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Interactions of a cationic cellulose derivative with an ultrathin cellulose support

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ABSTRACT

The adsorption behavior of cellulose-4-[*N*-methylammonium]butyrate chloride (CMABC) on two hydrophilic substrates is studied, namely nanometric cellulose model thin films and silicon dioxide substrates. The adsorption is quantified in dependence of electrolyte concentration and pH value using a quartz crystal microbalance with dissipation (QCM-D). In case of CMABC, at high ionic strengths (25–100 mM NaCl) high adsorption is observed at pH 7 (Δf_3: −15 to −17 Hz) while at lower ionic strengths (1–10 mM) less CMABC (Δf_3: −2 to −12 Hz) is deposited on the cellulose surfaces as indicated by the frequency changes using QCM-D. A change in pH value from 7 to 8 reveals an increase in adsorption. Atomic force microscopy shows that the coating of cellulose thin films with CMABC changes the morphology from a fibrillar to a particle like structure on the surface. The surface wettability with water increases with an increasing amount of CMABC on the surface compared to neat cellulose model films. At lower pH values (3 and 5), CMABC does not adsorb onto the cellulose model thin films. XPS is used to validate the results and to determine the nitrogen content of the surfaces. In addition, adsorption of CMABC onto another hydrophilic and negatively charged substrate, silicon dioxide coated quartz crystals, cannot be detected at different pH values and electrolyte concentrations as proven by QCM-D.

1. Introduction

In the past years, there has been growing interest in the development of biomimetic materials based on polysaccharides (Ishimaru & Lindström, 1984; Teeri, Brumer, Daniel, & Gatenholm, 2007; Zhou, Rutland, Teeri, & Brumer, 2007). In particular, cellulosic materials offer several promising perspectives for the design and preparation of such materials due to their intrinsic properties. It is known that the properties of cellulosic fibers such as mechanical strength or biocompatibility can be altered during chemical modifications. One methodology to overcome a disadvantageous harsh chemical treatment is to perform a compatibilization, which is usually done by coating cellulose fibers with structurally similar but water soluble derivatives (Christiernin et al., 2003; Eronen, Junka, Österberg, & Laine, 2011; Fras Zemljic, Stenius, Laine, & Stana-Kleinschek, 2011; Kondo, Koschella, Heublein, Klemm, & Heinze, 2008). In this context, the most commonly used material is carboxymethyl cellulose (CMC), which can be immobilized on different kinds of cellulose based supports (Liu, Choi, Gatenholm, & Esker, 2011). In many cases, the approach toward the attachment of CMC has been very pragmatic, for instance by using click chemistry or enzymes (Brumer, Zhou, Baumann, Carlsson, & Teeri, 2004; Filpponen et al., 2012). Moreover, a huge amount of technical studies does exist which use CMC or xyloglucans for the improvement of the properties of papers and fibers (Ahrenstedt, Oksanen, Salminen, & Brumer, 2008; Blomstedt, Kontturi, & Vuorinen, 2007; Fras Zemljic, Stenius, Laine, & Stana-Kleinschek, 2008; Laine et al., 2000; Laine, Lindström, Nordmark, & Risinger, 2000, 2002; Rakkolainen et al., 2009). In almost all of these studies, the adsorption can be controlled by variation of electrolyte concentration and pH value. However, the monitoring of adsorption on real samples such as fibers is sometimes tricky, laborious and requires a combination of analytical techniques. A more elegant way to investigate the adsorption behavior of water soluble cellulose derivatives onto a solid cellulose substrate is the use of cellulose model thin films in combination with a highly surface sensitive technique such as a quartz crystal microbalance with dissipation (QCM-D). The QCM-D method allows a monitoring of the adsorption process in real time and in situ, which reduces experimental errors in the course of the analysis, while providing high sensitivity (resolution: ~0.1 Hz; ca. 2 ng cm^{-2}).

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Amorphous cellulose model films can be prepared by exposing spin coated trimethysilyl cellulose (TMSC) to vapors of hydrochloric acid (Kontturi, Thüne, & Niemantsverdriet, 2003; Mohan et al., 2011; Schaub, Wenz, Wegner, Stein, & Klemm, 1993). Recently, the kinetics of this conversion was investigated by means of X-ray reflectivity (Kontturi & Lankinen, 2010), Raman spectroscopy (Woods, Petkov, & Bain, 2011), and QCM-D (Mohan, Spirk, Kargl, Doliška, Ehmann, et al., 2012) and it was shown that the amorphous nature of these films is also retained upon heating (Mohan, Spirk, Kargl, Doliska, Vesel, et al., 2012). Potential applications of cellulose model films include polyelectrolyte adsorption (Liu et al., 2011), enzymatic digestion (Cheng et al., 2011; Suchy et al., 2011; Mohan, Kargl, Doliška, et al., 2012) and biomolecule immobilization (Kargl, Mohan, Köstler, et al., 2012; Löscher, Ruckstuhl, Jaworek, Wegner, & Seeger, 1998; Mohan, Kargl, Köstler, et al., 2012; Orelma, Filpponen, Johansson, Laine, & Rojas, 2011; Orelma, Teerinen, Johansson, Holappa, & Laine, 2012), to mention just a few. While anionic (at pH 7) CMC has been used to immobilize biomolecules on such films (Mohan, Kargl, Köstler, et al., 2012), the use of cationic cellulosic polymers has not been demonstrated so far for this purpose. However, positively charged surfaces possess an enormous potential regarding the immobilization of biomolecules such as DNA and proteins (Orelma et al., 2011). Therefore, we became interested whether we can control the adsorption behavior of a water soluble cationic cellulose derivative onto thin solid cellulose supports. In this paper, the adsorption behavior of cellulose-4-[*N*-methylammonium]butyrate chloride (in the following referred to as cationic cellulose or CMABC) on cellulose substrates is investigated as a function of electrolyte concentration and pH value of the polymer solution. The results are set into contrast with the adsorption of CMABC on silicon dioxide substrates. For this purpose, a quartz crystal microbalance with dissipation (QCM-D) is employed to quantify the amount of deposited cationic cellulose.

