

Layer-by-Layer Adsorption of Two Cellulose-Based Polyelectrolytes on Cellulose Fibers. Dependence of pH and Ionic Strength on the Resulting Charge Density as Measured by Polyelectrolyte Titration

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The charge density of a bleached Kraft hardwood pulp, subjected to layer-by-layer adsorption of the oppositely charged cellulose derivative polyelectrolytes hydroxyethylcellulose ethoxylate, quaternised (HECE), and carboxymethyl cellulose (CMC), was studied by polyelectrolyte titration as a function of pH and ionic strength. The experimental design included a simultaneous variation of the experimental parameters, and the trends were evaluated with the help of partial least squares regression. As expected from the literature, the data indicate that both pH and ionic strength influence the charge of cationic fibers. It is also obvious that CMC as an outermost layer is more sensitive to changes in pH than the deprotonation of $\equiv\text{COOH}$ groups suggests. High ionic strength seems to be beneficial for the adsorption of HECE, while the pH dependence seems much more complicated. The non-linear pH dependence indicates that, in addition to electrostatic interactions, entropy factors and hydrogen bonding between OH groups on both the substrates and ligands are responsible for the adsorption, which is in agreement with literature on the subject.

Keywords: Layer-by-layer adsorption; Cellulosic polyelectrolyte; Fiber charge density

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INTRODUCTION

Nanostructured polyelectrolyte multilayer structures formed by layer-by-layer (LbL) deposition have been the focus of many studies since the first papers, by for example Decher *et al.* (1992), in the early 1990s. The interest in LbL materials virtually exploded after that, *cf.* the review in (Hammond 2004) and for example Boddohi *et al.* (2010), and the potential of multilayers is vast. LbL deposition has huge potential for applications ranging from biosensors, and electronic devices to membranes and microcontainers for molecular encapsulation, and controlled release (*e.g.* Ho *et al.* 2000; Nolte and Fery 2006; Haberska and Ruzgas 2009; Tian *et al.* 2013; Zhang *et al.* 2013). In the field of pulp and paper, the LbL technique has been part of the scope of several investigations, from surface science (*e.g.* Wågberg *et al.* 2008; Salmi *et al.* 2009), applied paper strength studies (*e.g.* Wågberg *et al.* 2002; Eriksson *et al.* 2006a,b), and tailored fibres (Gustafsson *et al.* 2012; Zechner and Kolednik 2013). A general conclusion from these investigations is that cellulose fibers modified by polyelectrolyte multilayers exhibit significantly enhanced fiber–fiber bond strength and make for strong paper sheets. However, combining cellulose surfaces with biopolyelectrolytes is almost

unexplored, and the potential of biorefinery products in this field is therefore unknown. Continued studies on LbL structures of cellulose are therefore greatly needed. Here, the most interesting thing is the use of biomaterials; multilayers with nanocellulose on cellulose have been reported (Ahola *et al.* 2008; Aulin *et al.* 2008; Olszewska *et al.* 2013). Although the last of these references reports on all-cellulose-based multilayers, layered structures formed by commercial cellulose-based polyelectrolytes have not been studied extensively. Haberska and Ruzgas (2009) studied the LbL deposition of chitosan and CMC on a gold surface, but the combination of cellulose model surfaces and the adsorption of bio-based polyelectrolytes is relatively unexplored. In most studies, the polyelectrolyte components are petroleum-based chemicals, *i.e.*, polyacrylamide and polyethyleneimine. A consequence of this is that the potential of biorefinery products for LbL modification of cellulose and fibers has not yet been extensively investigated. The use of cellulose-based polymers and polyelectrolytes in cellulose-surface modification also has the potential advantage of strong hydrogen bonding. The approach, therefore, possibly leads to an interesting source of more environmentally-friendly, new cellulose fiber-based materials with a “CO₂-neutral” backbone.

