# Determination of Dissociable Groups in Natural and Regenerated Cellulose Fibers by Different Titration Methods

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**ABSTRACT:** Different titration methods were applied with the purpose to determine the dissociation properties of a natural (cotton) and regenerated (viscose, modal and lyocell) cellulose fibers. Potentiometric and conductometric titration were used to determine the content of acidic groups. pK values were determined by potentiometric titration. Polyelectrolyte adsorption was used for surface and total charge determination, and to obtain information about charge location and accessibility of charged groups. It was found that the average content of acidic groups is higher in cotton fibers than in regenerated fibers. The fiber charge of cotton is due to the dissociation of two type of acidic groups, one with pK ≈3.5 and the other with pK ≈5.5. In regenerated fibers there is only one type of acidic groups (pK ≈3.5). The pK value of the stronger acid is typical for carboxyl group in uronic acids. The polyelectrolyte adsorption indicates that most of the carboxyl groups are located in an inner region of all cellulose samples (cotton and regenerated fibers). It is concluded that titration methods are powerful tools for monitoring the content, strength, and distribution of acidic groups, as well as the total charge of natural and regenerated cellulose fibers. The three methods give similar results on all analyzed samples and show good repeatability. The results of investigation make it quite clear that combination of all titrations yields relevant information about content and strength of acidic groups in both natural and regenerated cellulose fibers used in the manufacture of textiles. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3186–3195, 2004

**Key words:** fibers; macroporous polymers; electrochemistry; adsorption

## INTRODUCTION

It is well known that the charge of cellulosic fibers is an essential feature of their chemical and physical properties, and hence, it is also of importance for the final properties of textile products manufactured from these fibers. Most charged groups in cellulose fibers are carboxyl and hydroxyl groups. These dissociate in neutral or alkaline solutions, and then have a strong influence on the nature of adsorption (chemical or physical) and the adsorption kinetics of components present in the liquid phase, such as surfactants, dyes, polyelectrolytes, proteins, coatings, etc. Obviously, a better understanding of these interaction mechanisms will be achieved by a better knowledge about the dissociation behavior of the fibers (content of functional groups, pK values) and the accessibility of dissociated groups (surface and total charge). Both natural and regenerated cellulose fibers have a crystalline/amorphous microfibrillar structure.[1–3] Elementary fibrils consist of crystallites and intercalating less ordered, amorphous, domains. The differences between natural and different types of regenerated cellulose fibers are, above all, in the size and orientation of their crystallites and amorphous domains, the size and shape of the voids, and the number of interfibrillar lateral tie molecules. It can be assumed that all of these properties have an influence on accessibility and, therefore, are of importance for the dissociation–adsorption character and reactivity of cellulose materials.[1–3]

A number of methods are available to analyze the nature, content, and strength of acidic groups in wood material.[4–10] The amount of acidic groups (total charge) can be determined by dye adsorption, conductometric, and potentiometric titration and ion exchange.[7] Potentiometric titration and, to some extent, conductometric titration, can also be used to deter-

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**TABLE I**
**The Specifications and Structural Characteristics of Regenerated Cellulose Fibers[2]**

| Fiber type | | Viscose | Modal | Lyocell |
|---|---|---|---|---|
| Symbol | | CV | CMD | CLY |
| Linear density $T_1$ (dtex) | DIN 53 812 | 1.88 ± 0.15 | 1.78 ± 0.23 | 1.82 ± 0.30 |
| Fiber length 1 (mm) | DIN 53 808 | 39.9 ± 0.5 | 40.1 ± 0.3 | 39.4 ± 0.4 |
| Fiber diameter d ($\mu$m) | DIN 53 811 | 14.3 ± 1.4 | 14.2 ± 1.1 | 12.8 ± 1.0 |
| Density $\rho$ (g/cm$^3$) | DIN 53 479 | 1.5045 | 1.5141 | 1.5205 |
| Crystallinity index CrI[a] | | 0.25 | 0.37 | 0.44 |
| Orientation factor $f_{\Delta n}$[b] | | 0.58 ± 0.07 | 0.69 ± 0.08 | 0.71 ± 0.04 |
| Void volume $V_p$[cm$^3$/g][c] | | 0.68 | 0.49 | 0.62 |
| Void diameter $d$ [nm][c] | | 3.1 | 2.4 | 3.0 |
| Specific inner surface $S_p$ [m$^2$/g][c] | | 439 | 409 | 432 |

[a] Determined by X-ray wide angle diffraction ($2\theta$ = 5–45°).
[b] Determined by birefringence measurements of the fibers.
[c] Determined by size exclusion chromatography.

mine the dissociation constants of acidic groups in the fibers.[7,10] Adsorption of cationic polyelectrolytes gives information on the accessibility of anionic groups in the fibers.[7] Because the accessibility of different interiors of porous fibers depends on the molecular weight of the polymer,[7] polyelectrolyte adsorption can be used to determine both the surface charge (excluding the pores) and the total charge of cellulosic fibers including the charges in pores.[7] The surface charge can also be estimated by measurements of the zeta potential of fibers.[11,12] Although all these methods have been extensively used in investigations of cellulose fibers as raw materials in papermaking, for most of them there are only a few reports about their application to textile fibers.[13–15]

Our aim is to transfer and develop (modify) these methods for application in the field of textile chemistry. The dissociation properties of natural and regenerated cellulose fibers were determined using potentiometric and conductometric titration as well as polyelectrolyte adsorption. Our main objective is to compare the methods with regard to the amount of acid groups, their dissociation constants, and the repeatability of the analyses. Although the methods are well described in the literature,[5–9] they may not be so familiar to those engaged in research on textile fibers. A somewhat extended presentation of the principles of each method is given in the Appendix.

