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Film formation of ω-aminoalkylcellulose carbamates – A quartz crystal microbalance (QCM) study

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ABSTRACT

The film formation of novel ω-aminoalkylcellulose carbamates on gold surface was studied by means of quartz crystal microbalance with dissipation monitoring (QCM-D) and atomic force microscopy (AFM). The influence of the pH value of the buffer solution, the concentration, the degree of polymerization, and the structure (spacer length) of the polymers on the coating was investigated. The layer formation was explained based on the pK_a value and the degree of substitution of the ω-aminoalkylcellulose carbamates determined by potentiometric titration. This work provides novel supporting materials that might be applied in field of immobilization of biomolecules.

1. Introduction

Polymer coatings are very important in different fields of research and development, for example, the corrosion protection of industrial products (Šimunović & Juraga, 2005) and the modification of fiber surfaces (Samyn, 2013). Moreover, coating allows the design of responsive biomaterials (Yoshida, Langer, Lendlein, & Lahann, 2006). In particular polymeric monolayers are promising surface-active materials that gain increasing interest in the development of sensors, tailoring of surface chemistry and the use of micro- or nanofabrication techniques (Senaratne, Andruzzi, & Ober, 2005). Due to their inherent biocompatibility polysaccharide-based materials provide excellent polymer films for nanocomposites in biological applications. For instance, cellulose derivatives show often film-forming properties and they allow a wide range of possibilities for chemical modification in order to study structure–property relationships (Berlin et al., 2003).

Due to the protein-like behavior of 6-desoxy-6-aminocelluloses, resulting in a magnificent environment for biomolecules, thin films of these derivatives have been employed for the immobilization of enzymes (Berlin, Klemm, Tiller, & Rieseler, 2000; Heinze et al., 2011). However, the degree of substitution (DS) is limited to 0.8 in practice arising from the synthesis via nucleophilic displacement reaction of tosyl cellulose. Recently, the synthesis of ω-aminoalkylcellulose carbamates (Elschner, Ganske, & Heinze, 2013) was studied in detail and it was found that these new water soluble cellulose derivatives possess film forming properties. Cellulose carbamates are obtained by aminolysis of the corresponding carbonic acid ester. Cellulose phenyl carbonate with a DS of 3, e.g., could be synthesized and thus we overcome the limitations regarding the density of functional groups (Elschner, Kötteritzsch, & Heinze, 2014).

To investigate the film formation of polymers quartz crystal microbalance with dissipation monitoring (QCM-D) has become a powerful tool for studying adsorption/desorption processes of aqueous solutions of polymers at solid/liquid interface (Andersson et al., 2005; Gericke et al., 2011; Hook, Rodahl, Brzezinski, & Kasemo, 1998). This technique is based on the change of the oscillating frequency of a piezoelectric quartz crystal device upon mass

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loading and allows the detection of adsorbed mass on a surface (Coffey & Krim, 2005). Real-time measurements of the frequency shifts and energy dissipation allow conclusions about mass and viscoelastic properties of the layer. According to the Sauerbrey equation (Sauerbrey, 1959), the adsorbed mass (Δm) is proportional to the change in frequency (Δf):

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

where C is a mass sensitive constant that depends on the quartz crystal (17.7 ng Hz^{-1}cm^{-2} for f_0 = 5 MHz) and n the overtone number. This correlation is valid for thin, rigid, and evenly distributed monolayers because the change in dissipation has to be very small ($\Delta D \approx 0$).

In this work QCM-D is applied to study the layer formation of ω-aminoalkylcellulose carbamates on gold surface. The focus of this study is the adsorption of the biopolymer derivative in dependency of pH, degree of polymerization (DP), spacer length and polymer concentration. Moreover, the structure of the film is investigated by means of atomic force microscopy (AFM). The adsorption is evaluated by pK_a values of the amine groups obtained from potentiometric titration.