In this context, it must be observed that the very interesting and commercially available cellulose-based polyelectrolyte CMC is almost unexplored in multilayer studies on cellulose. CMC is a well-known, and thoroughly investigated, negatively charged cellulose-based polyelectrolyte. It is relatively cheap and easy to manufacture and has been used for several industrial applications for decades. It is therefore an interesting polyelectrolyte for several reasons, and its sorption onto cellulose fibers has been shown to significantly improve paper strength properties (Laine *et al.* 2003; Blomstedt and Vuorinen 2006). The buildup of multilayers involving CMC on cellulose is also interesting because CMC is both a polysaccharide-like material and a polyelectrolyte (Fig. 1).

Both anionic and cationic polyelectrolytes are needed for creating polyelectrolyte multilayers. For the reasons mentioned previously, a cellulose-based polyelectrolyte also was used as the cationic component. Because a cellulose derivative has a backbone structure that is similar to cellulose, the hydrogen-bonding possibilities could also be potentially high. For these reasons, the cationic cellulose derivative HECE (Fig. 1) was chosen for this study. The solution pH and ionic strength (I) affect the interactions between polyelectrolytes and surfaces (van der Schee and Lykema 1984), and it is probable that this is also the case for the presently studied polyelectrolytes. Layer-by-layer adsorption of these two cellulose-based polyelectrolytes on cellulosic fibers have therefore been investigated as a function of both pH and ionic strength. To find any hidden trends in the data, a partial least squares (PLS) regression analysis was performed, and the conclusions are presented here.

EXPERIMENTAL

Chemicals

0.1 M NaOH and 0.1 M HCl (Merck), NaCl (J. T. Baker), hydroxyethylcellulose ethoxylate, quaternised (Sigma-Aldrich), carboxyl methyl cellulose—sodium salt (Aldrich), NaH₂PO₄ (Sigma), Na₂HPO₄ (Fluka), CH₃COONa (Oy FF-Chemicals Ab), NaHCO₃ (VWR), polybrene (Sigma), and PES-Na, (Oy G. W. Berg Ab/BTG Müttek GmbH) were all used as received. Deionised water (Millipore Synergy UV) was used for

the preparation of all solutions. Solutions of the polyelectrolytes were prepared with a concentration of 1 g/dm³, and the ionic strength and pH of the solutions were adjusted before the final dilution. The pH values of the solutions were controlled using a combination pH electrode (Mettler Toledo) and calibrated using commercial buffer solutions (J. T. Baker). In Table 1, the polyelectrolytes used are presented, and in Fig. 1, the structure of the cellulose-based polyelectrolytes is shown. The fibre used was a bleached hardwood pulp from a Finnish Kraft mill, swollen for 72 h in MilliQ-H₂O, and then used without further purification.

Table 1. Names, Molar Masses, and Charge Densities of the Polyelectrolytes Used

Polyelectrolyte	M_w (g/mol)	Charge Density (mmol/g)
CMC, carboxymethyl cellulose (Aldrich)	90,000	-4.3
HECE, hydroxy ethylcellulose ethoxylate, quaternised (Aldrich)	?	+1.3
Polybrene poly(1,5-dimethyl-1,5-diazaundecylmethylene)bromide (Sigma)	8,000	+5.34
PES-Na, dium polyethansulphonate (Oy G. W. Berg Ab/BTG Müttek GmbH)	19,100	-7.69

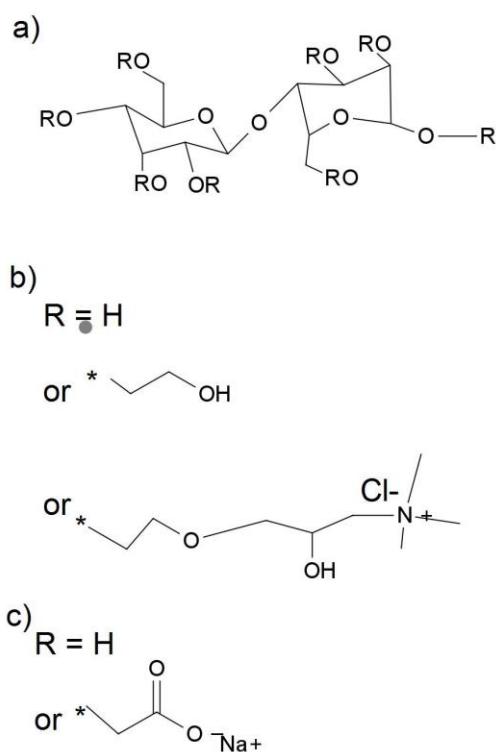


Fig. 1. Molecular structures of a) cellulose backbone, b) and c) the substituents in HECE (chloride salt) and CMC (sodium salt), respectively. In pure cellulose, R = H

