxylic acid groups bound to lignin.

Carboxylic acid groups are created during bleaching of chemical pulp, but the amount of acidic groups decreases due to dissolution of lignin and hemicellulose (Gellerstedt and Lindfors, 1987; Sjöström, 1993). It has been shown by Buchert et al. (1995) that ozone and chlorine dioxide almost completely destroy the hexenuronic acids, whereas peroxide and oxygen have no effect. Introduction of carboxylic acids groups occurs from bleaching agents oxidizing the polysaccharide chain, forming aldehydic groups after each cleavage. Depending on the prevailing bleaching conditions, the aldehydic groups are either oxidized to carboxylic acid groups or initiate a peeling reaction of the polysaccharide chain (Sjöström, 1993).
2 Polyelectrolyte adsorption

2.1 Theory

Two main approaches exist for the adsorption of polymers: mean-field theories (Flory, 1953; van der Schee and Lyklema, 1984; Fleer et al., 1993) and scaling concepts (de Gennes, 1981; Dobrynin et al., 2001). In the mean-field approach, interactions are the same for any segment because of identical local environments. Each segment experiences a mean-field interaction that represents an average of the neighboring interactions. Scaling concepts consider the solution as a close assembly of self-avoiding subchains represented as packed "blobs". The blob size is equal to the radius of gyration (below overlap) in dilute solutions, whereas the blob size decreases with increasing polymer concentration in semi-dilute solutions (beyond overlap).

Electrostatic interactions are important for the adsorption of polyelectrolytes onto an oppositely charged surface (Hesselink, 1977; Cohen Stuart et al., 1991). The charge density of both the polyelectrolyte and the surface affect the adsorption. Electrolyte concentration and, in some cases, pH are important factors as well.

In the presence of an (monovalent) electrolyte, polyelectrolyte adsorption onto an oppositely charged surface can either increase or decrease with increasing electrolyte concentration. If the interactions are purely electrostatic, theory predicts that the adsorption decreases due to the electrolyte screening both the segment-segment repulsion and the segment-surface attraction. In the case of non-electrostatic interactions, the repulsion between segments dominates the adsorption so that the screening of the repulsion at high electrolyte concentration causes the polyelectrolyte to behave as an uncharged polymer. The polyelectrolyte will conform in loops and tails, which enhance the adsorption. This is illustrated in Figure 2, where the adsorbed amount is plotted as a function of electrolyte concentration for various values of the adsorption energy parameter, $\chi_s$, which expresses the non-electrostatic affinity for the surface.

For pure electrostatic interaction ($\chi_s=0$), adsorption monotonically decreases with increasing electrolyte concentration. However, the screening effect is almost eliminated when a small non-electrostatic interaction ($\chi_s>0$) is introduced. A small increase in adsorption is seen before the adsorption decreases slightly. Higher $\chi_s$ values clearly enhance adsorption. A scaling theory by Dobrynin et al. (2001) also predicted that the adsorption will first increase at low ionic strength before decreasing at high ionic strength. Experiments have also shown that this is the case for various polyelectrolytes.
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Figure 2: Adsorbed amount as a function of electrolyte concentration for different values of $\chi_s$, the non-electrostatic interaction with the surface (van de Steeg et al., 1992).

onto silica (Cohen Stuart et al., 1991; Shubin, 1997), latex (Shubin et al., 1997), and cellulose (Tanaka et al., 1979; Lindström and Wågberg, 1983; van de Steeg et al., 1993).

Figure 3: Adsorption phase diagram (Netz and Andelman, 2003) as a function of substrate charge density, $\sigma$, and inverse screening length, $\kappa$.

The adsorption of polyelectrolytes onto a substrate has also been discussed by Netz and Joanny (1999) and Netz and Andelman (2003). These authors went beyond the mean-field theory and considered lateral correlation effects. An adsorption phase diagram was presented for strongly charged polyelectrolytes as a function of the substrate charge density and the inverse screening length (see Figure 3). At constant substrate charge
density, charge compensation occurs at low electrolyte concentrations. Increasing electrolyte concentration causes charge reversal of the substrate, followed by polyelectrolyte desorption. This affects the formation of, for instance, polyelectrolyte multilayer (Decher, 1997; Netz and Joanny, 1999). These aspects are further considered in this thesis.

2.2 Charge determination

In order to measure the fiber charge, the polyelectrolyte titration technique is often used. The direct polyelectrolyte titration technique was first developed by Terayama (1952). The concentration of cationic polyelectrolyte was determined by titration with an anionic polyelectrolyte in the presence of a cationic indicator, typically orthotoluidine blue (OTB). The color of the uncomplexed OTB indicator is blue, and changes color to pink when it complexes with excess anionic polyelectrolyte. This wavelength displacement is called metachromasy, and Figure 4 shows how the absorption spectrum of OTB changes in the presence of potassium polyvinylsulphate (KPVS) (Horn, 1978).

The complex formation can be written as:

\[ A + C \rightleftharpoons K_1 AC \]  

(1)

\[ A + I \rightleftharpoons K_2 AI \]  

(2)

where A is an anionic polyelectrolyte, C is a cationic polyelectrolyte and I the indicator. In order for this method to work, the complex formation of AC must be preferred over the AI complexation, i.e. \( K_1 \gg K_2 \).