2. Experimental

2.1. Materials

Microcrystalline cellulose (Avicel PH-101) with a $\bar{DP}_w$ of 330 was purchased from Sigma–Aldrich and dried at 60 °C in vaccum. Low molecular weight cellulose ($\bar{DP}_w$ of 50) was obtained by degradation of regenerated cellulosic fiber (*N*-methylmorpholine-*N*-oxide process, Thuringian Institute of Textile and Plastics Research, Rudolstadt, Germany) with hydrochloric acid (Meiland, Liebert, & Heinze, 2011). *N*-*tert*-Butoxycarbonyl-1,2-ethanediamine **3a** and *N*-*tert*-Butoxycarbonyl-1,4-butanediamine **3b** were obtained according to the procedure described by Krapcho and Kuell (1990). *N*-*tert*-Butoxycarbonyl-2,2′-(ethylenedioxy)diethylamine **3c** was synthesized according to the procedure described by Zuckermann et al. (1994). ω-Aminoalkylcellulose carbamates were synthesized according to a procedure published recently (Elschner, Ganske, et al., 2013). Other chemicals were purchased from Aldrich and were used without further treatment.

2.2. Measurements

Elemental analysis were performed by CHNS 932 Analyzer (Leco). Size-exclusion chromatography (SEC) was performed on an Agilent 1200 series LC system (G1310A pump, G1362A refractive-index detector) with PSS Gram30 and PSS Gram1000 columns in series. *N*,*N*-Dimethylacetamide (DMAc) with 0.21 wt.% LiCl was used as the eluent at 40 °C and a flow rate of 1 cm^3/min. Pullulan was used as calibration standard to determine the weight-average degree of polymerization ($\bar{DP}_w$). Moreover, SEC of ω–aminoalkylcellulose carbamates was performed with a Jasco system (PU-980 pump, RI-930 refractive-index detector) with a PSS SUPREMA-MAX 300 column. 0.05 M NaCl with 0.1 % TFA was used as the eluent at 30 °C and a flow rate of 1 cm^3/min.

Potentiometric titration was carried out under nitrogen atmosphere with a two-burette instrument (Mettler Toledo-70) equipped with a combined glass electrode (Mettler Toledo DG-111-SC). The burettes were filled with 0.1 M HCl and 0.1 M KOH prepared with degassed Milli-Q water (carbonate content < 10^{-5} M). 1 mL sample (2 wt.%) was diluted with Milli-Q water to a volume of 40 mL in the titration cell. The solutions were adjusted to an ionic strength of 0.1 M (adjusted with KCl) and titrated forth and back between the initial pH 2.8 to the preset pH 11.5. The titrant was added dynamically within a preset interval of 0.001–0.25 mL. The equilibrium criteria for the timed addition was set to E/dt < 0.1 V/s during 10 s. The time to reach equilibrium conditions between two additions of the titrant was set to 10–180 s.

Table 1
Conditions for and results of QCM-D measurements: change in frequency (ΔF) and dissipation (ΔD) for ω-aminoethylcellulose carbamates depending on pH and degree of polymerization.

No	DS[a]	pH	V[b] [mL]	ΔF [Hz]	ΔD [10^{-6}]
7a	1.17	5	8.8	−0.5	−0.2
7a	1.17	7	8.8	−25	−0.1
7a	1.17	10	8.8	−30	3.4
7b	1.43	5	8.2	−4.5	−0.3
7b	1.43	7	8.2	*[c]	*[c]
7b	1.43	10	8.2	−30	7
7c	1.20	5	7.4	−7.5	0
7c	1.20	7	7.4	*[c]	*[c]
7c	1.20	10	7.4	−39	11.5

[a] Degree of substitution determined by means of elemental analysis (nitrogen content).
[b] Average values of elution volume obtained from size exclusion chromatography corresponding reverse to degree of polymerization.
[c] No value of equilibrium.

The adsorption of ω-aminoalkylcellulose carbamates was studied with a QCM (QCM-D E4) from Q-Sense AB (Gothenburg, Sweden) at 23 °C. The relative resonant frequency (ΔF) of the crystals as well as the relative dissipation factor (ΔD) were determined in comparison to the zero values at the beginning of the experiment (third overtone). For the adsorption experiments, gold coated sensor crystals were rinsed (1 mL/min) in the QCM device until constant values of frequency as well as dissipation were observed. Before and after each adsorption step the crystals were rinsed with Milli-Q water and 10 mM sodium phosphate buffer. All adsorption experiments were repeated at least three-times. This procedure was optimized as described in literature (Indest et al., 2008, 2009). The quartz crystals (supplied by Q Sense AB) were AT-cut quartz with gold plated electrodes and with gold on the active surface. The fundamental frequency of quartz crystals is $f_0 \approx 5$ MHz and the sensitivity constant C = 17.7 ngHz^{-1}cm^{-2}.