Multilayer Buildup

First, 1 g/dm³ solutions of the polyelectrolytes for adsorption were prepared by diluting stock solutions with 0.5 mM buffers (HAc/Ac⁻ for pH = 4.5, H₂PO₄⁻/HPO₄²⁻ for the other pH values), NaCl (aq) and H₂O, to an approximate volume. NaCl was added to keep a constant ionic strength (I). The pH was then fine-tuned, and the solutions were finally diluted in volumetric flasks. Vacuum-filtered pulp was put in a beaker, and an aliquot of the above-described polyelectrolyte solutions was added to a fibre concentration of approximately 2% in the first suspension. The pulp/polyelectrolyte mixtures were mixed for 30 s with a spoon, and the suspension was left for 10 to 15 min for the adsorption to be completed.

Subsequently, the fiber/polyelectrolyte suspension was vacuum-filtered in a glass filter and gently rinsed with MilliQ-H₂O. A fiber sample was collected for analysis, and the rest of the fiber material was used for the formation of additional layers of polyelectrolyte. The procedure was repeated for each layer: HECE, CMC, HECE, CMC, and finally HECE, *i.e.*, five layers, for six combinations of pH and ionic strength conditions.

Polyelectrolyte Titration for Charge Density Measurement

The procedure is described elsewhere, *e.g.* Koljonen *et al.* (2004), and was only slightly modified. The fibers were put in different amounts of excess of cationic polybrene (negative fibers) or anionic PES-Na (positive fibers) in 0.1 M NaCl for 30 min. The fibers were separated from the polyelectrolyte solutions via vacuum filtration. The solutions were then titrated with the polyelectrolyte of opposite charge until charge reversal. The equivalence point in these titrations was determined using a streaming current detector (Mütek PCD 03, Germany). From the data, the fiber charge densities were calculated by extrapolation to zero excess of polyelectrolyte.

PLS Regression

PLS is a regression tool where latent variables are used to explain the maximal variance and is herein used to maximize the covariance between two data blocks, a block of experimental variables and a block of response values. The computer program SIMCA-P 10.5 (2004) was used for these evaluations, and the evaluated model consisted of two components.

RESULTS AND DISCUSSION

Although it is outside the aim of this study, we have found that the potential to alter the surface chemistry of cellulose fibers via the use of cellulose-based polyelectrolytes widens the applicability of bio refinery products.

After a few titrations, it was already obvious that the multilayer adsorption of both HECE and CMC was successful inasmuch as the charge was always overcompensated, *i.e.*, the charge of the fibers became positive each time they were exposed to HECE and negative after each exposure to CMC (charge reversal). The data from the charge density measurements are illustrated as symbols in Fig. 2 as a function of the number of layers.

In the data presented in Fig. 2, it is possible to discern pH dependence; higher pH values give a weight to the anionic side, which is logical and expected. However, although the different experiments are illustrated using different symbols, it is apparent

from the raw plotted data that any more trends are difficult to assess using such a graphical approach. To dig a bit deeper into the data and the trends, the data were statistically treated by means of PLS regression. The outcome of the PLS analysis is shown as lines in Fig. 2 and Fig. 3 (created with Simca-P 10.5).