The polyelectrolyte titration procedure is basically independent of molecular mass (Horn, 1978) and the polyelectrolyte complex is stoichiometric with respect to charge if the charge density of the polyelectrolytes are sufficiently high (Horn, 1979) or the ionic strength is sufficiently low (Tanaka, 1983a,b; Sjödin and Ödberg, 1996; Kam and Gregory, 1999). Winter et al. (1986) developed the method to be used for charge determination of cellulosic fibers (indirect titration). This method is based on a 1:1 stoichiometric relationship between the polyelectrolyte charges and the charges on the fiber. Several publications from Wågberg and co-workers (Wågberg et al., 1985, 1987, 1988, 1989; Wågberg and Ödberg, 1989; Winter et al., 1986) have shown that this is the case in the limit of zero ionic concentration. Kokufuta and Takahashi (1986) found that stoichiometry prevails between poly-DADMAC and silica in deionized water but deviates in ionic solutions.
A requirement for adsorption stoichiometry is the absence of non-ionic interactions. The driving force for polyelectrolyte adsorption onto an oppositely charged surface is of an electrostatic nature (Andelman and Joanny, 2000). It has been suggested that this is also the case for many cationic polyelectrolytes onto cellulosic surfaces (Tanaka et al., 1979; Wågberg et al., 1988; Wågberg and Ødberg, 1989; Wågberg, 2000).

### 2.2.1 Adsorption isotherm

The adsorbed amount of polyelectrolyte onto fibers and the equilibrium concentration in solution can be calculated from the inflection point in the (direct) polyelectrolyte titration curve. The adsorbed amount of polyelectrolyte as a function of the equilibrium concentration is compiled in an adsorption isotherm, see Figure 5.

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**Figure 4**: Metachromatic band displacement of orthotoluidine blue (OTB) in the presence of potassium polyvinylsulphate (KPVS). (Horn, 1978)
In theory, the adsorption isotherm for a charged polyelectrolyte would have two main features. First, a vertical line would exist on the abscissa because all the polyelectrolyte is adsorbed at low addition levels. Secondly, a plateau region at higher equilibrium concentrations, represented by the dashed line in Figure 5, because the additional polyelectrolyte remains in solution once the available surface is saturated (Lindström, 1989). In practice, however, the adsorption isotherms deviate from this prediction. The rounding of the isotherm is due to at least three effects:

I. The polydispersity in the adsorbing polyelectrolyte causes curved isotherms because high molecular mass material is preferentially adsorbed at the accessible fiber surfaces, displacing low molecular mass material (Cohen Stuart et al., 1980).

II. A low molecular mass polyelectrolyte has higher accessibility to charges in the fiber cell wall than a high molecular mass polyelectrolyte (Wågberg et al., 1987).

III. A decrease in stoichiometry for the adsorbed polyelectrolyte molecules, most probably due to an increased interaction between the polyelectrolyte molecules on the surfaces, seen as an expansion of the adsorbed polyelectrolyte layer out from the surface (Wågberg and Ödberg, 1989).

The number of adsorbed charges can be evaluated from the adsorption isotherm by an extrapolation of the "plateau region" of the adsorption
Figure 6: Charge ratio, i.e. the number of adsorbed polyelectrolyte charges divided by the total amount of fiber charges, as a function of poly-DADMAC molecular mass. (Wågberg and Ödberg, 1989)

An example of the charge ratio as a function of the molecular mass of a cationic polyelectrolyte is shown in Figure 6. A charge ratio equal to one means that all fiber charges can be reached by the polyelectrolyte. Above a certain molecular mass, the charge ratio drops drastically, i.e. the adsorption decreases. This is because larger molecular mass polyelectrolytes have less accessibility to the charges in the fiber pores and will almost only be adsorbed on the fiber surface.

The electrolyte concentration and molecular mass are two important factors to consider when determining the fiber surface charge. The charge ratio for pulps determined by different authors are listed in Table 1, along with the electrolyte concentration and molecular mass. Although the charge ratio is practically constant within each individual publication, the difference in charge ratio between cited publications is quite large. Therefore, it is important that caution is taken when comparing results from the literature.
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**Table 1:** Conditions used for determining the charge ratio from various authors for bleached softwood pulps. Charge ratio = surface charge (polyelectrolyte titration with poly-DADMAC)/ total charge (conductometric titration)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Pulp</th>
<th>Molecular mass</th>
<th>Electrolyte conc. [M]</th>
<th>Charge ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ampulski (1985)</td>
<td>CTMP</td>
<td>$10^{64}$</td>
<td>-</td>
<td>$\sim 53$</td>
</tr>
<tr>
<td>Zhang et al. (1994)</td>
<td>CTMP</td>
<td>$2 \cdot 10^5$</td>
<td>$10^{-2}$</td>
<td>$\sim 11$</td>
</tr>
<tr>
<td>Höök (1995)</td>
<td>Kraft</td>
<td>$5 \cdot 10^5$</td>
<td>$10^{-2}$</td>
<td>$\sim 6$</td>
</tr>
<tr>
<td>Laine and Stenius (1997)</td>
<td>Kraft</td>
<td>$&gt;3 \cdot 10^5$</td>
<td>$10^{-2}$</td>
<td>$\sim 18^*$</td>
</tr>
<tr>
<td>Wågberg et al. (1988)</td>
<td>Kraft$^|$</td>
<td>$4 \cdot 10^{61}$</td>
<td>0</td>
<td>$\sim 4$</td>
</tr>
</tbody>
</table>