## EXPERIMENTAL

### Materials

In this work natural (cotton) and regenerated (viscose, modal and lyocell) cellulose fibers were investigated.

Natural cellulose fibers (NC) were cotton fibers (type Ronda) with a fiber length of 31 mm, micronaire value of 4.4, and regain of 7.2%. To obtain a well-defined reference substance, the following purifying processes were applied:[4]

1. Boiling-alkaline cleaning: removal of noncellulose compounds (hemicellulose, waxes, pectin, proteins) by treatment for 90 min in 0.5 *M* NaOH at 95°C.
2. Oxidative bleaching: degradation of natural dyes and pigments by treatment for 30 min with 0.1 *M* $H_2O_2$ at pH = 11.2 and 95°C.

After each treatment the fibers were washed with distilled water until conductivity of less than 3 $\mu$S/cm was reached. The processed material was air dried.

Regenerated cellulose fibers were viscose (CV), modal (CMD), and lyocell (CLY) fibers produced by Lenzing AG, Austria. The structural parameters of these fibers have been determined previously and are given in Table I.[1–3]

The regenerated fibers were pretreated (only washed) according to the pretreatment processes conventionally used in textile praxis.[1,2]

Alkaline washing: treatment for 30 min at 60°C in a solution of 1 g/L Sandoclean PC (nonionic detergent) and 1 g/L $Na_2CO_3$ at pH = 10.9.

The fibers were then rinsed with distilled water until a constant conductivity of the washing liquid was obtained.

Before titrations, all cellulose fibers (natural and regenerated) were ground into small particles. The prewashed fibers were ion-exchanged into acid form by suspending them in 0.1 *M* HCl for 15 min. To remove excess acid, the fibers were washed with deionized water until the conductivity of the filtrate was less than 3 $\mu$S/cm. After washing, most of the water was removed from the fibers by filtering (Büchner funnel). The fibers were stored in a refrigerator at 4–6°C in wet form and were not dried before titrations.

Polymers: poly (1,5- dimethyl-1,5-diazaundecamethylene) bromide, "Polybrene" (molecular weight $M_w$ = 8000), from Sigma was used for total charge

determination and poly(dimethyldiallylammonium) chloride, "PDMDAAC" ($M_w > 100\ 000$), from Ciba was used for the surface charge determination. The anionic polymer used for polymer titration was sodium poly (etylenesulfonate) (PesNa) from MT Instruments Oy.

Other chemicals: in all analyses ion exchanged, distilled, and degassed water and analytical grade chemicals were used.

## Analytical methods

### Potentiometric titration

Details about the method of titration, including determination of equivalence point as well as the calculation of the amounts of acidic groups and pK values are described in Appendix A.1.

Oven-dry fibers (0.5 g) were added to 100 $cm^3$ of 0.5 *M* NaCl. The titration was started with a neutral fibers suspension to which 10 $cm^3$ of 0.1 *M* HCl in 0.5 *M* NaCl was added using a precision burette. The titration was carried out by adding a of 0.1 *M* NaOH in 0.5 *M* NaCl from a precision burette. During titration, the solution was stirred with a glass propeller and kept in airtight titration vessel. All experiments were carried out under thermostatically controlled conditions at 25°C. An inert atmosphere was maintained by continuous flow of argon. After each addition, the potential was recorded automatically with Methrohm 715 GPD titrator. It usually took 2.5 h until a stable potential was attained. The stability criterion was a drift of less than 0.5 mV/min. The amount of impurities not stemming from the fibers was determined by performing titrations exactly in the same way as with fibers, but without fibers present. The stability of the electrode system used was checked by calculation of the standard potential of the cell in the presence of excess acid or alkali (see Appendix A.1). All presented values are the mean values of five parallel measurements.

### Conductometric titration

Details about the method of titration, including determination of the equivalent point, are described in Appendix A.2. An amount of wet fibers corresponding to 1 g oven-dry fibers was added to an airtight titration vessel. About 500 $cm^3$ distilled water and 1 $cm^3$ 0.5 *M* NaCl was added to the vessel to obtain a 1 m*M* NaCl solution concentration during titration. Furthermore, 0.5 $cm^3$ HCl (0.1 *M*) was added to the vessel. During titration, the solution was stirred with a magnetic stirrer at 25°C under an argon atmosphere. The titration was performed by adding 0.1 *M* NaOH from precision burette in steps of 0.04 $cm^3$ with 1-min intervals. After each addition pH was recorded potentiometrically. Conductivity was recorded with a Metrohm 712 conductometer. Typically, titrations were finished at pH $\approx$ 10.5, which makes proper extrapolation of the intersection/end point possible.[16,17] A blank titration without fibers was performed to calibrate the system and to eliminate effects of impurities effects. The total amount of acidic groups was obtained by extrapolating the second and the third linear parts of the titration curve until they intersect (letter A on the Fig. 6 in Appendix A.2). The total acidic group content (X) was calculated from:

$$X = \frac{C_{\mathrm{OH}} \cdot V_t}{m_{\mathrm{dry}}}, \tag{1}$$

where $C_{\mathrm{OH}}$ is the concentration of the sodium hydroxide solution, $V_t$ is the volume of the sodium hydroxide solution consumed at the second intersection point and $m_{\mathrm{dry}}$ is the oven-dry weight of sample. All presented values are the mean values of three parallel measurements.