2. Experimental

2.1. Materials and methods

Trimethylsilyl cellulose (TMSC), with a degree of substitution (DS) of 2.55 with $M_w = 175.000\,\mathrm{g\,mol^{-1}}$, and $M_n = 36.000\,\mathrm{g\,mol^{-1}}$ was used as starting material for the cellulose model film preparation (Köhler, Liebert, & Heinze, 2008). Cellulose-4-[*N*-methylamino]butyrate hydrochloride with degree of substitution (DS) of 0.86 and degree of polymerization (DP) of 415 (DP_n) and 1188 (DP_w), denoted in this work as cationic cellulose (CMABC), was synthesized from cotton linters (Fluka) via the ring-opening reaction of *N*-methyl-2-pyrrolidone (NMP, Acros) with *p*-toluenesulfonyl chloride (TosCl, Fluka) as previously reported (Zarth, Koschella, Pfeifer, Dorn, & Heinze, 2011). QCM-D gold (QSX-301) and SiO_2 coated crystals (QSX-303) were purchased from LOT-Oriel (Germany). Sodium chloride (NaCl, ≥99.0%) was obtained from Sigma–Aldrich. A MilliQ water system was the source of pure water (resistivity = 18.2 MΩ cm at 25 °C) used for sample preparation and for measurements. For the QCM-D measurements, cellulose-4-[*N*-methylamino]butyrate hydrochloride ($c = 1\,\mathrm{mg\,ml^{-1}}$, native pH: 4) is dissolved in NaCl electrolyte solution (1, 10, 25, 50, 100 mM) and adjusted to different pH values (3, 5, 7, 8) using 0.1 M HCl and 0.1 M NaOH, respectively.

2.2. Substrate cleaning and film preparation

In the course of the cleaning procedure, the Au coated QCM sensors were soaked in a mixture of H_2O/H_2O_2 (30 wt.%)/NH_4OH (5:1:1, v/v/v) for 10 min at 70 °C, then immersed in a "piranha" solution containing H_2O_2 (30 wt.%)/H_2SO_4 (1:3, v/v) for 60 s, followed by rinsing with water and finally dried in a stream of nitrogen. For cellulose film preparation, TMSC ($10\,\mathrm{g\,l^{-1}}$) was dissolved in toluene and 50 μl of the solution were deposited on the static Au-crystal and subjected to spin coating ($\nu = 4000$ rpm, $a = 2500\,\mathrm{rpm\,s^{-1}}$, $t = 60$ s). The regeneration of the spin coated TMSC to cellulose was performed by vapor phase hydrolysis according to a modified literature procedure (Kontturi et al., 2003). A detailed description of the spin coating and regeneration procedure can be found elsewhere (Mohan et al., 2011; Mohan, Spirk, Kargl, Doliska, Vesel, et al., 2012). Resulting cellulose film thickness is 25 ± 1 nm.

The SiO_2 coated QCM sensors were cleaned by treatment with a "piranha" solution for 60 s, rinsing with water and drying in a stream of nitrogen.

2.3. Quartz crystal microbalance with dissipation (QCM-D)

A QCM-D instrument (model E4) from Q-Sense, Gothenburg, Sweden was used. The instrument simultaneously measures changes in the resonance frequency (Δf) and energy dissipation (ΔD) when the mass of an oscillating piezoelectric crystal changes upon adsorption on the crystal surface (Marx, 2003; Rodahl et al., 1997). Dissipation refers to the frictional losses that lead to damping of the oscillation depending on the viscoelastic properties of the material. Thus, by measuring the frequency and dissipation it is possible to analyze the state of molecular layers bound to the sensor surface during the adsorption and/or desorption process. For a rigid adsorbed layer that is fully coupled to the oscillation of the crystal, Δf_n is given by the Sauerbrey equation

$$\Delta m = -\frac{C\Delta f_n}{n} \tag{1}$$

where Δf_n is the observed frequency shift, C is the Sauerbrey constant ($17.7\,\mathrm{ng\,Hz^{-1}\,cm^{-2}}$ for a 5 MHz crystal), n is the overtone number ($n = 1, 3, 5, \ldots$), and Δm is the change in mass of the crystal due to the adsorbed layer. The mass of a soft film is not fully coupled to the oscillation and the Sauerbrey relation is not valid since energy is dissipated in the film during the oscillation. The damping (or dissipation) (D) is defined as

$$D = \frac{E_{\mathrm{diss}}}{2\pi E_{\mathrm{stor}}} \tag{2}$$

where E_{diss} is the energy dissipated, and E_{stor} is the total energy stored in the oscillator during one oscillation cycle. The QCM-D records the change in D (ΔD) as a function of adsorption time. For the data analysis in this study, the changes in the third overtone's frequency and dissipation (Δf_3, ΔD_3) were determined.

The regenerated cellulose film attached to Au-crystals was mounted in the QCM-D chamber. Before the adsorption measurements, in each run pure MilliQ water was pumped into the chamber for 15 min to ensure the stability of the baseline frequency. In a subsequent step, MilliQ water was replaced by electrolyte solutions and equilibrated until the frequency remained at a stable level. Afterwards, the frequency was reset to zero and CMABC ($c = 1\,\mathrm{mg\,ml^{-1}}$, dissolved in MilliQ water with electrolyte at adjusted pH) was allowed to adsorb onto the cellulose surfaces for 90 min. In the end, the surfaces were rinsed with electrolyte solutions (30 min) and MilliQ water (30 min) to remove loosely attached material and the changes in frequency and dissipation were calculated. All experiments were conducted in continuous flow mode at a flow rate of $0.1\,\mathrm{ml\,min^{-1}}$. The temperature was kept at 21.0 ± 0.1° C for the duration of the measurement. All measurements were repeated three times in order to ensure the reproducibility of the results. Experiments have been performed at pH values of 3, 5, 7 and 8, respectively, for all substrates.

2.4. Contact angle measurements

The wettability of the surfaces was determined by contact angle measurements. Static water contact angles (SCA) were determined on a Dataphysics (Filderstadt, Germany) contact angle measurement system OCA15+ using the sessile drop method and a drop volume of 3 μl. All measurements were carried out at room temperature on regenerated cellulose surfaces and cellulose surface that were coated with CMABC. Determination of the SCA was based on the analysis of the drop shape (Young–Laplace approach) using the software provided by the manufacturer (software version SCA 20.2.0) of the instrument. All the measurements were performed on at least two independent pure surfaces and CMABC coated surfaces with a minimum of three drops per surface.

2.5. X-ray photoelectron spectroscopy (XPS)

XPS spectra were performed with a monochromatic K-Alpha spectrometer equipped with an Al X-ray source (1486.6 eV) operating with a base pressure in the range of 10^{-8} to 10^{-10} mbar. Survey scans were acquired with a pass energy of 100 eV and a step size of 1.0 eV. All spectra have been normalized to the Au $4f_{7/2}$ peak. Charge compensation was performed with an argon flood gun. The average chemical composition was calculated from wide scan spectra in two different locations on each surface. The peaks were fitted using a Gaussian/Lorenzian mixed function employing Shirley background correction. All analyses were performed at room temperature.

2.6. Atomic force microscopy

Surface morphology of cellulose surfaces on the QCM-D crystals that are incubated with CMABC were characterized by AFM in the intermittent contact mode with an Agilent 5500 AFM multimode scanning probe microscope (Digital Instruments, Santa Barbara, CA). The images were acquired after drying the films in a stream of dry nitrogen. Silicon cantilevers (ATEC-NC-20, Nanosensors, Germany) with a resonance frequency of 210–490 kHz and a force constant of 12–110 N m^{-1} were used. The scanned image size was 1 μm × 1 μm. All measurements were performed at room temperature in ambient atmosphere.