$^*\)$ Total charge determined by polyelectrolyte titration, Mw = $8 \cdot 10^3$
$^\|$ Carboxymethylated to various degrees of substitution
$^\|$ Methyl glycol-chitosan
$^\|$ C-PAM

This work has therefore been aimed to resolve the appropriate electrolyte concentration (Paper I) and molecular mass (Paper II) for determining surface charge of cellulosic fibers with the polyelectrolyte titration technique. The method was also externally validated by the ESCA-technique (Paper II). Finally, the charge ratio of various pulps and treatments was examined (Paper III).
3 Materials

The reference pulp used in Paper I and II is an ECF-bleached (Elementary Chlorine Free) softwood (spruce) kraft pulp from M-real, Husum, Sweden. Before various treatments, the fines were removed with 100 µm screening slots. Pulps used in paper III are from various mills located in Sweden.

3.1 Pulp treatments

3.1.1 Pretreatment

All pulps were washed according to the following procedure:

**Hydrogen form.** In order to remove all metal ions, pulps were washed with HCl. Pulps were immersed into 10⁻² M HCl and adjusted to pH 2. The pulps were then soaked for 30 min and finally rinsed with deionized water until the conductivity of the filtrate was below 5 µS/cm.

**Sodium form.** The pulps were transferred to their sodium form by soaking in a 10⁻³ M NaHCO₃ solution for 10 min. pH was adjusted to 9 with NaOH and kept constant for 30 min. The pulps were again rinsed with deionized water to remove excess of electrolyte until the conductivity of the filtrate was below 5 µS/cm.

3.1.2 Bulk carboxymethylation

Bulk carboxymethylation was carried out according to a method developed by Walecka (1957). The pulp was placed in 95% ethanol, stirred and then filtered after 10 min. This was repeated three times, the final time with 99% ethanol. Solutions consisting of various amounts of monochloroacetic acid dissolved in isopropanol were prepared. The added amount of monochloroacetic acid theoretically determines the amount of carboxylic acid groups introduced into the pulp, i.e. the degree of substitution (DS). The added amount and the achieved DS are listed in Table 2. The pulps were impregnated with these solutions for 30 min. NaOH was dissolved in methanol and then added to isopropanol. Each of the impregnated pulps was added to the NaOH/isopropanol solutions, which had been heated close to the boiling point. The reactants were refluxed for one hour. The pulp samples were then filtered and washed with a sequence of deionized water, 0.1M acetic acid, and deionized water again. The pulps were
finally placed in a 4% $NaHCO_3$ (consistency $\sim$1%) solution for one hour, filtered, and then washed with deionized water.

Table 2: The various amounts of added monochloroacetic acid with the theoretical and achieved degree of substitution for bulk carboxymethylated pulp.

<table>
<thead>
<tr>
<th>Monochloroacetic acid (mg/g pulp)</th>
<th>Theoretical DS</th>
<th>Achieved DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>13.7</td>
<td>0.015</td>
<td>0.009</td>
</tr>
<tr>
<td>45.5</td>
<td>0.050</td>
<td>0.045</td>
</tr>
<tr>
<td>90.9</td>
<td>0.100</td>
<td>0.076</td>
</tr>
</tbody>
</table>

3.1.3 Surface carboxymethylation (CMC-grafting)

Laine et al. (2000) developed a method where charges were irreversibly introduced to the fiber surface by grafting of carboxymethyl cellulose (CMC). The CMC used in these experiments was Finnfix WRH (Mets-Serla, Finland) with $M_w = 1 \cdot 10^6$ Da and DS = 0.52.

A 10 g/l CMC solution was prepared. The pulp was washed into its sodium form according to the above procedure. The CMC solution was added to a pulp suspension and subjected to the conditions in an autoclave, listed in Table 3. After the grafting of CMC, the pulp was washed with deionized water until the conductivity of the filtrate was below 5 $\mu$S/cm. The pulp was subsequently transferred to its hydrogen form, followed by a two hour leaching period to its sodium form in order to remove excess CMC, which had not been attached to the fibers.

Table 3: Conditions for irreversible grafting of carboxymethyl cellulose onto ECF-bleached softwood kraft pulp.

| Temperature | 120°C |
| Time        | 2 h   |
| Consistency | 5%    |
| Ionic conditions | $5 \cdot 10^{-2}$M $CaCl_2$  |
| Buffer      | $10^{-2}$M $NaHCO_3$ |
| pH          | 8 (adjusted with NaOH) |
| Added CMC   | 10, 20 and 40 mg/g pulp |
3.1.4 Enzymatic treatment

An enzymatically treated pulp was used in Paper III. The pulp used was a never dried, laboratory cooked ECF-bleached (ODEDD) softwood spruce kraft pulp with fines removed (100 \( \mu \text{m} \) screening slots). The pulp was acetone extracted before enzyme treatment with Pulpzyme HC, batch CKN 00021. Pulp was treated with the enzymes at 40°C for 21 h (3% pulp consistency, 50 mM Tris HCl buffer, pH 7). The pulp was then washed with deionized water and set in 80°C water for 40 min (10% pulp consistency) in order to inactivate the enzymes. The pulp was finally washed three times with deionized water. Three different dosages of enzyme were used: 0.00, 0.05 and 0.90 ml/g.