Both the potentiometric and the conductometric titration were controlled by a computer system, so that additions of NaOH and potentiometric and conductometric data were controlled and collected automatically.

### Polyelectrolyte adsorption

Details about the polyelectrolyte adsorption method of titration are described in Appendix A.3. All acid groups were first converted into their Na form by treating the cellulose fibers with $1 \cdot 10^{-3}$ *M* $NaHCO_3$ at pH 9 (adjusted with NaOH). Prior to the adsorption experiments, excess electrolyte was removed by washing the fibers with deionised water until the supernatant had conductivity less than 2 $\mu$S/cm. After that, about 0.3 g of dry fibers were weighted into a 100-mL beaker. At least four samples were prepared. To each sample 40 $cm^3$ of 0.1 *M* NaCl was added and pH was adjusted to 7. Then varying excess amounts of cationic polymer were added to the fiber suspension. The suspensions were stirred for 30 min to reach adsorption equilibrium and then filtered through weighted filter paper using a Büchner funnel. After that, fibers were washed with some water so that the total amount of filtrate was 55 $cm^3$; 10 $cm^3$ of filtrate (which contains nonadsorbed polyelectrolyte) were titrated with PesNa using a Mütek particle charge detector to detect the end point (zero potential). Blank samples, which contained only cationic polymers, were titrated in the same way as the fibers so that effects of polymer adsorption by the glassware and a glass fiber filter could be eliminated. The filtrated samples on the filter paper were dried in an oven at 105°C for at least 4 h. The dried fibers samples were placed in a dry desiccator to cool down and were weighted afterwards. The

**TABLE II**
**Total Anionic Groups Determined by Potentiometric, Conductometric Titrations, and Polyelectrolyte Adsorption for Cotton (NC), Viscose (CV), Modal (CMD), and Lyocell Fibers (CLY)**

| Method | Potentiometric titration | Conductometric titration | Polyelectrolyte adsorption | |
|---|---|---|---|---|
| Sample | Acidic groups (mmol/kg) | Acidic groups (mmol/kg) | Total charge (mmol/kg) | Surface charge (mmol/kg) |
| NC | 52.3 ± 5.0 | 43.2 ± 1.3 | 25 ± 1.5 | 18.5 ± 1.7 |
| CV | 40.6 ± 3.1 | 48.6 ± 1.0 | 24 ± 1.4 | 4.7 ± 0.4 |
| CMD | 26.1 ± 1.5 | 27.2 ± 0.5 | 16 ± 0.8 | 3.5 ± 0.08 |
| CLY | 18.4 ± 1.0 | 20.6 ± 0.5 | 15 ± 0.9 | 3.5 ± 0.04 |

following equation was used for calculating the charge ($Q$) of the fibers:[18]

$$Q = \frac{(V_0 - V_{\text{tit}}) \cdot C_{\text{polymer}}}{m_{\text{dry}}} \cdot \frac{V_{\text{tot}}}{V_{\text{sample}}} \quad (2)$$

where $V_0$ is the volume of PesNa consumed by the blank sample, $V_{\text{tit}}$ is the volume of PesNa solution consumed in titration of the fiber sample, $C_{\text{polymer}}$ is the weight concentration of cationic polymer, $V_{\text{tot}}$ is the total volume of filtrate, $V_{\text{sample}}$ is the volume of filtrate suspension taken to the titration, and $m_{\text{dry}}$ is the dry mass of the sample. The charge on the fibers was estimated from adsorption isotherms by extrapolating the plateau level of adsorption to the zero polymer concentration (see Appendix A.3). The amount of charge adsorbed with the polymer at this point (in $\mu$g/g or mmol/kg) was taken as the charge of the fibers.[5,7,17] All presented values are the mean values of three parallel measurements.

## RESULTS AND DISCUSSION

### Potentiometric titration

The amount of acid or basic impurities not stemming from the fibers was found to be about 15 $\mu$mol/L or less in all titrations. The standard potential of the electrode system was found to be stable within ±0.1 mV or less during each titration and also, using the same set of electrodes, varied changed by less than 1 mV between titrations. This indicates excellent stability of the electrode system. The total amount of acid groups obtained by the potentiometric titration is presented in Table II. The calculated pK values and amounts of different acid groups are given in Table III.

The highest amount of acidic groups is detected in raw cotton sample (52.3 mmol/kg). The content of acid groups in CV is about 22% lower (40.6 mmol/kg) than in raw cotton. CLY fibers contain the lowest amount of acidic groups content (18.4 mmol/kg), which is about 30% less than the value for CMD (26.1 mmol/kg). The differences in acid content of the analyzed samples are a consequence of different structural parameters, such as: molecular mass, degree of polymerization, crystallinity index, orientation factor, etc. The most important structural parameters expected to have a certain influence on the dissociation and accessibility of acidic groups in the fibers are the degree of crystallinity and/or the amount of amorphous domains. The amount of amorphous material of regenerated fibers increases (the crystallinity index decreases, see Table I) from lyocell to modal fibers, and a significant increase of this amount is evident in the case of viscose fibers:[1–3]

Comparison of Tables I and II indicates that the content of accessible carboxyl groups is lowered by an increase in the degree of crystallinity, i.e., with a reduction of the amorphous regions. The structural analysis shows that the highest molecular weight, of the three regenerated fibers, CLY, has highest degree of crystallinity and the highest molecular orientation (see Table I).[1–3]