3. Results and discussion

The adsorption of a positively charged polyelectrolyte onto negatively charged solid surfaces is usually influenced by electrolyte concentration/ionic strength, concentration of the adsorbent, pH value of the solution as well as by the intrinsic properties of the solid surfaces (Dobrynin & Rubinstein, 2005; Dobrynin et al., 2000; Dobrynin, Deshkovski, & Rubinstein, 2000, 2001; Findenig et al., 2012). For polysaccharides and their derivatives, additional factors may influence the adsorption behavior, namely the degree of substitution, the solubility, the intrinsic viscosity, as well as the degree of polymerization (Kontturi, Tammelin, Johansson, & Stenius, 2008; Liu et al., 2011). These factors have an impact on the conformation of the polymers in solution. In particular, the conformation of positively charged polymers in solution strongly depends on the strength of the inter- and intramolecular repulsion between the cationic moieties (Kontturi et al., 2008). Intramolecular repulsion between the charged moieties along the polymer chain as well as between the single polymer chains can be minimized by an increase in electrolyte concentration in solution. As a consequence, the conformation of these polymers is changed from a flat toward a coil-like structure. This change in conformation, in turn, influences also then the adsorption behavior of the polymers on an oppositely charged surface. In both cases, the adsorbed layer consists of adsorbed polymer, electrolyte, and solvent, which are embedded inside the layer. A detailed description of the theories on the polyelectrolyte adsorption can be found elsewhere (Dobrynin et al., 2000, 2001; Dobrynin & Rubinstein, 2005).

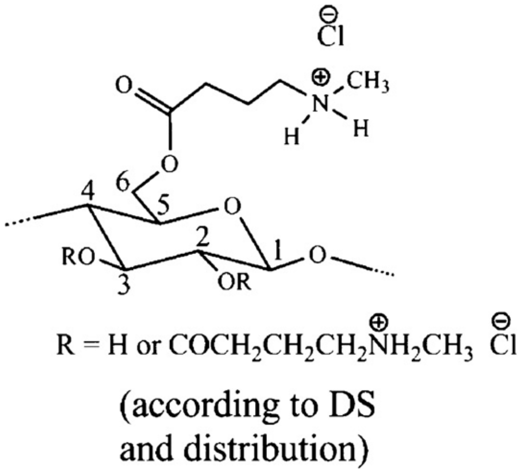

Fig. 1. Molecular structure of cellulose-4-[*N*-methylamino]butyrate hydrochloride (CMABC). DS means the degree of substitution.

In case of CMABC (Fig. 1), the adsorption is studied using different electrolyte concentrations (NaCl; 1, 10, 25, 50 and 100 mM) in combination with four different pH values (pH 3, 5, 7 and 8). The use of a QCM-D device allows for a quantification of the deposited material in a very convenient way. It has been kept in mind that the adsorbed layer consists of CMABC, NaCl, and water. Therefore, when we mention adsorption of CMABC on the different surfaces in the following, we always refer to the adsorption of CMABC including NaCl, and water.

While there is not any detectable adsorption of CMABC on cellulose model films at pH 3 and 5 in combination with various electrolyte concentrations (1, 10, 100 mM), respectively (see Fig. 2a), at pH 7 and pH 8 irreversible adsorption takes place, even at low NaCl concentrations (Figs. 3 and 4).

At pH 7, the frequency and dissipation increase with increasing electrolyte concentration, implying that the adsorption of cationic cellulose is favored at higher electrolyte concentration (Figs. 3 and 4). At the lowest investigated NaCl concentration (1 mM), only a small frequency (−2 ± 0.1 Hz; low adsorption) and dissipation change ($1.2 \pm 0.2 \times 10^{-6}$) is observed during adsorption of CMABC. These rather small frequency changes can be related to the adsorption of CMABC in a flat conformation at low ionic strength which probably results in the formation of a monolayer like coating. Moreover, the adsorption is due to the electrostatic interaction between weakly charged cellulose surfaces and CMABC, as known from the related cases, such as adsorption of cationic starch on a cellulose surface (Kontturi et al., 2008). As mentioned above, with an increase in electrolyte concentration (from 10 to 100 mM NaCl), CMABC adopts a more coiled-like conformation due to the reduced repulsion between the charged polymer moieties.

In addition, the solubility of CMABC is reduced due to the increase in electrolyte concentration which favors a higher degree of adsorption onto the surfaces. Consequently, more material is deposited onto the cellulose substrate, which is reflected in the increased frequency shift as the electrolyte concentration increases (Fig. 4). The changes in the frequency and dissipation reach a plateau between 50 and 100 mM NaCl indicating adsorption to be independent from electrolyte concentrations larger than 50 mM. The net charge of the cellulose surfaces is decreased during the adsorption and the surface charge is overcompensated by addition of CMABC. The dissipation increased with electrolyte

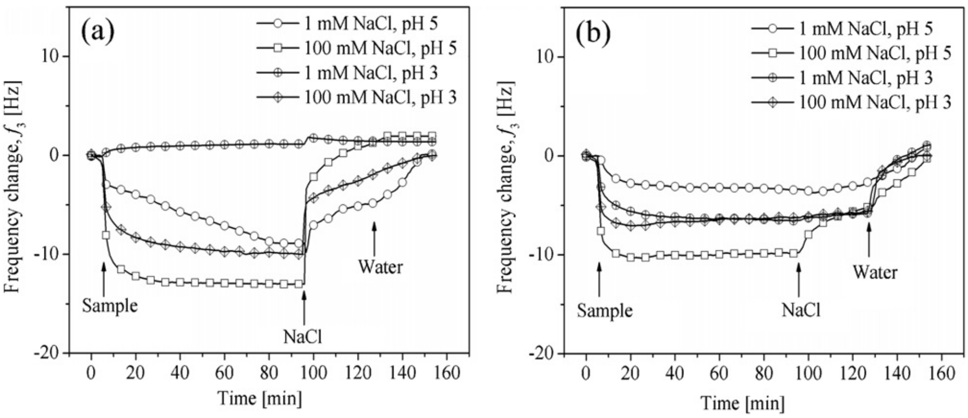

Fig. 2. Comparison of the adsorption behavior of CMABC on cellulose (a) and silica (b) surfaces at pH 3 and 5, respectively, as function of electrolyte concentration.