3.1.5 PFI beating

PFI beating was used as a mechanical fiber treatment in Paper III. The beating followed the standard method SCAN-C 24:96 with some modifications. The reference pulp (also used in Paper I and II) was washed into its sodium form prior to beating for 0, 1000, 5000 and 10000 revolutions.

3.2 Polyelectrolytes

A fractionated poly-diallyldimethylammonium chloride (poly-DADMAC) (Ciba, Yorkshire, UK) was used in Paper I and II, see Table 4. The charge density was determined to be 5.9 \( \cdot 10^{-3} \text{eq/g} \) by direct titration (theoretical value is 6.19 \( \cdot 10^{-3} \text{eq/g} \)). The high molecular mass polyelectrolyte, with \( M_w 9.2 \cdot 10^5 \), was used in Paper III.

Table 4: Properties of poly-DADMAC.

<table>
<thead>
<tr>
<th>Molecular mass (Da)</th>
<th>( M_w/M_N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4.0 \cdot 10^3 )</td>
<td>1.4</td>
</tr>
<tr>
<td>( 2.2 \cdot 10^4 )</td>
<td>2.1</td>
</tr>
<tr>
<td>( 1.4 \cdot 10^5 )</td>
<td>2.8</td>
</tr>
<tr>
<td>( 9.2 \cdot 10^5 )</td>
<td>6.3</td>
</tr>
</tbody>
</table>
4 Methods

4.1 Charge determination

4.1.1 Conductometric titration

The total charge was determined by conductometric titration according to Katz et al. (1984). 1 g dry pulp in its hydrogen form was suspended in deionized water to a total volume of 485 ml. 10.0 ml of $10^{-2}$M NaCl and 5.0 ml of $10^{-2}$M HCl were added. The conductivity was recorded as $10^{-1}$M NaOH was added. The pulp was then filtered and oven-dried over night after the titration in order to record the actual dry weight.

4.1.2 Polyelectrolyte adsorption

Polyelectrolyte adsorption was performed according to a method developed by Winter et al. (1986). Various amounts of poly-DADMAC, seen in Figure 7(a), was added to a pulp suspension (5 g/l). The ionic conditions were varied in Paper I and $10^{-5}$M NaHCO$_3$ was used in Paper II and III. The pulp suspension was shaken 30 min immediately after the polyelectrolyte addition. The suspension was then filtered and the pulp was dried in an oven over night in order to record the actual dry weight. The filtrate was saved and titrated according to the method developed by Terayama (1952).

![Chemical structure of polyelectrolytes and indicator used in direct polyelectrolyte titration.](a) poly-DADMAC  (b) OTB  (c) KPVS

Figure 7: Chemical structure of polyelectrolytes and indicator used in direct polyelectrolyte titration.

A $\leq$40 g sample of filtrate from the adsorption was weighed and then diluted to 40 g with the same electrolyte concentration as used in the polyelectrolyte adsorption. The amount of filtrate in the sample was recorded. 1 ml orthotoluidine blue (OTB, see Figure 7(b)) was added before titrations.
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with an anionic polyelectrolyte, potassium polyvinylsulfate (KPVS, see Figure 7(c)). The equivalence volume was recorded and corrected for the OTB consumed by KPVS. Duplicate samples were always conducted.

4.2 ESCA

Electron Spectroscopy for Chemical Analysis (ESCA) was used in Paper II to measure the nitrogen content on the surface and compare it with the amount of adsorbed nitrogen determined by polyelectrolyte adsorption.

The ESCA measurements were carried out at the Helsinki University of Technology using an AXIS-HS spectrometer from Kratos Analytical. Monochromatized Al Kα radiation was used to excite the electrons. Analyses were made on three different locations in each sample. The amount of adsorbed poly-DADMAC was detected by monitoring the nitrogen (N 1s) content on the fiber surfaces.

Different dosages of poly-DADMAC (only Mw 7.0·10^3 and 9.2·10^5) were adsorbed onto modified pulp in 10^{-5} M NaHCO₃. After 30 min of shaking, the pulp was filtered and washed twice with 100 ml of 10^{-5} M NaHCO₃ in order to remove excess poly-DADMAC. The filtrate was saved for polyelectrolyte titrations. Handsheets (grammage 60 g/m²) were made from the fibers in 10^{-5} M NaHCO₃, according to the standard SCAN-C 26:76 method, and subjected to ESCA analysis. Four different amounts of poly-DADMAC were added to obtain an adsorption isotherm.

4.3 Water Retention Value

The Water Retention Value (WRV), a measure of the swelling of the pulp, was determined according to the proposed SCAN method (SCAN-C 102 XE; 15 min, 3000 g). The WRV of the pulp in its sodium form was determined in 10^{-4} M NaCl.
5 Summary of results from ”Indirect poly-electrolyte titration of cellulosic fibers. Parts 1-3”

5.1 Paper I: The effects of electrolyte concentration on the adsorption of poly-diallyldimethylammonium chloride.

5.1.1 Effect of electrolyte concentration on poly-DADMAC adsorption

The adsorption of high molecular mass poly-DADMAC onto bleached softwood kraft pulp was carried out at various electrolyte (\(NaHCO_3\)) concentrations. Adsorption isotherms (e.g. Figure 5) were determined in electrolyte concentrations between \(10^{-6}\) and 1M. The amount of polyelectrolyte adsorbed was determined by extrapolating the linear region back to an equilibrium concentration of zero. The charge ratio was then calculated as the amount of adsorbed polyelectrolyte charges divided by the total amount of fiber charges (Equation 3). The results are shown in Figure 8.