It is known[18,19] that raw cotton has a higher degree of crystallinity than regenerated fibers and, therefore, the lowest amount of amorphous regions. Thus, it is expected that cotton will show the lowest value of accessible acidic groups. The experimental results did not agree with this prediction. Raw cotton actually contains the highest amount of carboxyl groups (52.3 mmol/kg). This may be the consequence of impurities such as hemicellulose, pectins, and waxes (low molecular fractions), which were not totally removed by pretreatment processes. This is confirmed by the cal-

**TABLE III**
**Dissociation Constants and Relative Amounts of Acid Groups for Cotton (NC), Viscose (CV), Modal (CMD), and Lyocell (CLY) Fibers**

| Sample | $pK_1$ | $pK_2$ | Acid 1 (mmol/kg) | Acid 2 (mmol/kg) |
|---|---|---|---|---|
| NC | 3.51 | 5.72 | 47.4 | 4.9 |
| CV | 3.6 | / | 40.6 | / |
| CMD | 3.49 | / | 26.1 | / |
| CLY | 3.54 | / | 18.4 | / |

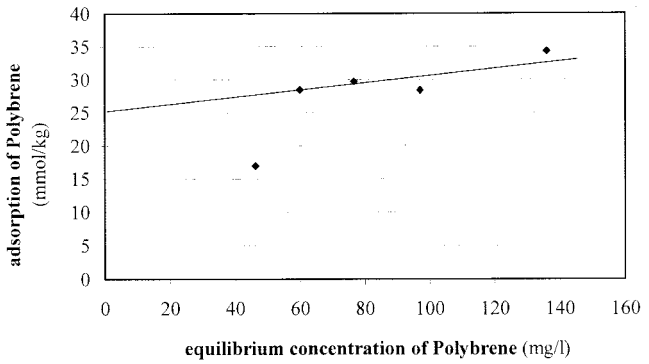


**Figure 1** Adsorption of Polybrene on cotton fibers as a function of equilibrium concentration of polymer.

culated pK values, which clearly show that the highest amount of acidic groups in raw cotton is a consequence of the presence of two different types of acidic groups (Table III), while regenerated fibers (viscose, modal, and lyocell) contained only one type of acidic group.

Within experimental error (which is about 2% in the case of all samples), a predominating acid with dissociation constant (pK ≈3.5) is found in all fibers. In raw cotton there is about 10% of an additional acidic group with pK 5.7. The pK value (3.5) of the strong acid agrees well with the value expected for carboxyl groups in uronic acids.[17] The amount of the weaker acid (pK ≈5.7), in raw cotton could be due to residual (rest) components in the cellulose fibers (low molecular fractions). It is, however, difficult to clearly identify the possible sources of weak anionic groups in the fibers. In earlier studies it has been suggested that they may be ester or lactone groups.[20,21] The small amount impurities of in the cotton fibers may also contain some fatty and resin acids. To verify this hypothesis, ESCA studies of the cotton surfaces are in progress and will be reported in a subsequent article.

The amount of the weaker acid detected in the NC fibers corresponds to a concentration of about 25 μmol/L in the titration, which about twice as large as the amount of impurities detected in the blank titration. Thus, although there is no doubt that there is a significant amount of weaker acid in the NC fibers, the actual amount of these is not very precisely determined.

## Conductometric titration

The results of conductometric titration differ somewhat from those of potentiometric titrations (Table II). The cotton fibers contain 43.2 mmol/kg of acidic groups. The viscose fibers contain the highest amount of —COOH groups (48.6 mmol/kg), i.e., 13% more than the cotton fibers. The modal fibers contain 27.2 mmol/kg of carboxyl groups, which is ≈44% less than in the viscose fibers and ≈37% less than in cotton. The differences between the amounts of —COOH groups in modal and lyocell fibers are the same as found by potentiometric titration. The lyocell fibers contain the lowest amount of acidic groups (20.6 mmol/kg), which is ≈32% les than in the CMD fibers (27.2 mmol/kg). The reasons (structural parameters) for this were already discussed.

## Polyelectrolyte titration

Examples of adsorption isotherms for cotton fibers are shown in Figures 1 and 2. These isotherms showed a well-defined plateau level, which made total (Fig. 1) and surface charge determination unequivocal (Fig. 2). This was also the case for regenerated fibers.

The amount of charge (total and surface) varies in the same way as the amount of carboxyl groups determined by potentiometric and conductometric titration (Table II).

Cotton and viscose samples show almost the same total charge. Total charge for raw cotton is 25 mmol/kg, while for viscose fibers it is only 4% lower. The charges of modal and lyocell fibers are lower and roughly equal (16 and 15 mmol/kg, respectively). The surface charge of raw cotton fibers is 18.5 mmol/kg, what is almost four times higher than the surface charge of viscose fibers, which is only 4.7 mmol/kg. The surface charges of modal and lyocell fibers are equal and lower than those of viscose fibers (3.5 mmol/kg). It is likely that because of the very low specific surface area of regenerated fibers, PDMDAAC, which has a very high charge density, can react only with some of the acidic groups on the surface. Another possible explanation is that most of carboxyl groups are located in an inner region of regenerated cellulose fibers. Another possible explanation is that most of carboxyl groups are lcoated in an inner region of regenerated fibres, which can be confirmed by approximate ratios be-