The surface roughness of the layers of the adsorbed cellulose derivative was characterized by Atomic force microscopy (AFM) in tapping mode with an Agilent 5500 AFM multimode scanning probe microscope (Digital Instruments, Santa Barbara, CA). The images were scanned using silicon cantilevers (ATEC-NC-20, Nanosensors, Germany) with a resonance frequency of 210–490 kHz and a force constant of 12–110 N/m. The scanned image size was 5 μm × 5 μm. All measurements were performed at ambient temperature in air.

3. Results and discussion

3.1. Synthesis of ω-aminoalkylcellulose carbamates

The synthesis and characterization of ω-aminoalkylcellulose carbamates **7a–c**, **8** and **9** (Fig. 1) was published recently (Elschner, Ganske, et al., 2013). In brief, cellulose (**1**) is allowed to react with phenyl chloroformate in the presence of pyridine. The cellulose phenyl carbonate (**2**) obtained is converted with the corresponding mono-protected diamine (**3a–c**) to yield functional cellulose carbamates (**4–6**). A subsequent deprotection by an acidic treatment yield the ω-aminoalkylcellulose carbamates (**7a–c**, **8** and **9**). The degree of substitution (DS) determined by elemental analysis and potentiometric titration is in the range from 0.72 to 1.50 (Tables 1 and 2). Moreover, the products were analyzed by means of size exclusion chromatography (SEC, Table 2).

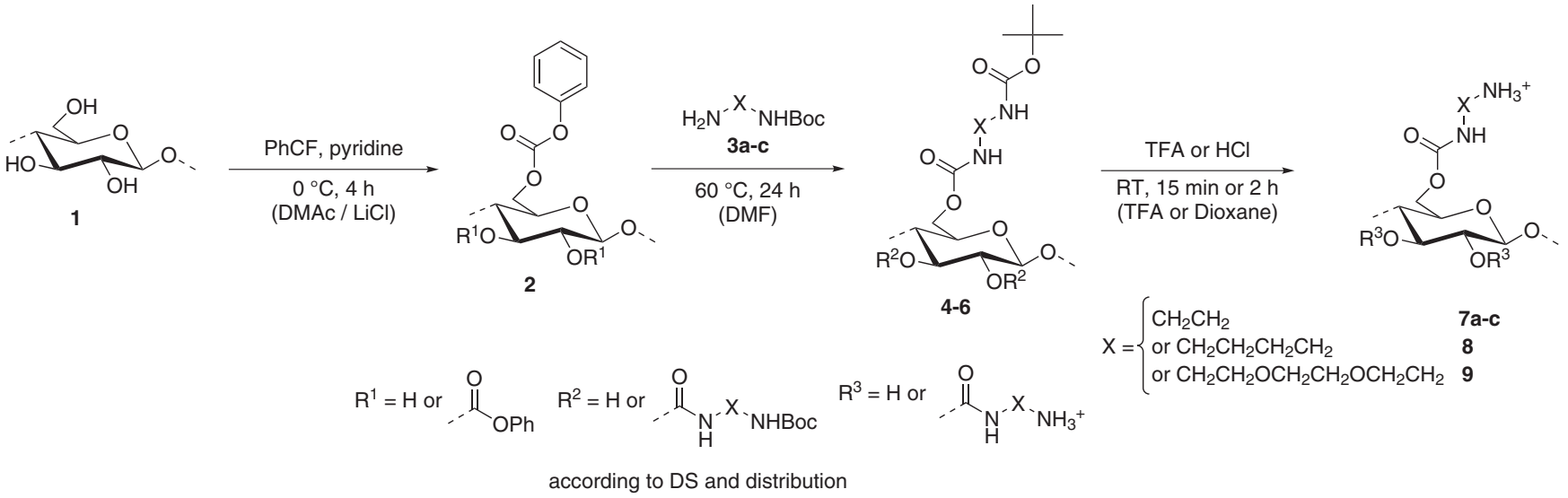

Fig. 1. Reaction scheme of the synthesis of ω-aminoalkylcellulose carbamates.