![Figure 8: Charge ratio as a function of electrolyte concentration (NaHCO_3) for adsorption of poly-DADMAC, molecular mass 9.2 \(\cdot\) 10^5 Da, onto bleached softwood kraft pulp. (Paper I)](image)

A prerequisite for adsorption stoichiometry is the absence of non-electrostatic interactions. As shown in Figure 8, adsorption vanished when the electrolyte concentration is sufficiently high.
5.1.2 Effects of bulk and surface charge density on poly-DADMAC adsorption

In order to investigate how the electrolyte concentration affects polyelectrolyte adsorption onto fibers with different charge profiles, a reference pulp was carboxymethylated according to Walecka (1957). This method is based on substituting hydroxyl groups for carboxylic acid groups using monochloro-acetic acid in isopropanol. The degree of substitution (DS) is controlled by the amount of monochloroacetic acid added to the reaction. Results from the adsorption of high molecular mass poly-DADMAC in various electrolyte concentrations onto fibers with different DS-values are shown in Figure 9. It can be seen that the charge ratio is 0.05 regardless of the degree of substitution, i.e. 5% of the charges are located on the fiber surface when measured in $10^{-5}$M $NaHCO_3$. This suggests that charges are distributed evenly throughout the fiber and the treatment is non-surface selective. A higher surface charge ratio for the highest DS (0.076) is probably due to extensive swelling of the fiber, resulting in an increased accessibility of poly-DADMAC to the fiber charges. A significant observation is that the increase in adsorption is shifted towards higher electrolyte concentrations for pulp with higher DS.

![Figure 9: Charge ratio of bulk carboxymethylated pulp as a function of electrolyte concentration during adsorption. The polyelectrolyte used was poly-DADMAC with molecular mass 9.2·$10^5$Da. (Paper I)](image)

In a second set of fiber modifications, the reference pulp was treated with carboxymethyl cellulose (CMC) according to Laine et al. (2000). In this method, high molecular mass CMC is grafted onto the fiber surface, making it possible to increase the surface charge ratio with the amount of
CMC grafted, see Figure 10. It was possible to increase the charge ratio from 5% to 30%. It can also be seen that the relative increase in adsorbed amount changes by a much larger factor with electrolyte concentration for pulps with low surface charge density.

Figure 10: Charge ratio of CMC grafted pulp at different electrolyte concentrations. The polyelectrolyte used was poly-DADMAC with molecular mass $9.2 \cdot 10^5$ Da. (Paper I)
5.2 Paper II: Verification of the polyelectrolyte titration method by the ESCA-technique for determining the fiber surface charge.

5.2.1 Effect of Mw on poly-DADMAC adsorption

The effect of molecular mass on the adsorption of cationic polyelectrolytes on cellulosic fibers has been investigated by a number of authors (Wågberg and Ödberg, 1989; Swerin and Wågberg, 1994; Lindström and Sörenmark, 1976; Horn and Melzer, 1977). In order to resolve the appropriate molecular mass needed to measure the surface charge, polyelectrolytes with varying molecular mass were adsorbed on a high charge density pulp (506 \( \mu \)eq/g) in \( 10^{-5} \text{M} \text{NaHCO}_3 \), as determined in Paper I. The number of adsorbed polyelectrolyte charges (determined from adsorption isotherms) was plotted against molecular mass, showing that a low molecular mass polyelectrolyte could penetrate into the fiber pores to a larger extent, see Figure 11. The adsorbed amount of poly-DADMAC is rather constant for polyelectrolytes with molecular mass \( \geq 10^5 \text{Da} \). This means that only the surface charges can be reached for polyelectrolytes with high molecular mass (\( > 1.4 \cdot 10^5 \)). Therefore, poly-DADMAC with Mw \( 9.2 \cdot 10^5 \) was used in subsequent experiments.

![Figure 11: Amount of polyelectrolyte charges adsorbed onto a carboxymethylated bleached kraft pulp as a function of poly-DADMAC molecular mass. (Paper II)](image-url)
The polyelectrolyte titration method was verified with ESCA (Electron Spectroscopy for Chemical Analysis), which detects the amount of nitrogen on the surface of a sheet at a reported analysis depth of 6-12 nm for polymeric materials (Ashley and Williams, 1980). Different amounts of high molecular mass ($9.2 \cdot 10^5$ Da) and low molecular mass ($7.0 \cdot 10^3$ Da) poly-DADMAC were adsorbed onto fiber suspensions (electrolyte concentration $10^{-5}$M $NaHCO_3$). The filtrate was used to determine the adsorbed amount by polyelectrolyte titrations. Handsheets were made from the fibers and the amount of nitrogen was analyzed using ESCA. The results are displayed in Figure 12.

As can be seen in Figure 12(a), the adsorbed amount of low Mw poly-DADMAC is about ten times higher when determined by polyelectrolyte titration. This is of course expected since the smaller polyelectrolyte has access to the charges in the fiber pores, whereas the larger polyelectrolyte can only reach the charges on the fiber surface. On the other hand, the surface nitrogen content determined by ESCA (Figure 12(b)) shows similar adsorbed amount regardless of molecular mass. In the case of stoichiometry, it is expected that the surface nitrogen content would be the same for a fiber surface. However, the fibers onto which high molecular mass poly-DADMAC has been adsorbed have a somewhat higher nitrogen content, indicating a less flat conformation.
5.2.2 Effect of fiber charge profile on poly-DADMAC adsorption

ESCA was also used to examine the nitrogen content after poly-DADMAC adsorption onto fibers with different charge profiles. Bulk carboxymethylation (Walecka, 1957) and surface carboxymethylation (Laine et al., 2000) were used in order to achieve the profiles. The surface charge is plotted as a function of total charge in Figure 13 to show the different charge profiles.