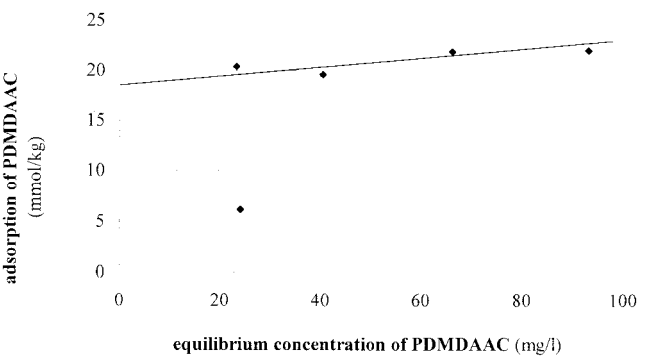


**Figure 2** Adsorption of PDMDAAC on cotton fibers as a function of equilibrium concentration of polymer.

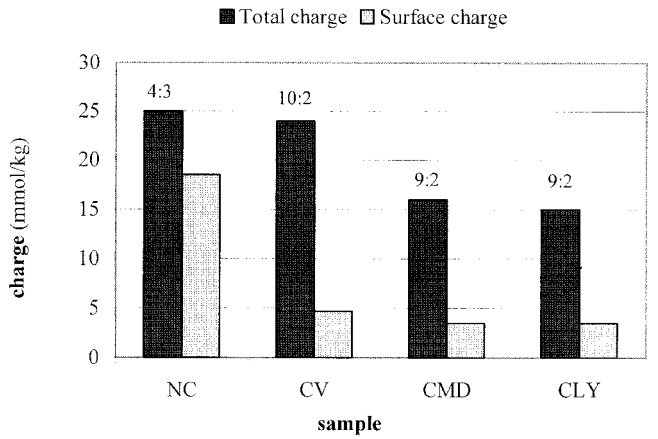


**Figure 3** Amount of total and surface charge using polyelectrolyte adsorption. Approximate ratios of the amounts are given for each sample.

tween total and surface charge for each sample as shown in Figure 3.

### Comparison of methods

Figure 4 shows total acidic groups content determined by potentiometric, conductometric titration, and polyelectrolyte adsorption.

The trends in the results of all titration methods are equal. Potentiometric and conductometric titration are direct methods, and therefore, give very similar results for all samples. The exception is result for raw cotton sample determined by potentiometric titration, which is higher that determined by conductometry. The weak acids (pK ≈5.7) located on the fiber could give rise to this difference. Such groups were not detected using conductometric titration, but they were seen in the potentiometric measurements. We believe that the small differences can be due differences in the evaluation of the near-neutral end point. As noted in the discussion of the results from potentiometric titration, the amount of the weaker acid is quite small and might be difficult to detect as a separate slope in the evaluation of conductometric data. The reproducibility was the best for the conductometric titration with coefficients of variation (CV) in the range of 1–3% and was much better than the reproducibility of the potentiometric titration, with CV 5–10% (Table II). This may be due to the amount of strong acid added prior to the titration and the determination of low concentrations of acid groups in the presence of an excess of a strong acid.[20,21] The coefficient of variation for the total charge determination is in the range of 5–6%. For the surface charge determination using polyelectrolyte titration it is in the range of 1–10%. Polyelectrolyte titration gives a lower content of acidic groups than potentiometric and conductometric titration (Fig. 4). These differences between the three methods are not unexpected, because polyelectrolyte titration is an indirect method, while potentiometric and conductometric titrations are direct methods.

In the case of polyelectrolyte titration, the amount of cationic polymer adsorbed into/onto the fiber does not seem to correspond to the stoichiometric amount of anionic groups determined by direct titration methods. Assuming that the potentiometric and conductometric results are correct, it is obvious that the stoichiometric reaction between fibers and the Polybrene used for total charge determination is not complete. On average (an exception is raw cotton determined with potentiometric titration), 50% of the acids groups determined with potentiometric and conductometric titrations were accessible to the Polybrene polymer. This indicates that charges in the smallest pores of fibers are not accessible even for a polyelectrolyte with a molecular weight as low as $M_w$ = 8000. This may be due to either steric hindrance or a slow adsorption process. In addition, small amounts of impurities (specific cations) on the surface may cover some carboxyl groups, and therefore, block the ion-exchange reaction with polymer. Comparison of the results for surface charge shows higher values for cotton fibers than regenerated fibers. For the cotton sample, about 40% of all acidic groups, which were determined by potentiometric and conductometric titration, were accessible to PDMDAAC, while in the case of regenerated fibers, only 20% were accessible to the same polymer. It can be concluded that, assuming that PDMDAAC adsorbs in the same way on cotton and regenerated fibers, the surface of cotton fibers contains higher amounts of accessible —COOH groups than regenerated fibers. For all fibers, it can be concluded that most of the carboxyl groups are located in an inner region of the cellulose fibers that is not accessible for polycations with molecular weight >100,000. A combination of the three-titration methods described above constitutes a

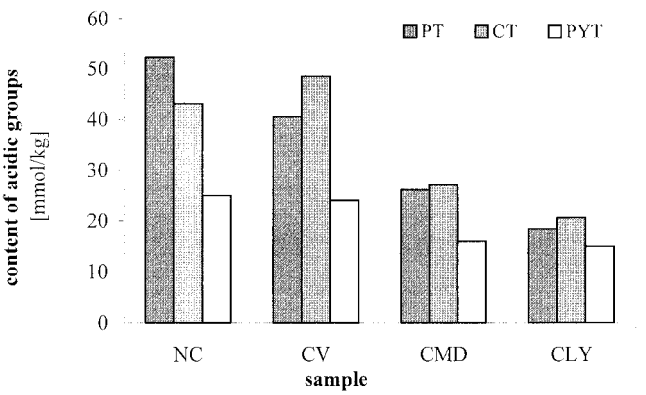


**Figure 4** Anionic groups in cotton (NC), viscose (CV), modal (CMD), and lyocell fibers (CLY) determined using potentiometric (PT), conductometric (CT), and polyelectrolyte titration (PYT).

promising tool for the investigation of the content of acidic groups of natural and regenerated cellulosic textile fibers. The advantage of the potentiometric method in comparison with other two titration is that it allows determination of pK values of the strong acids as well as determination of very weak acids, which gives a direct insight into the nature of these acids.