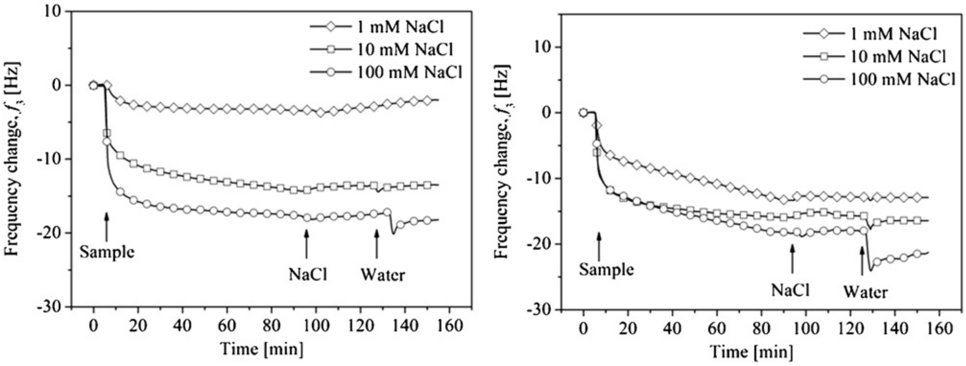

Fig. 3. Changes in the third overtone frequency (Δf_3) for the adsorption of CMABC onto cellulose surfaces at pH 7 (left) and pH 8 (right) as a function of NaCl concentration.

concentration up to 100 mM which indicates a high degree of swelling of the material and incorporation of water and electrolyte in the film.

A similar trend in the changes of frequency (Δf_3) and dissipation (ΔD_3) is observed when the adsorption is carried out at pH 8 (Fig. 3, right). Similar to adsorption at pH 7, the adsorption at pH 8 increases with increasing electrolyte concentration. Interestingly, a frequency change of -13.0 ± 2.3 Hz is observed when the adsorption is carried out applying a 1 mM NaCl solution. This value is 10-fold higher than that of the adsorption carried out at pH 7. This behavior is unexpected since the cellulose surface net charge does not strongly depend on the pH in the range between pH 7 and 10 as shown by zeta potential studies on various cellulosic substrates (Geffroy, Labeau, Wong, Cabane, & Cohen Stuart, 2000). In contrast to the cationic starch used in a previous study for similar purposes, CMABC bears two hydrogens at the amine functionality which allows protonation/deprotonation of the amine group upon a change in the pH value. This protonation/deprotonation influences the solubility of CMABC to a large extent and results in a reduced solubility at higher pH values (Zarth et al., 2012). The reduced solubility and the induced change in conformation in turn lead to a higher adsorption capacity of CMABC on the cellulose surfaces.

The cationic cellulose does not show any adsorption in the absence of electrolyte at both pH values which is an indication that

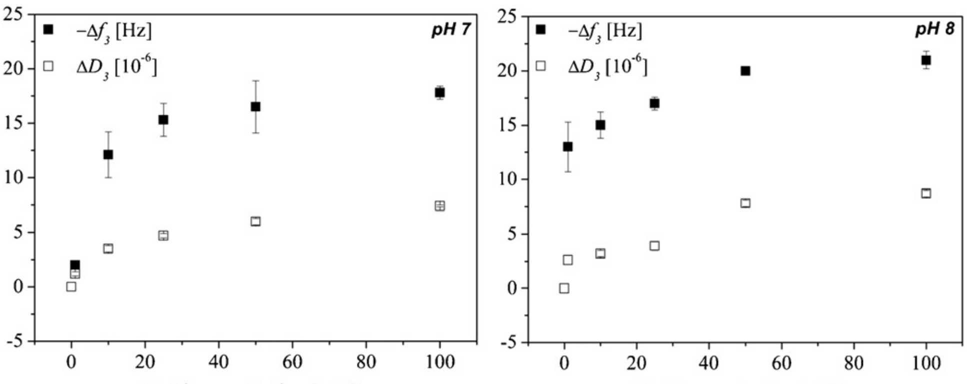

Fig. 4. QCM-D changes in the frequency (Δf_3) and dissipation(ΔD_3) of CMABC (1 mg ml^{-1}) adsorption onto cellulose film as a function of NaCl electrolyte concentration at pH 7 (left) and pH 8 (right).

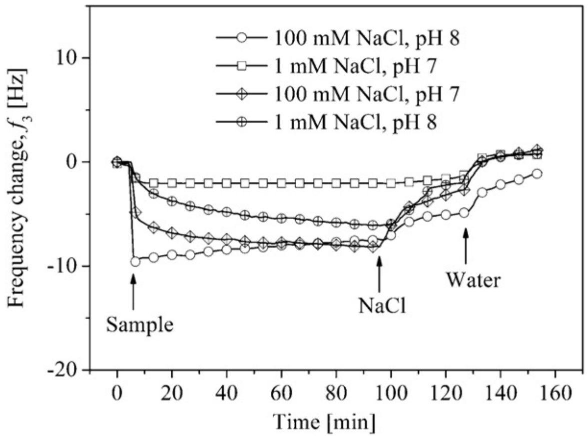

Fig. 5. Comparison of the adsorption behavior of CMABC on silica surfaces at pH 7 and 8, respectively, as function of electrolyte concentration.

the conformation and solubility of CMABC in water are the driving forces for the adsorption of CMABC onto cellulose rather than electrostatic interactions. The summary of changes in frequency (Δf_3) and dissipation (ΔD_3) for the adsorption of CMABC onto thin solid cellulose surfaces at pH 7 and 8 as a function of electrolyte concentrations are shown in Fig. 4.

These findings inspired us whether CMABC can be adsorbed onto other negatively charged, hydrophilic surfaces bearing many OH groups on the surface. A suitable candidate are SiO_2 surfaces which have a significant lower zeta potential (down to −80 mV at pH 7 for ‘piranha’ cleaned glass slides (Spirk et al., 2010) compared to cellulose (ca. −5 to −10 mV, Stana-Kleinschek, Kreze, Ribitsch, & Strnad, 2001). Therefore, the electrostatic interaction and the adsorption capacity should be much larger compared to the cellulose supports. Similar studies, which have been performed using hydrophilic and hydrophobic cationic starch as the adsorbent, yielded high adsorption onto SiO_2 surfaces (Kontturi et al., 2009, 2008; Tammelin, Merta, Johansson, & Stenius, 2004). The authors argued that electrostatic interactions are the driving force for adsorption of the cationic starch. Subsequently, the adsorption behavior of CMABC onto SiO_2 was investigated using the same parameters (pH, ionic strength, same CMABC concentration) as on the cellulose model films (Figs. 2b and 5). If the adsorption was based on mere electrostatic interactions, adsorption of CMABC (including water and electrolyte) would be at least in a similar range on SiO_2 surfaces as for the cellulose model films. Surprisingly, CMABC did not show any adsorption at all on SiO_2 surfaces neither at low nor high pH values nor at high ionic strength and only negligible frequency and dissipation changes were observed after rinsing. Therefore, it must be taken into consideration that adsorption of CMABC onto cellulose surfaces is possibly not mainly driven by electrostatics. However, there is a difference regarding the swelling behavior of cellulose and SiO_2 based surfaces. While cellulose tends to swell extensively (resulting also in a higher RMS roughness), the SiO_2 surfaces are hydrated but are not prone to swelling. As a consequence, the total surface area available for adsorption is much larger in case of a swollen cellulose model film than for SiO_2 substrates. Moreover, the rather soft cellulose surface may allow a penetration of the adsorbent into the cellulose film, which can be excluded for rigid SiO_2 surfaces.