![Figure 13: Surface charge as a function of total charge (using conductometric titration) for various carboxymethylated pulps. The surface charge was analyzed by polyelectrolyte titration using a poly-DADMAC with a Mw of 9.2·10^5. (Paper II)](image)

Eight pulps were then used to compare the polyelectrolyte titration method with ESCA measurements. High molecular mass poly-DADMAC was adsorbed, corresponding to an equilibrium concentration of 8.50 ± 3 mg/l in the adsorption isotherm, and handsheets were made. The nitrogen content was measured by polyelectrolyte titration and ESCA. It can be seen in Figure 14 that there is a good correlation between the two methods, meaning that the surface charge content of cellulosic fibers can be measured using high molecular mass poly-DADMAC.
Appropriate Conditions for Polyelectrolyte Titration to Determine the Charge of Cellulosic Fibers

Figure 14: Relation between ESCA-analysis and polyelectrolyte titration to analyze surface charge of surface- and bulk carboxymethylated pulps with different charge profiles. The Mw of the poly-DADMAC was $9.2 \cdot 10^5$. (Paper II)
5.3 Paper III: Surface and bulk charges of cellulosic fibers.

It was determined in Paper I and II that surface charge can be measured with polyelectrolyte titration using a high molecular mass polyelectrolyte (poly-DADMAC Mw \( \sim 10^6 \) Da) at low ionic strength (10\(^{-5}\)M \( NaHCO_3 \)).

Paper III examined the relationship between total charge (as determined by conductometric titration) and surface charge (using polyelectrolyte titration with the conditions mentioned above) for various pulps. Pulps from various mills in Sweden, that had been subjected to different bleaching sequences and treatments, were investigated. Different types of pulping processes were also investigated, as shown in Table 5. Although the total and surface charge vary to a large extent between the different types of pulping, the charge ratio does not change significantly for chemical (kraft) and semi-chemical (NSSC) pulping. However, the (thermo) mechanical pulping (TMP) process gives a much higher charge ratio, probably due to the large amount of fines material released during pulping. Fines material has a higher specific surface area, resulting in an increased charge ratio.

Table 5: Different types of unbleached pulp from various mills in Sweden. (Paper III)

<table>
<thead>
<tr>
<th>Mill/Mill Treatment type</th>
<th>Total charge (( \mu\text{eq/g} ))</th>
<th>Surface charge (( \mu\text{eq/g} ))</th>
<th>Charge ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stora Enso/Skoghall Kraft/SW</td>
<td>107</td>
<td>3.4</td>
<td>0.03</td>
</tr>
<tr>
<td>M-real/Husum Kraft/HW</td>
<td>137</td>
<td>6.3</td>
<td>0.05</td>
</tr>
<tr>
<td>Billerud/Skärblacka NSSC/HW</td>
<td>156</td>
<td>6.0</td>
<td>0.04</td>
</tr>
<tr>
<td>Holmen/Hallsta TMP/SW</td>
<td>83</td>
<td>11</td>
<td>0.14</td>
</tr>
</tbody>
</table>

A bleaching sequence was examined by collecting pulp after each bleaching stage and measuring the charge content, see Table 6. The number of charges decreases as the kappa number (lignin removal) decreases. The increase in charges after the first bleaching stage is due to the oxidation of end groups and cleavage of polysaccharide chains, forming aldehydic end groups that can be oxidized to carboxylic acid groups (Sjöström, 1993). However, the charge ratio is virtually the same, which means the bleaching is not very surface selective.
Appropriate Conditions for Polyelectrolyte Titration
to Determine the Charge of Cellulosic Fibers

Table 6: Bleaching sequence for softwood (60:40 spruce:pine) kraft pulp from Stora Enso, Skoghall. (Paper III)

<table>
<thead>
<tr>
<th>Bleaching sequence</th>
<th>Kappa number</th>
<th>Total charge (µeq/g)</th>
<th>Surface charge (µeq/g)</th>
<th>Charge ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached</td>
<td>34.8</td>
<td>107</td>
<td>3.4</td>
<td>0.03</td>
</tr>
<tr>
<td>O</td>
<td>18.8</td>
<td>115</td>
<td>5.9</td>
<td>0.05</td>
</tr>
<tr>
<td>O OP</td>
<td>10.7</td>
<td>98</td>
<td>4.8</td>
<td>0.05</td>
</tr>
<tr>
<td>O OP D</td>
<td>4.0</td>
<td>59</td>
<td>3.1</td>
<td>0.05</td>
</tr>
<tr>
<td>O OP D Q</td>
<td>3.6</td>
<td>62</td>
<td>2.8</td>
<td>0.05</td>
</tr>
<tr>
<td>O OP D Q PO</td>
<td>1.9</td>
<td>58</td>
<td>2.6</td>
<td>0.04</td>
</tr>
</tbody>
</table>

The effect of mechanical treatment can be seen in Table 7, where a fully bleached softwood kraft pulp was investigated with the fines material being removed before beating. The total charge is unchanged since charges are not created during the treatment. On the other hand, the surface charge increased because more surface is exposed as fines material is created during beating. Also, it is possible with this treatment to increase the charge ratio, which could therefore be used as a measure for the extent of beating.