## CONCLUSIONS

Good agreement was obtained between the results determined by potentiometric and conductometric titration. Both techniques may be used to determine the content of acidic groups; the potentiometric titration technique is also capable of providing information about the actual strength of acidic groups. Results of polyelectrolyte adsorption show that adsorption of polyelectrolytes onto/into the cellulose fiber is limited by the accessibility of the groups to polymers of different size. The Polybrene adsorption method shows the same trends as potentiometric and conductometric titration, but it gives lower total charge. If this indirect method is used, it has to base on the assumption that only about 50% of the total charge is neutralized by the polymer. On the other hand, adsorption of polycations with different molecular weight gives important information on the accessibility of anionic groups in the fibers. The surface charge of the fibers could not be accurately determined in this study. Only a rough estimation of their amount could be made. From polyelectrolyte adsorption results it can be concluded that polymer with a molecular mass of 8000 (Polybrene) has stronger ability to sorb into pores than polymer with a molecular mass ≈300,000 (PDMDAAC) used for surface charge determination, which has only very limited access.

This work has shown that the combination of different titration analysis contributes to a better and detailed understanding about content and strength of acidic cellulose (natural and regenerated) fiber's groups, related to their dissociation–adsorption ability.

## APPENDIX

### Methods to determine fiber charge

#### A.1. Principle of potentiometric titration

The methods described below have been extensively applied in high-precision titrations aiming at determinations of complex equilibria in solution. However, because the original papers were published a rather long time ago and the methods, to our knowledge, have not been applied to textile fibers before, we give a brief explanation of them below.

In the potentiometric titration of fibers the concentration of free hydrogen ions [H+], was determined after each sodium hydroxyl (NaOH) addition by measuring the potential of the electrochemical cell $E$ of the cell:

$$-\mathrm{Hg,Hg_2Cl_2/0.1\ M\ NaCl//\ fibers}$$
$$\text{suspension in 0.5 M NaCl/glass electrode} + \quad \text{(A1.1)}$$

At high ionic strength it can be assumed that the activity coefficients of hydrogen and hydroxyl ions are constant. In this case, the potential of the cell is given by the Nernst equation in the form:

$$E = E_{\mathrm{H}}^{\mathrm{o}} + k_E\mathrm{pH} + E_j = E_{\mathrm{H}}^{\mathrm{o}} - k_E\mathrm{pOH} + k_E\mathrm{pK}_w + E_j = E_{\mathrm{OH}}^{\mathrm{o}} - k_E\mathrm{pOH} + E_j \quad \text{(A1.2)}$$

where $E°_{\mathrm{H}}$ and $E°_{\mathrm{OH}}$ are standard potentials, pH = $-\log\ [\mathrm{H}^+]$, pOH = $-\log\ [\mathrm{OH}^-]$, and $K_w = [\mathrm{H}^+][\mathrm{OH}^-]$ is the ionic product of water. $E_j$ is the diffusion potential due to the salt bridge, which is frequently found to be linearly but weakly dependent on $[\mathrm{H}^+]$ and $[\mathrm{OH}^-]$. $k_E = RT\ln 10/F$ (=59.16 mV at 25°C), where $R$ is the universal gas constant, $T$ is temperature, and $F$ is Faraday's number.[22,23]

In the presence of excess hydrogen ions over those bound to the weak acids or excess hydroxyl ions over those required to neutralize all acids, $[\mathrm{H}^+]$ and $[\mathrm{OH}^-]$ can be calculated from:

$$[\mathrm{H}^+] = \frac{(V_{\mathrm{ekv}} - V_{\mathrm{t}})C_{\mathrm{OH}}}{V_{\mathrm{o}} + V_{\mathrm{t}}} \quad \text{(A1.3)}$$

and

$$[\mathrm{OH}^-] = \frac{(V_{\mathrm{t}} - V_{\mathrm{ekv}})C_{\mathrm{OH}}}{V_{\mathrm{o}} + V_{\mathrm{t}}} \quad \text{(A1.4)}$$

respectively. Here, $V_o$ is the initial volume of the solution, $V_t$ is the added volume of NaOH solution with concentration $C_{\mathrm{OH}}$ and $V_{ekv}$ is the volume of NaOH required to neutralize all acids in the solution.[22,23]