Probably, we have to consider that there is a kind of interaction that is based on the structural similarities between these two polysaccharides; a phenomenon known for the CMC/cellulose (Kargl, Mohan, Bracic, et al., 2012) and xyloglucan/cellulose systems (Mishima, Hisamatsu, York, Teranishi, & Yamada, 1998). In this case, the change in conformation and solubility of the CMABC enable adsorption onto the surface, while interaction via structural similarity anchor the material onto the surface leading to an irreversible deposition of CMABC on the cellulose supports. However, from the discussion above there is no reason why CMABC should not adsorb onto SiO_2 based surfaces. It may be assumed that cationic celluloses themselves are compounds possessing somehow special properties. There are few examples where cationic celluloses exhibit unusual physicochemical behavior, cationically modified cellulose nanocrystals for instance. Aqueous suspensions of these nanocrystals form readily thixotropic gels instead of expected chiral nematic liquid crystalline phases, which is probably also associated with the charge density on the cellulose nanocrystals (Hasani, Cranston, Westman, & Gray, 2008). However, when a hydrophilic, highly charged mica surface is offered, adsorption of these cationic crystals takes place. In addition, the very few existing adsorption studies of cationic celluloses (namely commercially available ones) showed that adsorption takes place on silica as well as on hydrophobized silica surfaces in the presence of an electrolyte e.g. NaCl (Terada, Samoshina, Nylander, & Lindman, 2004a,b). These studies showed that distinct differences in the adsorption can be observed depending on the employed cationic cellulose. Derivatives with a low charge density adsorbed much better on silica than those with high charge density. CMABC can be considered as a highly charged cationic cellulose derivative exhibiting in average 0.86 positive charges per AGU; therefore a priori only low adsorption can be expected on SiO_2 surfaces. The result obtained – that adsorption on these surfaces does not take place – is quite surprising but must be related to the unique nature of CMABC rather than by general physicochemical properties of cationic celluloses. The main difference to the previously studied cationic celluloses for adsorption on SiO_2 is that CMABC bears hydrogen atoms at the charged nitrogen atom. These hydrogen atoms are able to participate in inter- and intramolecular hydrogen bonding leading to a steric protection of the charged moieties of the CMABC. As a consequence, the charge is screened by steric hindrance, the interaction via electrostatics is diminished and the adsorption on SiO_2 does not take place. Such a view is consistent with the observations made in the adsorption of CMABC on cellulose surfaces since electrostatics plays a minor and is not the driving force for adsorption in this case.

Although QCM-D is a highly sensitive technique, its main weakness is that only mass differences can be determined. Therefore, for an analysis of the elemental composition other techniques must be employed. A standard technique for the determination of the elemental composition of surfaces is XPS. The XPS wide scan spectra

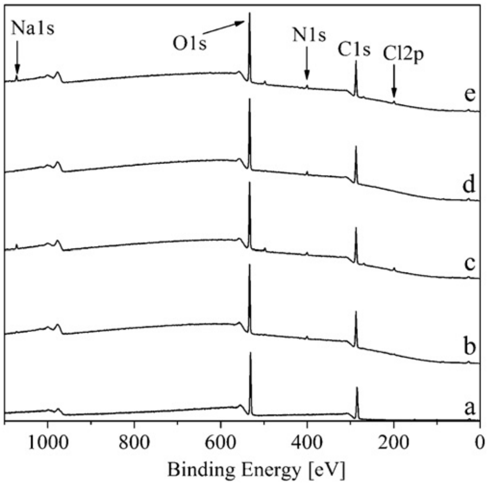

Fig. 6. Comparison of XPS wide scan spectra of CMABC adsorbed on cellulose model thin films. (a) Neat cellulose surface; (b) pH 7, 1 mM NaCl; (c) pH 7, 100 mM NaCl; (d) pH 8, 1 mM NaCl; and (e) pH 8, 100 mM NaCl.