Table 7: Effect of beating on the charge ratio of a never dried ECF-bleached (ODQPDP) softwood kraft pulp from M-real, Husum. The fines material was removed using a screen with 100 µm slots prior to beating. (Paper III)

<table>
<thead>
<tr>
<th>PFI revolutions</th>
<th>Total charge (µeq/g)</th>
<th>Surface charge (µeq/g)</th>
<th>Charge ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>37</td>
<td>2.3</td>
<td>0.06</td>
</tr>
<tr>
<td>1000</td>
<td>37</td>
<td>2.6</td>
<td>0.07</td>
</tr>
<tr>
<td>5000</td>
<td>38</td>
<td>4.9</td>
<td>0.13</td>
</tr>
<tr>
<td>10000</td>
<td>40</td>
<td>6.0</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Methods are also available to increase the charge content chemically. As described in Paper I and II, pulp was carboxymethylated by substituting hydroxyl groups with carboxylic acid groups. The results are shown in Table 8. Both the surface and the total charge was increased, although the charge ratio is unchanged. This means that the method was non-surface selective and charges are distributed evenly throughout the fiber cell wall. This method was therefore called bulk carboxymethylation.
Table 8: Bulk carboxymethylation of never dried ECF-bleched (ODQPDP) softwood Kraft pulp from M-real Husum. Fines material was removed with 100 µm slots prior to modification. (Paper III)

<table>
<thead>
<tr>
<th>Degree of substitution</th>
<th>Total charge (µeq/g)</th>
<th>Surface charge (µeq/g)</th>
<th>Charge ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>37</td>
<td>1.7</td>
<td>0.05</td>
</tr>
<tr>
<td>0.009</td>
<td>89</td>
<td>4.1</td>
<td>0.05</td>
</tr>
<tr>
<td>0.045</td>
<td>314</td>
<td>16</td>
<td>0.05</td>
</tr>
<tr>
<td>0.076</td>
<td>506</td>
<td>34</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Another method to modify fibers chemically is to graft carboxymethylcellulose (CMC) onto the fiber surface. Sufficiently high molecular masses of CMC could only be grafted to the fiber surface. Table 9 lists treatments with four different amounts of CMC grafted onto the fibers. The charge content increases with increasing amount of CMC. However, this modification is surface selective. The decrease in surface selectivity (= increased charges on the surface divided by the increased total amount of charges) is due to surface swelling (Laine et al., 2003). When the amount of grafted CMC increases, the surface swells because of electrostatic repulsion between CMC chains. This results in some of the pores and cavities opening up and allowing more CMC chains to be grafted below the surface of the fiber. Although the selectivity decreases with CMC treatment, the surface charge increases, which is why the method is referred to as surface carboxymethylation.

Table 9: Surface carboxymethylation of a never dried ECF-bleched (ODQPDP) softwood kraft pulp from M-real Husum. Fines material was removed with 100 µm slots prior to modification. (Paper III)

<table>
<thead>
<tr>
<th>Grafted CMC (mg/g)</th>
<th>Total charge (µeq/g)</th>
<th>Surface charge (µeq/g)</th>
<th>Charge ratio</th>
<th>Selectivity † (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>34</td>
<td>1.6</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>10</td>
<td>0.22</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>57</td>
<td>17</td>
<td>0.29</td>
<td>67</td>
</tr>
<tr>
<td>14</td>
<td>74</td>
<td>21</td>
<td>0.29</td>
<td>49</td>
</tr>
</tbody>
</table>

†) ∆ surface charge / ∆ total charge
6 Discussion

The ionic conditions near a charged surface can be considered as a diffuse electric double layer with thickness $\kappa^{-1}$, called the Debye length. The thickness of the double layer is very much dependent on the electrolyte concentration and can be calculated as:

$$
\kappa^{-1} = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{2z^2 e^2 \rho_\infty}}
$$

where $\varepsilon$ is the medium dielectric constant, $\varepsilon_0$ the permittivity in vacuum, $k_B$ Boltzmann’s constant, $T$ the temperature, $z$ the valency of a $z:z$ electrolyte, $e$ the charge in the bulk medium and $\rho_\infty$ the number concentration of counterions.

At a low electrolyte concentration (e.g. $<10^{-4}$M in Figure 8), the distance between the charges ($d$) will be smaller than the thickness of the diffuse double layer (compare Netz and Andelman (2003)). The interaction of the fiber surface and the polyelectrolyte, illustrated in Figure 15(a), can be considered as the interaction of two mean-fields rather than point-charges, and 1:1 stoichiometry will prevail (charge compensation (Netz and Andelman, 2003)).