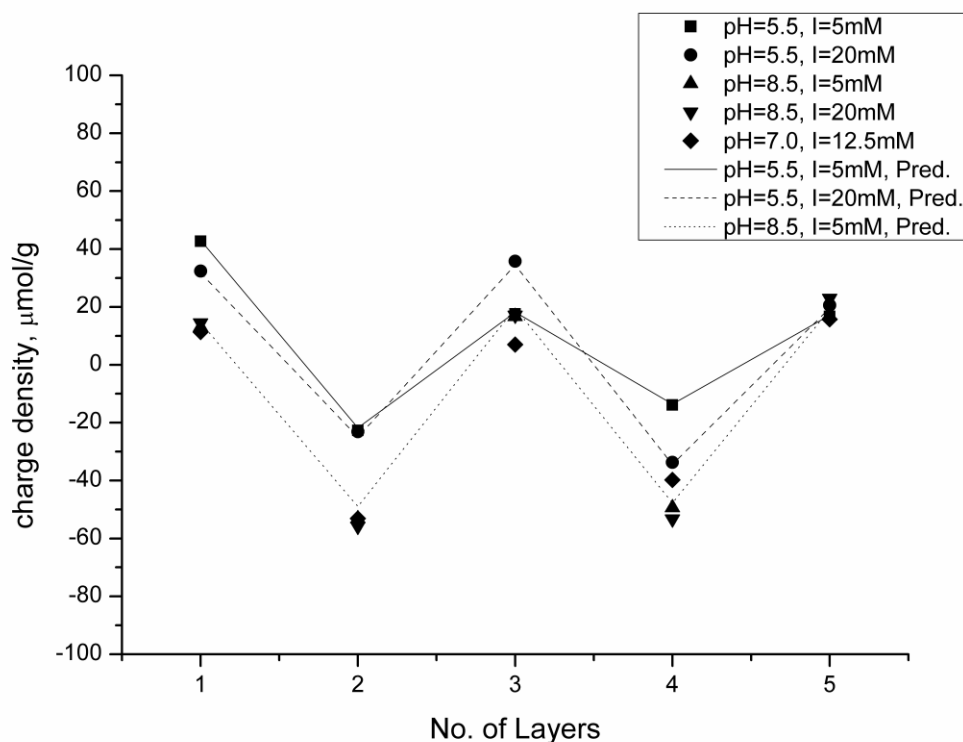


Fig. 2. Data of the charge density determination of the fibers for the different experiments, as analysed by polyelectrolyte titration (symbols) and predicted values (lines) for three experimental points. The pH and ionic strength for each series, presented as different symbols, are indicated in the legend of the figure. The predicted values are calculated by a PLS model in Simca software (2004) at the integer values of “No. of layers” and are shown here as connecting lines for easier comparison with the data.

The discussion below is based on a purely statistical model that does not reveal any molecular information at all and has only been used to uncover the trends in the data.

As can be seen in Fig. 2, the predicted charge densities of the fibers were quite reliable and could be used to create estimations. To illustrate the variation of the predicted charge density with pH and I (ionic strength), surface resonance plots were constructed and are illustrated in Fig. 3. Here, both the negative charge density (Fig. 3a and 3c) and positive charge density (Fig. 3b and 3d) of the fibers are shown as a function of ionic strength and pH. Although quite good, *cf.* Fig. 2, it is important to keep in mind that the plots in Fig. 3 are calculated predictions and must not be overly interpreted. Nonetheless, the surface resonance plots presented in Fig. 3 give a good idea of how the variation in pH and I, within the range studied, influence the resulting fiber charge density.