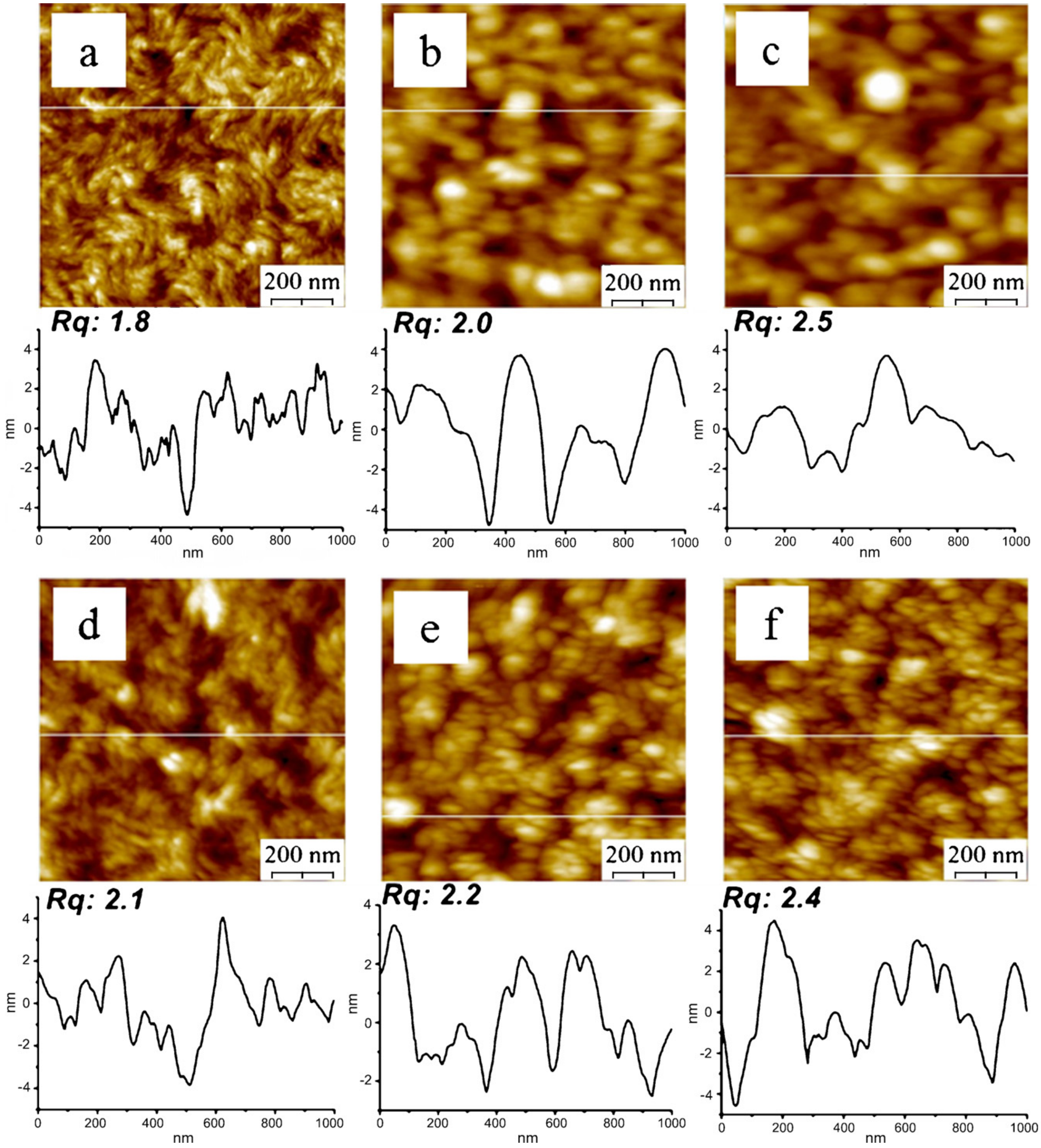

Fig. 7. Comparison of AFM images (1 μm × 1 μm) of cellulose films from the QCM-D experiments treated with cationic cellulose at 1 mM (a, pH 7; d, pH 8), 10 mM (b, pH 7; e, pH 8), and 100 mM (c, pH 7; f, pH 8) NaCl concentration. The images were acquired after drying in a stream of nitrogen. Z-scale: 10 nm. For all images, height profiles are determined at the white line.

of pure cellulose and CMABC coated cellulose at different pH values and electrolyte concentrations are compared in Fig. 6. The peak corresponding to elemental nitrogen, N 1s, is detected for all CMABC treated cellulose surfaces, whereas the lack of element nitrogen is evident in the untreated cellulose surface.

As expected, at both investigated pH values the nitrogen content of CMABC treated cellulose is increasing with increasing electrolyte concentration (1–100 mM), which is in line with results from QCM-D. As for the QCM-D experiments, where adsorption of CMABC is higher at pH 8, the same trend can be followed by XPS. The QCM-D experiments showed that the adsorption at pH 7 (100 mM NaCl) and pH 8 (10 mM) gave the same amount of adsorbed CMABC. This result is perfectly reproduced by XPS where for these samples a nitrogen content of 3.2 at% is determined. An overview of the elemental composition of the different experiments is given in Table 1.

In addition, XPS is able to prove whether there is an incorporation of the electrolyte into the film by simple scanning for

Table 1
Surface elemental composition of pure cellulose and cationic cellulose adsorbed on cellulose surfaces obtained from XPS measurements. All values are given in at%. The penetration of the XPS beam is much deeper than the thickness of the CMABC coating resulting in lower experimentally determined nitrogen contents in comparison to the theoretical values.

	C 1s	O 1s	N 1s
Neat cellulose	59.5	39.2	–
Neat CMABC (DS 0.86)	60.5	34.4	5.1
pH 7			
1 mM NaCl	59.6	39.3	0.4
10 mM NaCl	58.5	37.8	2.8
100 mM NaCl	56.1	36.9	3.2
pH 8			
1 mM NaCl	58.3	39.0	2.7
10 mM NaCl	57.8	37.8	3.2
100 mM NaCl	55.1	37.1	3.8

sodium and chlorine. While it was not possible to determine unambiguously incorporated sodium chloride for the 1 and 10 mM NaCl samples (<1 at%), for the 100 mM samples approximately 2% Na 1s and Cl 2p have been detected.

The different adsorption modes (flat vs. coil-like) should lead to different surface structures and morphologies. Indeed, such differences are observed using different ionic strengths in the course of the adsorption experiment. In Fig. 7, a series of AFM images (acquired after drying the films in a stream of nitrogen) is depicted which compare pure cellulose surfaces and those where cationic cellulose has been deposited. There is an influence of the electrolyte concentration on the morphology, which is related to the conformation of CMABC at different electrolyte concentrations. In a 1 mM NaCl solution, CMABC exhibits a flat like structure and adsorbs onto the fibrils forming a kind of monolayer coating. Therefore, the fibrillar motif of the cellulose surface is retained. By employing higher electrolyte concentrations, the structure of the CMABC changes and a coil like structure is present which is reflected in a particle like structure on the surface.

The wettability of the cellulose surfaces with water increases with an increasing amount of adsorbed CMABC at higher ionic strength and pH value (Fig. 8). This behavior can be explained by the amount of positive charges on the surface and by the incorporation of ions which results in lower contact angles at higher amounts of deposited CMABC on the cellulose. A comparison of CMABC adsorbed at pH 7 (100 mM NaCl) with adsorption at pH 8 (10 mM NaCl) leads, as for all the other experiments, to similar results.

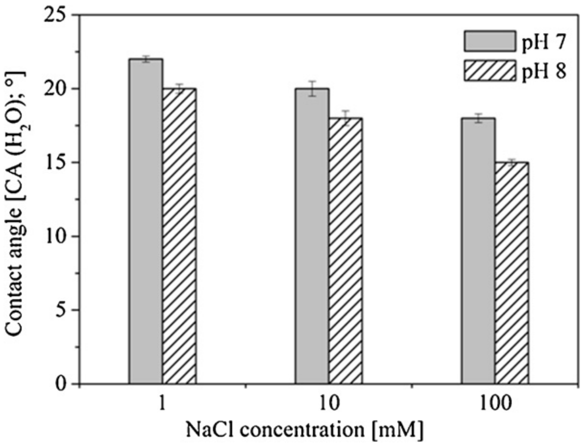

Fig. 8. Static water contact angle of cellulose surface that is treated with cationic cellulose at different pH and electrolyte concentration. The water contact angle of the neat cellulose model films is 25 ± 1°.