An increase in adsorption occurs when the electrolyte concentration increases. This is due to the distance between the charges becoming greater than the thickness of the double layer as the electrolyte concentration increases ($d > \kappa^{-1}$, see Figure 15(b)). The polyelectrolyte and fiber charges

Figure 15: Schematic of polyelectrolyte adsorption at (a) low and (b) high electrolyte concentration. (Also in Paper I)
behave more as discrete charges instead of as a mean field of charge, and the deviation from stoichiometry will be more profound. At the same time, the conformation of the polyelectrolyte will change. When the electrolyte concentration increases, the polyelectrolyte charges will be further screened from each other and the repulsion will decrease. The polyelectrolyte will adsorb in loops and tails instead of in the flat conformation that occurs at low electrolyte concentrations. This results in an increase in the adsorption. At very high electrolyte concentrations, the adsorption decreases because the charges are entirely screened by the electrolyte so that there are essentially no electrostatic interactions. Increased adsorption occurs at higher electrolyte concentration when the surface charge density is increased by different chemical modifications, i.e. the deviation from stoichiometry occurs at higher electrolyte concentrations for pulp with higher surface charge density. This is not surprising since the distance between the charges is smaller, requiring a thinner diffuse double layer, which occurs at higher electrolyte concentrations, to fulfil the limiting condition \( d > \kappa^{-1} \) for deviation from stoichiometry.

A Critical Electrolyte Concentration (CEC) was defined in order to test when adsorption stoichiometry starts to deviate from 1:1. The CEC was defined as the electrolyte concentration where the apparent surface charge had increased by 20%. \( \kappa^{-1} \) was then calculated from each CEC and plotted against the distance between the charges on the surface calculated according to Equation 5:

\[
d = \sqrt[3]{\frac{V_S}{\sigma_S \cdot N_A}} = \sqrt[3]{\frac{W RV_{Na} \times 5\%}{\sigma_S \cdot N_A}}
\]

where \( V_S \) is the ”surface volume”, \( \sigma_S \) the surface charge density, \( N_A \) Avogadro’s number and \( W RV_{Na} \) the water retention value for untreated pulp in its sodium form. The ”surface volume” was introduced as a more straightforward way to define and calculate the distance between the charges, because a wet fiber surface is an ill-defined property. Assuming uniform charge distribution and swelling across the cell wall of the fiber, the surface volume can be calculated as \( 5\% \times W RV_{Na} \), where the WRV is a measure of fiber swelling (Scallan and Carles, 1972) and \( 5\% \) is the charge ratio for bulk carboxymethylated fibers. The results are shown in Figure 16. It can be seen that \( d \approx \kappa^{-1} \) (the dashed line represent where \( d = \kappa^{-1} \)) for all the different pulp treatments. The hypothesis that \( d \ll \kappa^{-1} \) in order for 1:1 stoichiometry to prevail is therefore a useful and simple assumption.
Figure 16: Surface charge distance ($d$) as a function of the thickness of the diffuse electric double layer ($\kappa^{-1}$), calculated from the critical electrolyte concentration (CEC) (see Equation 5). ♦ denotes surface carboxymethylation and • denotes bulk carboxymethylation. (Paper I)
7 Conclusions

The main objective of this thesis was to investigate the appropriate conditions for surface charge determination of cellulosic fibers using the indirect polyelectrolyte titration method. The electrolyte concentration was first investigated. It was concluded that stoichiometry prevailed at low electrolyte concentrations, but started to deviate already at moderate concentrations as the distance between the charges approached the thickness of the double layer. Adsorption was enhanced as the polyelectrolyte coiled and charge reversal occurred. As the electrolyte concentration increased further, the screening of the charges increased and the adsorption decreased. Increasing the surface charge density decreased the distance between the charges and, hence, the adsorption deviated from stoichiometry at higher electrolyte concentrations.

Secondly, the suitable molecular mass of the polyelectrolyte for accurate measurement of the surface charge was examined. It was found from polyelectrolyte titrations that a high molecular mass polyelectrolyte (\(9.2 \cdot 10^5 \text{Da}\)) should not be able to enter the pore system. This was further investigated by a comparison with ESCA-measurements, a method that measures the nitrogen content on the surface. Since the same amount of high and low molecular mass polyelectrolyte was found on the surface, it was concluded that stoichiometry prevailed between the surface charges and polyelectrolyte charges. The nitrogen content was measured by polyelectrolyte titration for pulps with different charge profiles and compared with ESCA-measurements. A good agreement was found between the two methods. This suggested that the surface charges can be quantitatively measured with the polyelectrolyte titration method if a high molecular mass polyelectrolyte is used.

Finally, the total and surface charge were measured for various pulps and treatments. It was found that the total and surface charge content varied a lot between different types of wood and bleaching sequences. However, the charge ratio was virtually the same for the chemical pulps. Mechanical pulping increased the charge ratio due to an increase in fines material. This was also found for chemical pulp that had been beaten. Surface carboxymethylation (CMC grafting) of fibers increased the charge ratio, but bulk carboxymethylation did not. As beating increased the charge ratio, it could be used as a measurement for the extent of beating.
8 Acknowledgments

This work has been carried out at the Swedish Pulp and Paper Research Institute, STFi. I would like to express my gratitude to my supervisor Professor Tom Lindström for giving me the opportunity to do this work and for the support he has given me. I would also like to thank Gunborg Glad-Nordmark and Gunnel Risinger for all the help in the laboratory and for giving me some of their knowledge and experience. All the help Marco Lucisano gave with \LaTeX{} is deeply appreciated. The financial support from STFi is gratefully acknowledged. My parents are thanked for steering me in this direction and supporting me. Last but not least, I would like to thank my husband Andrew and our dog Oden for being there whenever I need them.

Stockholm, December 9\textsuperscript{th}, 2003

Elisabet Horvath
A. Elisabet Horvath

Literature


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