Table 2
Amount of amino groups, degree of substitution (DS) and pK_a of ω-aminoalkylcellulose carbamates obtained by potentiometric titration.

No	Spacer X[a]	Amino groups [mmol/g]	DS[b]	pK_a
7a	$-(CH_2CH_2)-$	3.73	1.11	8.6
7b	$-(CH_2CH_2)-$	4.34	1.50	8.6
7c	$-(CH_2CH_2)-$	3.81	1.16	8.6
8	$-(CH_2CH_2CH_2CH_2)-$	2.68	0.72	9.7
9	$-(CH_2)_2O(CH_2)_2O(CH_2)_2-$	2.70	1.02	9.0

[a] According to Fig. 1.
[b] Degree of substitution determined by means of potentiometric titration.

On one hand, ω-aminoethylcellulose carbamates with various degrees of polymerization (DP) were obtained starting from celluloses with different DP and applying different procedures of acidic deprotection. On the other, amines with different spacer length *X* (Fig. 1) were used for the synthesis of ω-aminoalkylcellulose carbamates starting from cellulose with a DP of 330. Thus, a set ω-aminoalkylcellulose carbamates of different structures become available in order to study structure–property-relationships, here the film formation was of particular interest.

3.2. Adsorption of ω-aminoalkylcellulose carbamates on gold surfaces

The layer formation of ω-aminoalkylcellulose carbamates (**7a–c**, **8** and **9**) on a gold surface was studied by means of quartz crystal microbalance with dissipation monitoring (QCM-D), adjusting the pH of the polymer solution with sodium hydroxide to 5 or 10. It became obvious that ω-aminoethylcellulose carbamate **7c** does not adsorb onto a gold surface in the presence of hydroxide- or chloride-ions. Therefore, buffered solutions containing carbonate- or phosphate-ions were used in further experiments. Comparing carbonate- and phosphate-buffer solutions, the equilibrium values of change in frequency ($\Delta F = -40$ Hz) and dissipation ($\Delta D = 11 \times 10^{-6}$) are similar at pH 10. These results indicate that carbonate- and phosphate-ions adsorb onto the gold surface to form a negatively charged anchor layer as known (Weber & Nart, 1996). Subsequently, the positively charged polymer is adsorbed on the surface. This phenomenon was already observed in studies of adsorption of proteins onto surfaces, like hydroxyapatite (Tagaya et al., 2010; Wei, Kaewtathip, & Shing, 2009). While carbonate buffer is limited to alkaline pH scale, phosphate buffer covers a broad range of pH values and was used for further adsorption studies.

The adsorption of ω-aminoethylcellulose carbamates (**7a–c**) in dependence on the pH value and DP was studied systematically (Table 1). For the experiments 10 mM sodium phosphate buffer solutions containing 0.07 % ω-aminoalkylcellulose carbamate were applied. In general, increasing molecular weight leads to an increase of adsorbed mass.

At a pH value of 5 no ($\Delta F = -0.5$ Hz, **7a**) or a small amount of adsorbed mass (≈3–44 ng/cm^2, **7b** and **c**) was observed, while the amount of polymer adsorbed on the gold surface increases significantly at pH 7 (Figs. 2 and 3). Especially, ω-aminoethylcellulose carbamate (**7c**) with a high $\bar{D}P_w$ of 330 (starting material) forms a multilayer at neutral pH. This phenomenon of quasi-linear adsorption, which was already observed during the adsorption of proteins (Wei et al., 2009), could be clearly revealed by means of QCM-D. In Fig. 2, the adsorption of polymer (**7c**) does not reach an equilibrium indicated by the continuous linear increase of the absolute value of ΔF. After rinsing with buffer and water, loosely bound polymer is desorbed from the surface and the layer become soft due to swelling indicated by increasing ΔF and ΔD. Sample **7c** shows a more pronounced formation of multilayers due to the highest $\bar{D}P_w$ that cause an increased entanglement of the polymer chains.