$V_{\mathrm{ekv}}$ can be obtained from the steepest point of a titration curve (pH vs. $V_t$), but to increase accuracy of the end-point determination, linearization of the titration curve (the so-called Gran plot) is recommended.[9,17,23] For the parts of the titration curve where only hydrogen ions in excess of those bound in weak acids react with added $\mathrm{OH}^-$ (low pH) or $\mathrm{OH}^-$ is added in excess of the equivalence points, the functions:

$$Y = K(V_0 + V_t)10^{E/k_E} \quad \text{(A1.5)}$$

at low pH and

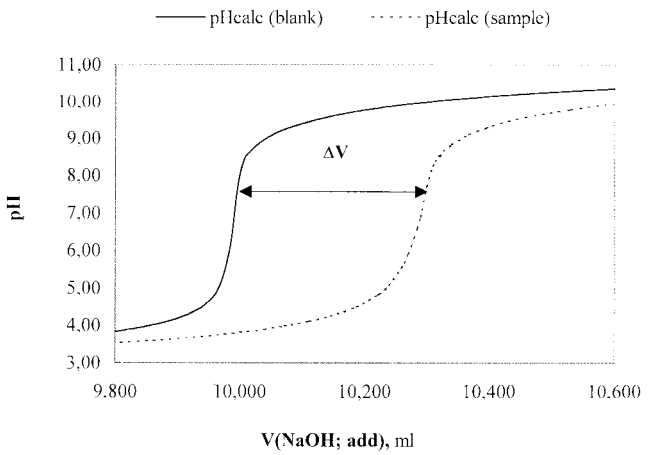


**Figure 5** Titration curves (pHcalc) for blank and pulp electrolyte solutions in 0.5 M NaCl.

$$Y' = K'(V_0 + V_t)10^{-E/k_E} \qquad \text{(A1.6)}$$

at high pH (where $K$ and $K'$ are arbitrary scaling constants) are plotted against $V_t$. Provided that the electrode system is stable and has reached equilibrium after each addition of $OH^-$, these plots are linear and can, with high accuracy, be extrapolated to their intercept with the abscissa. The value of $V_t$ at $Y' = 0$ is $V_{ekv}$; the value of $V_t$ at $Y = 0$ ($V_f$) is the volume of NaOH solution required to neutralize the free hydrogen ions in excess of those bound to weak acids. Thus, the difference $V_{ekv} - V_t$ gives the volume of NaOH required to neutralize the weak acids.

Knowing $V_{ekv}$, $[H^+]$ and $[OH^-]$, using eqs. (A1.3) and (A1.4) can be calculated for the parts of the titration where excess free hydrogen ions or hydroxyl ions are titrated. Then equation (A1.2) can be used to calculate values of $E°_H + E_j$ and $E°_{OH} + E_j$ as functions of $[H^+]$ and $[OH^-]$. Because $E_j$ depends linearly on $[H^+]$ and $[OH^-]$, these functions can be extrapolated to $[H^+]$ and $[OH^-] = 0$, respectively, to yield values of $E°_H$ and $E°_{OH}$.[24]

In addition to being an accurate way of calibrating the electrode system in each titration, this method also provides an excellent test of the stability of the electrode system. If the cell is not stable, or $E$ is measured before equilibrium is reached, it will not be possible to obtain reasonably linear plots of $E°_H + E_j$ and $E°_{OH} + E_j$. The variation due to the diffusion potential should be a few mV at most. In the titrations reported in this article, both $E°_H$ and $E°_{OH}$ were actually constant within the accuracy of the potentiometric system used. If there are no weak acids and bases present in the blank titrations, the intercepys of both Gran plots should be the same, i.e. $V_f = V_{ekv}$. Usually this is not the case, because very small amounts of impurities usually cannot be avoided. The gap between $V_f$ and $V_{ekv}$ then yields a direct measure of the amount of such impurities and provides further control of the accuracy of the tiration, which is essential if very small amounts of acid are titrated.[24]

The methods described above were used to check the stability of the electrode system and the amount of impurities for several titrations. It was found that the system generally was very stable and the amount of impurities quite small compared to the amounts of acid in the samples, in most cases the total amount of acidic groups was calculated from the difference ($\Delta V$) in added NaOH volume between the blank ($V_{t,\text{Blank}}$) and fiber sample ($V_t$) at any given pH (Fig. 5).[25–27] Potentiometric titration can also be used to evaluate the dissociation constants of the acids and the titration has been interpreted using the method of Herrington et al.,[9] as modified by Rasanen et al.[25,26] In this model the apparent dissociation constant of the acids in fiber surface will depend on the degree of dissociation ($\alpha$) of fibers, due to increased electrostatic interaction between hydrogen ions and the fiber as $\alpha$ increases. In the Donnan model of ion distribution between fibers and surrounding solution, the apparent dissociation constant is given by:

$$K_i = \lambda \cdot K_i' \qquad \text{(A1.7)}$$

where $K_i$ is the intrinsic dissociation constant and $\lambda$ is the Donnan distribution coefficient.

However, at high ionic strength (0.5 $M$ NaCl) the Donnan distribution coefficient is equal to one ($\lambda = 1$) and, therefore, the apparent dissociation constants approach the intrinsic ones ($K_i = K_i'$).[25] The dissociation of fiber-bound groups is described by the following equation:

$$n_A \cong V_f \sum \frac{[A_i]_f \cdot K_i}{10^{-\text{pH}} + K_i} \qquad \text{(A1.8)}$$

where $n_A$ is total amount of dissociated acids in the fiber, and $[A_i]_f$ is concentration of fiber-bound acids.[25–27]

On the mentioned assumptions the dissociation constants as well as the quantities of the fiber-bound groups can be determined by minimizing the sum of squares of errors:

$$\sum (n_{A_j}(V_t - V_{t,\text{Blank}})_j C_{OH})^2 = \sum_j U_j^2 \qquad \text{(A1.9)}$$

where the summation is taken over all experimental points $j$.[25–27]

The full details of the principle of potentiometric titration for determination of pK values, as well as data treatment are given in refs. 25–27.