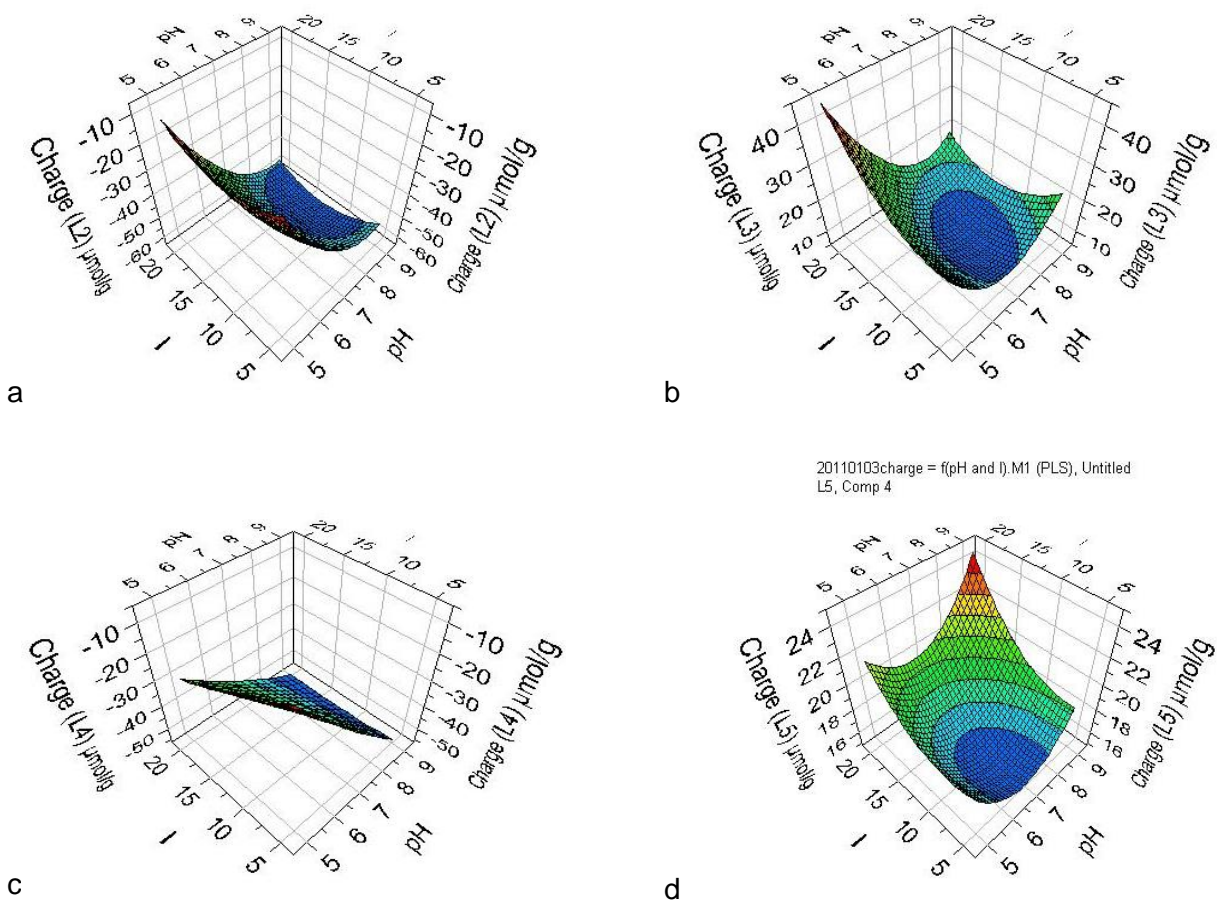


Fig. 3. Surface response plot of the negative charge density of the fibers after a) the first layer of CMC (Layer 2), and b) the positive charge density of the fibers after adsorption of the second layer of HECE (Layer 3), c) the second layer of CMC (Layer 4), and d) the third layer of HECE (layer 5) illustrated as $\mu\text{mol/g}$ and as a function of pH and I ($[\text{Na}^+]$). The surfaces are values predicted by the evaluated PLS model and are therefore estimations.

As previously mentioned, it is important to remember that evaluation of the experimental data using PLS regression is a statistical tool and that no molecular level information is found in this kind of evaluation. Nevertheless, the trends found can to some extent be discussed in molecular terms. It is, however, very important to remember that all conclusions are drawn from a macroscopic level and that the conclusions should therefore be treated with some caution. The findings presented here are unique in the sense that unusual polyelectrolytes have been studied. For layer-by-layer studies, a significant influence from polyelectrolyte complexes (*e.g.* Fatehi *et al.* 2009; Fatehi *et al.* 2010) has been reported on when washing between the layers is insufficient. As a consequence, the pulp was washed between each layer in the process and layer-by-layer adsorption was thereby achieved (it is believed). The use of MilliQ-H₂O instead of the appropriate buffer may, however, have affected the result by removing excessive amounts of the adsorbed polyelectrolytes.

Another issue that might have affected the outcome of the experiments is the presence of fines in the fibers. The important influence of fines on polymer adsorption has previously been discussed in the literature (Fatehi *et al.* 2010). Therefore, the

presence of fines on the fiber material (pulp) used here might have affected the observed results, especially the first layers. The presence of fines naturally increases the surface area of the cellulosic solid material as a whole, increasing the availability for, and thus the adsorption of, polyelectrolytes. However, for the large molecules used here, this may not be as important. Furthermore, it was considered important to keep a somewhat realistic scenario; hence, the fines were not removed prior to the adsorption of the polymers.