4. Conclusion

The adsorption behavior of cellulose-4-[*N*-methylamino]butyrate hydrochloride (CMABC) onto cellulose model surfaces is investigated by a quartz crystal microbalance as a function of electrolyte concentration and pH value. CMABC irreversibly adsorbs onto cellulose surfaces in the presence of an electrolyte such as NaCl at pH 7 and 8 while for lower pH values (3 and 5) adsorption could not be detected. The adsorption increases with increasing electrolyte concentration and is favored at pH 8 over pH 7. XPS results agree well with those obtained by QCM-D and it was possible to estimate the amount of electrolyte incorporated into the films by surface elemental analysis. Atomic force microscopy reveals that the conformation of the CMABC at low ionic strengths seems to be flat like leading to a thin layer, probably a monolayer of CMABC, on the cellulose substrate. By increasing the electrolyte concentration, the conformation of the polymer is changed to a particle like structure and the solubility of CMABC is reduced. While high electrolyte concentrations provide more adsorption on the surface by a change in conformation and solubility of CMABC, interactions caused by structural similarity between cellulose and CMABC are probably responsible for the irreversibility of this adsorption process. These results are consistent with adsorption experiments of CMABC on highly negatively charged silicon dioxide surfaces using different pH values and electrolyte concentrations where any adsorption of CMABC was not observed despite the higher negative charge of SiO_2 surfaces compared to cellulosic ones. A possible explanation for this phenomenon includes several parameters such as the high charge, the steric hindrance induced by inter- and intramolecular hydrogen bonding and reduced affinity of CMABC to the rather rigid SiO_2 surfaces. Detailed studies to evaluate the exact mechanisms in the adsorption behavior of CMABC on several types of surfaces are on the way.

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References

Ahrenstedt, L., Oksanen, A., Salminen, K., & Brumer, H. (2008). Paper dry strength improvement by xyloglucan addition: Wet-end application spray coating and synergism with borate. *Holzforschung*, *62*, 8–14.

Blomstedt, M., Kontturi, E., & Vuorinen, T. (2007). Optimising CMC sorption in order to improve tensile stiffness of hardwood pulp sheets. *Nordic Pulp and Paper Research Journal*, *22*, 336–342.

Brumer, H., Zhou, Q., Baumann, M. J., Carlsson, K., & Teeri, T. T. (2004). Activation of crystalline cellulose surfaces through the chemoenzymatic modification of xyloglucan. *Journal of the American Chemical Society*, *126*, 5715–5721.

Cheng, G., Liu, Z., Murton, J. K., Jablin, M., Dubey, M., Majewski, J., et al. (2011). Neutron reflectometry and QCM-D study of the interaction of celluloses with films of amorphous cellulose. *Biomacromolecules*, *12*, 2216–2224.

Christiernin, M., Henriksson, G., Lindström, M., Brumer, H., Teeri, T. T., Lindström, T., et al. (2003). The effects of xyloglucan on the properties of paper made from bleached kraft pulp. *BioResources*, *18*, 182–187.

Dobrynin, A. V., Deshkovski, A., & Rubinstein, M. (2000). Adsorption of polyelectrolytes at an oppositely charged surface. *Physical Review Letters*, *84*, 3101–3104.

Dobrynin, A. V., Deshkovski, A., & Rubinstein, M. (2001). Adsorption of polyelectrolytes at oppositely charged surfaces. *Macromolecules*, *34*, 3421–3436.

Dobrynin, A. V., & Rubinstein, M. (2005). Theory of polyelectrolytes in solutions and at surfaces. *Progress in Polymer Science*, *30*, 1049–1118.

Eronen, P., Junka, K., Österberg, M., & Laine, J. (2011). Interaction between water-soluble polysaccharides and native nanofibrillar cellulose thin films. *BioResources*, *6*, 4200–4217.

Filpponen, I., Kontturi, E., Nummelin, S., Rosilo, H., Kolehmainen, E., Ikkala, O., et al. (2012). Generic method for modular surface modification of cellulosic materials in aqueous medium by sequential click reaction and adsorption. *Biomacromolecules*, *13*, 736–742.

Findenig, G., Leimgruber, S., Kargl, R., Spirk, S., Stana-Kleinschek, K., & Ribitsch, V. (2012). Water vapor barriers from hydrophilic components. *ACS Applied Materials & Interfaces*, *4*, 3199–3206.

Fras Zemljic, L., Stenius, P., Laine, J., & Stana-Kleinschek, K. (2008). Topochemical modification of cotton fibres with carboxymethyl cellulose. *Cellulose*, *15*, 315–321.

Fras Zemljic, L., Stenius, P., Laine, J., & Stana-Kleinschek, K. (2011). The effect of adsorbed carboxymethyl cellulose on the cotton fibre adsorption capacity for surfactant. *Cellulose*, *13*, 655–666.

Geffroy, C., Labeau, M. P., Wong, K., Cabane, B., & Cohen Stuart, M. A. (2000). Kinetics of adsorption of polyvinylamine onto cellulose. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *172*, 47–56.

Hasani, M., Cranston, E. D., Westman, G., & Gray, D. G. (2008). Cationic surface functionalization of cellulose nanocrystals. *Soft Matter*, *4*, 2238–2244.

Ishimaru, Y., & Lindström, T. (1984). Adsorption of water-soluble nonionic polymers onto cellulosic fibers. *Journal of Applied Polymer Science*, *29*, 1675–1691.

Kargl, R., Mohan, T., Bracic, M., Kulterer, M., Doliska, A., Stana-Kleinschek, K., et al. (2012). Adsorption of carboxymethyl cellulose on polymer surfaces: Evidence of a specific interaction with cellulose. *Langmuir*, *28*, 11440–11447.

Kargl, R., Mohan, T., Köstler, S., Spirk, S., Doliska, A., Stana-Kleinschek, K., et al. (2012). Functional patterning of biopolymer thin films using enzymes and lithographic methods. *Advanced Functional Materials*, in press. http://dx.doi.org/10.1002/adfm.201200607

Köhler, S., Liebert, T., & Heinze, T. (2008). Interactions of ionic liquids with polysaccharides VI. Pure cellulose nanoparticles from trimethylsilyl cellulose synthesized in ionic liquids. *Journal of Polymer Science Part A: Polymer Chemistry*, *46*, 4070–4080.

Kondo, T., Koschella, A., Heublein, B., Klemm, D., & Heinze, T. (2008). Hydrogen bond formation in regioselectively functionalized 3-mono-O-methyl cellulose. *Carbohydrate Research*, *343*, 2600–2604.

Kontturi, E., & Lankinen, A. (2010). Following the kinetics of a chemical reaction in ultrathin supported polymer films by reliable mass density determination with X-ray reflectivity. *Journal of the American Chemical Society*, *132*, 3678–3679.

Kontturi, E., Thüne, P. C., & Niemantsverdriet, J. W. (2003). Cellulose model surfaces simplified preparation by spin coating and characterization by X-ray photoelectron spectroscopy, infrared spectroscopy and atomic force microscopy. *Langmuir*, *19*, 5735–5741.

Kontturi, K. S., Holappa, S., Kontturi, E., Johansson, L.-S., Hyvärinen, S., Peltonen, S., et al. (2009). Arrangements of cationic starch of varying hydrophobicity on hydrophilic and hydrophobic surfaces. *Journal of Colloid Interface Science*, *336*, 21–29.

Kontturi, K. S., Tammelin, T., Johansson, L.-S., & Stenius, P. (2008). Adsorption of cationic starch on cellulose studied by QCM-D. *Langmuir*, *24*, 4743–4749.