### A.2. Principle of conductometric titration

The conductometric titration of fibers suspension is similar to that of soluble acids. The measured parameter is conductance, which is an additive function of the products of concentration and equivalent conductance of each type of ion present in solution.[16,28] Marked increases or decreases in conductance are associated with the changing concentrations of the two most highly conducting ions—the hydrogen and hydroxyl ions. However, as in any titration of a fiber suspension or polyelectrolyte, it is necessary to carry out the procedure in the presence of a neutral salt.[28] In the absence of salt, the Donnan equilibrium causes a very unequal distribution of the mobile ions between the interior of the fiber wall and the external solution, with the result that the strength of the fiber-bound acids will appear to depend on the degree of dissociation. The presence of 0.001 *M* sodium chloride was found to be optimal for the conductometric titration.[16,28] A higher concentration of salt, although bringing a more uniform distribution of ions, introduces a background conductance, which swamps the examined effects.[16,28] When fibers are conductometrically titrated they are first converted to the $H^+$ form, what means that all acidic groups have proton as a counterion. After this, the fibers are titrated with NaOH. For carboxylic acid groups, respectively, the following reaction takes place:

$$\text{Fiber-COOH} + OH^- \Rightarrow \text{Fiber-COO}^- + H_2O \quad \text{(A2.1)}$$

As already discussed, prior to the titration, some salt (NaCl) is added to the titration vessel to improve the accuracy of the determination of the acidic groups. The titration of cotton fibers suspension is characterized by three distinct phases,[16,28] as is evident from appearance of the titration curve (Fig. 6): Phase 1: neutralization of liberated protons slightly lowers the conductivity; Phase 2: neutralization of carboxylic groups, which does not change the conductivity. The added sodium ions ($Na^+$) are adsorbed as counterions to the carboxylic acidic groups, and the dissociated protons are neutralized by the added hydroxide ions ($OH^-$). Phase 3: accumulation of NaOH in excess leads to an increased conductivity.

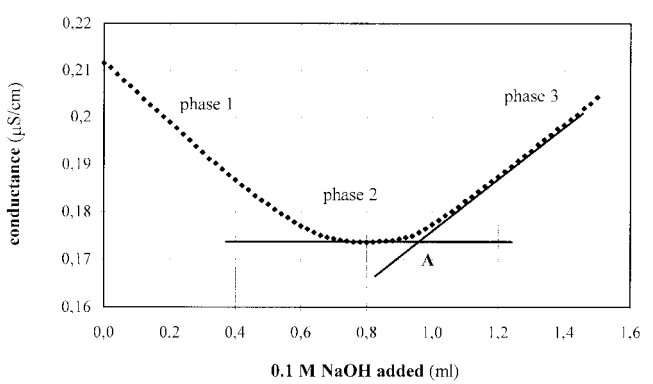


**Figure 6** Conductometric titration of cotton fibers in the presence of 0.5 mL 0.1 *M* hydrocloric acid.

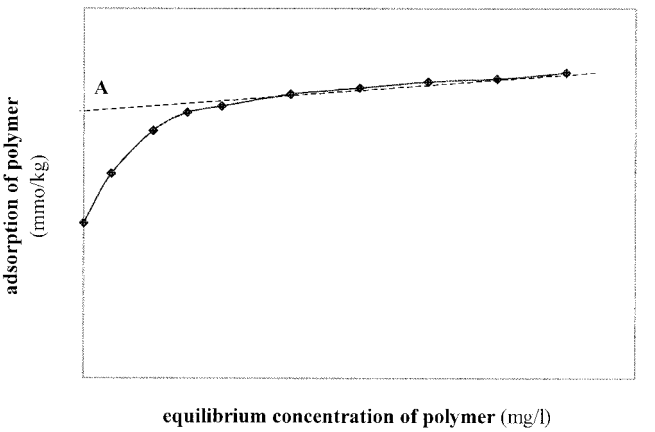


**Figure 7** Adsorption of polymer, as a function of equilibrium concentration of polymer in solution. A is the amount of adsorbed polymer used for calculation of the charge on the cellulosic fibers.

The total amount of acidic groups can be determined from the intersection point (A), as shown in Figure 6.

### A.3. Principle of polyelectrolyte adsorption

Adsorption of cationic polymers with high charge density has been proven to be a powerful method to characterize the charge of cellulosic fibers.[5,7,17] A basic assumption of this method is that there is a 1 : 1 stoichiometric relationship between the number of cationic groups bound to the fiber surface and the number of anionic groups on the surface neutralized by the cationic groups.[5] This assumption is generally valid as long as the adsorbed polymer is bound in a flat conformation, which will be the case as long as the charge density of the polymer is high and electrostatic interactions are not screened by a simple electrolyte in the solution. The accessible charge of fibers depends on the molecular weight of the adsorbed polymer. Polymers with a low molecular weight have access to all charges in the interior of the fiber, representing the total charge. Polymers with a high molecular weight neutralize only the charge located at the fiber surface, giving information about the surface charge. The amount of adsorbed polymer on the fibers is determined by titrating the excess (nonadsorbed) polymer with polyanion. The end point of titration is detected by measuring the streaming current of the filtrate. The usual way to describe adsorption is to determine the amount of polymer adsorbed onto fibers as a function of the equilibrium concentration of polymer in solu-

tion. This function is called the adsorption isotherm (Fig. 7). From these isotherms the charge on the fibers can be evaluated by extrapolating the plateau value of adsorption to the zero polymer concentration; i.e., to the point A in Figure 7.[5,7,17]

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