As discussed in several papers, *e.g.*, Wågberg (2000), the size of the polyelectrolyte molecules is a crucial factor in the adsorption mechanism onto cellulose fibers and also in what part of the fibers they have access to. In this study, four different polyelectrolytes were adsorbed on fibers, for two different purposes. First, the relatively large CMC and HECE were used. Both of these two polyelectrolytes are cellulose-based and were adsorbed to modify the charge density of the fibers. Second, PES-Na and polybrene were used to measure the charge of these fibers. Even for a reader with only minor experience in polyelectrolyte chemistry, it is to be expected that the accessibility for fiber surfaces is not nearly the same for, for example a huge CMC polyelectrolyte, as it would be for the much smaller polybrene. This is, however, not a problem, as the large molecules were adsorbed on the accessible surface (as they were supposed to be) while the smaller molecules used for charge density measurement accessed the whole fiber and thus gave an indication of the total charge density of the fibers. It is known from previous research that CMC adsorption on anionic cellulose is strongly dependent on the presence of an electrolyte (Laine *et al.* 2000). From the present data, this is not as obvious, but it can be hypothesized that CMC adsorbs best at intermediate ionic strengths (only a very small difference), while HECE adsorbs more at higher ionic strengths (in the interval studied). There is as-yet-unpublished data that suggest that the LbL adsorption of HECE and CMC gives thick and water-filled layers at pH values reaching ≈ 7 , and this could also explain the effect seen here. It is obvious from Fig. 3b and 3d that the positive charge density of fibers with a HECE layer as an outermost layer shows a complex dependence on pH and ionic strength. This is most likely due to a number of related, and unrelated, physical phenomena. This can partly be explained with the more “coiled” conformation of the polyelectrolytes at higher ionic strength (van der Schee and Lykema 1984; Steitz *et al.* 2000; Smits *et al.* 1993), which normally gives rise to a higher polyelectrolyte adsorption (Liu *et al.* 2008). For the fibers with an outermost layer of CMC, it is obvious that the charge density was very dependent on pH, and it seemed to become more negative with increasing pH within the whole range investigated. At these high pH values, carboxylic acids on both CMC and the fibers are fully deprotonated, so the observed effect at high pH does not originate in deprotonation alone. It must be remembered, however, that no information on the dependence outside of the investigated area can be extracted from the present study.

As expected (v. Klitzing 2006), it is seen throughout this experimental series that a significant overcompensation of the fiber charge always took place. This was expected and is an indication that electrostatic attraction only plays a minor role in the adsorption of these cellulose based polyelectrolytes. According to the literature (v. Klitzing 2006), entropy factors are very important for polyelectrolyte multilayer formation. Moreover, we believe that attractive hydrogen bonding between $-OH$ groups on the cellulose backbones also may be important. The non-linear relationship between the adsorption of HECE and the previous CMC layer is highly dependent on the ionic strength, which indicate that structure is very important (Liu *et al.* 2008). Furthermore, the non-linear increase of

positive fibre charge density with increasing ionic strength is possibly the result of an exponential growth of the multilayers at higher ionic strength (Kiryukhin *et al.* 2011). It is possible that the amount of adsorbed CMC is higher at low pH, but because this is not seen as charge density, there is no evidence of this. More studies focusing on adsorption kinetics and thermodynamics may unravel the nature of HECE and CMC sorption on cellulose surfaces.

CONCLUSIONS

1. It is confirmed that the adsorption of HECE and CMC on cellulose is not determined by electrostatic attraction only, and other factors are much more important for the adsorption of these cellulose derivatives.
2. It is seen that the charge density of fibers with CMC as the outermost layer is strongly dependent on pH, while the charge density of fibers with HECE as the outermost layer is more dependent on the ionic strength.
3. It is obvious that the anionic charge of both CMC and cellulose fibers that arise with increasing pH does not prevent adsorption, possibly in part because the fibers are positively charged due to previous HECE adsorption.

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