Laine, J., Lindström, T., Nordmark, G. G., & Risinger, G. (2000). Studies on topochemical modification of cellulosic fibres. Part 1. Chemical conditions for the attachment of carboxymethyl cellulose onto fibres. *Nordic Pulp and Paper Research Journal*, *15*, 520–526.

Laine, J., Lindström, T., Nordmark, G. G., & Risinger, G. (2002). Studies on topochemical modification of cellulosic fibres Part 2. The effect of carboxymethyl cellulose attachment on fibre swelling and paper strength. *Nordic Pulp and Paper Research Journal*, *17*, 50–56.

Liu, Z., Choi, H., Gatenholm, P., & Esker, A. R. (2011). Quartz crystal microbalance with dissipation monitoring and surface plasmon resonance studies of carboxymethyl cellulose adsorption onto regenerated cellulose surfaces. *Langmuir*, *27*, 8718–8728.

Löscher, F., Ruckstuhl, T., Jaworek, T., Wegner, G., & Seeger, S. (1998). Immobilization of biomolecules on Langmuir–Blodgett films of regenerative cellulose derivatives. *Langmuir*, *14*, 2786–2789.

Marx, K. A. (2003). Quartz crystal microbalance: A useful tool for studying thin polymer films and complex biomolecular systems at the solution–surface interface. *Biomacromolecules*, *4*, 1099–1120.

Mishima, T., Hisamatsu, M., York, W. S., Teranishi, K., & Yamada, T. (1998). Adhesion of β-D-glucans to cellulose. *Carbohydrate Research*, *308*, 389–395.

Mohan, T., Kargl, R., Doliška, A., Ehmann, H. M. A., Ribitsch, V., & Stana-Kleinschek, K. (2012). Enzymatic digestion of partially and fully regenerated cellulose model films from trimethylsilyl cellulose. *Carbohydrate Polymers*, in press

Mohan, T., Kargl, R., Doliška, A., Vesel, A., Köstler, S., Ribitsch, V., et al. (2011). Wettability and surface composition of partly and fully regenerated cellulose thin films from trimethylsilyl cellulose. *Journal of Colloid and Interface Science*, *358*, 604–610.

Mohan, T., Kargl, R., Köstler, S., Doliška, A., Findenig, G., Ribitsch, V., et al. (2012). Functional polysaccharide conjugates for the preparation of microarrays. *ACS Applied Materials & Interfaces*, *4*, 2743–2751.

Mohan, T., Spirk, S., Kargl, R., Doliška, A., Ehmann, H. M. A., Köstler, S., et al. (2012). Watching cellulose grow – Kinetic investigations on cellulose thin film formation at the gas–solid interface using a quartz crystal microbalance with dissipation (QCM-D). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *400*, 67–72.

Mohan, T., Spirk, S., Kargl, R., Doliska, A., Vesel, A., Salzmann, I., et al. (2012). Exploring the rearrangement of amorphous cellulose model thin films upon heat treatment. *Soft Matter*, *8*, 9807–9815.

Orelma, H., Filpponen, I., Johansson, L.-S., Laine, J., & Rojas, O. J. (2011). Modification of cellulose films by adsorption of CMC and chitosan for controlled attachment of biomolecules. *Biomacromolecules*, *12*, 4311–4318.

Orelma, H., Teerinen, T., Johansson, L.-S., Holappa, S., & Laine, J. (2012). CMC-modified cellulose biointerface for antibody conjugation. *Biomacromolecules*, *13*, 1051–1058.

Rakkolainen, M., Kontturi, E., Isogai, A., Enomae, T., Blomstedt, M., & Vuorinen, T. (2009). Carboxymethyl cellulose treatment as a method to inhibit vessel picking tendency in printing of eucalyptus pulp sheets. *Industrial and Engineering Chemical Research*, *48*, 1887–1892.

Rodahl, M., Hook, F., Fredriksson, C., Keller, A., Krozer, C., Brzezinski, A., et al. (1997). Simultaneous frequency and dissipation factor QCM measurements of biomolecular adsorption and cell adhesion. *Faraday Discussions*, *107*, 229–246.

Schaub, M., Wenz, G., Wegner, G., Stein, A., & Klemm, D. (1993). Ultrathin films of cellulose on silicon wafers. *Advanced Materials*, *5*, 919–922.

Spirk, S., Ehmann, H., Kargl, R., Hurkes, N., Reischl, M., Novak, J., et al. (2010). Surface modifications using a water-stable silanetriol in neutral aqueous media. *ACS Applied Materials & Interfaces*, *2*, 2956–2962.

Stana-Kleinschek, K., Kreze, T., Ribitsch, V., & Strnad, S. (2001). Reactivity and electrokinetical properties of different types of regenerated cellulose fibres. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, *195*, 275–284.

Suchy, M., Linder, M. B., Tammelin, T., Campbell, J. M., Vuorinen, T., & Kontturi, E. (2011). Quantitative assessment of the enzymatic degradation of amorphous cellulose by using a quartz crystal microbalance with dissipation monitoring. *Langmuir*, *27*, 8819–8828.

Tammelin, T., Merta, J., Johansson, L.-S., & Stenius, P. (2004). Viscoelastic properties of cationic starch adsorbed on quartz studied by QCM-D. *Langmuir*, *20*, 10900–10909.

Teeri, T. T., Brumer, H., Daniel, G., & Gatenholm, P. (2007). Biomimetic engineering of cellulose-based materials. *Trends in Biotechnology*, *25*, 299–306.

Terada, E., Samoshina, Y., Nylander, T., & Lindman, B. (2004a). Adsorption of cationic cellulose derivative/anionic surfactant complexes onto solid surfaces II. Hydrophobized silica surfaces. *Langmuir*, *20*, 6692–6701.

Terada, E., Samoshina, Y., Nylander, T., & Lindman, B. (2004b). Adsorption of cationic cellulose derivatives/anionic surfactant complexes onto solid surfaces I. Silica surfaces. *Langmuir*, *20*, 1753–1762.

Woods, D. A., Petkov, J., & Bain, C. D. (2011). Surfactant adsorption by total internal reflection Raman spectroscopy. Part III: Adsorption onto cellulose. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *391*, 10–18.

Zarth, C., Koschella, A., Pfeifer, A., Dorn, S., & Heinze, T. (2011). Synthesis and characterization of novel amino cellulose esters. *Cellulose*, *18*, 1315–1325.

Zarth, C. S. P., Zemljič, L. F., Čakara, D., Bračič, M., Pfeifer, A., Stana-Kleinschek, K., et al. (2012). Charging behavior and stability of the novel amino group containing cellulose ester cellulose-4-[*N*-methylamino]butyrate hydrochloride. *Macromolecular Chemistry and Physics*, *213*, 1669–1676.

Zhou, Q., Rutland, M., Teeri, T., & Brumer, H. (2007). Xyloglucan in cellulose modification. *Cellulose*, *14*, 625–641.