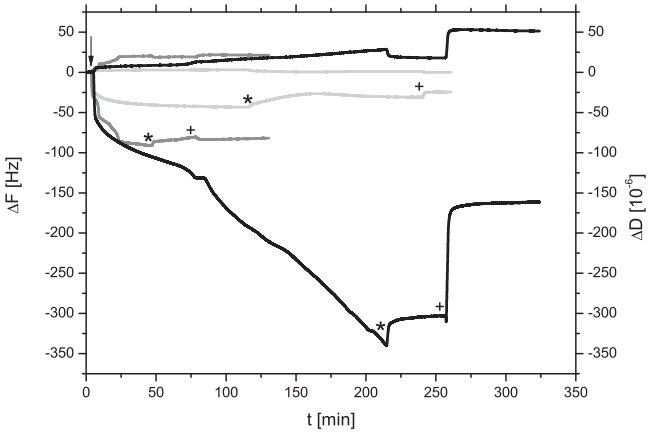

Fig. 2. Change in frequency and dissipation (third overtone) as function of time during adsorption of ω-aminoethylcellulose carbamates **7a** (light gray), **7b** (gray) and **7c** (black) at pH 7. Addition of sample (arrow) and start of rinsing (*buffer, $^+$water) are marked.

However, the graph in Fig. 2 indicates that the rinsing of **7c** with water leads to a huge loss of mass that might be explained by the wash out of phosphate ions. Thus, the adhesion between the multiple layers is reduced and the polymer coils are removed from the surface. Beyond the QCM-D data, the AFM images show film formation of ω-aminoethylcellulose carbamates (**7a–c**) at pH 7 depending on DP (Fig. 3). In comparison to the pure gold surface (top left, S_a 0.3 nm), the roughness increases to S_a = 1.7–3.1 nm and moreover, aggregates become visible (**7c**, bottom right).

In contrast to experiments carried out at pH 7, a uniform, rigid and thin film is formed at pH 10 (Fig. 4). After addition of ω-aminoalkylcellulose carbamates ΔF and ΔD reach equilibrium values. Comparing the ω-aminoethylcellulose carbamates, **7a** and **7b** show identical ΔF and almost identical ΔD due to the less pronounced coiling of the short polymer chains and thus, the film is more rigid and less swellable. ΔF is similar for **7a** and **7b** (−30 Hz) but the absolute value for **7c** is increased (−40 Hz) and ΔD increases with increasing DP from 3.4 to 11.5 (Table 1). Varying the spacer length of amine from ethylene (**7**, solid) to butylene (**8**, dashed) to 2,2′-(ethylenedioxy)bis(ethylene) (**9**, dotted) has almost no influence on the layer formation (Fig. 4).

Moreover, the dependency of the adsorbed mass on the polymer concentration was investigated. From the graph shown in Fig. 5 it is obvious that an increasing polymer concentration does not cause a thicker layer at concentrations above 0.1 %. This behavior indicates that a monolayer is formed at a pH value of 10 under the conditions applied. The adsorbed mass can be calculated by the Sauerbrey equation (Sauerbrey, 1959) because the dissipation shift is very small ($\Delta D \approx 0$). A frequency shift of −32 Hz leads to 189 ng/cm^2 (0.61 nmol/cm^2). The adsorbed amount is equivalent to 3.7×10^{14} repeating units/cm^2 and fits to the same magnitude of a repeating unit of cellulose (500–600 pm) assuming a regular, completely covered arrangement of squares on the surface. Thus, a monolayer is probably formed if the coating is carried out in phosphate buffer at pH 10.

3.3. Potentiometric titration of ω-aminoalkylcellulose carbamates

The pH dependent amount of charged groups of ω-aminoalkylcellulose carbamates was investigated in order to explain the film-forming properties of the polymers at different pH values by means of pH-potentiometric titrations. The forth and back isotherms coincided with each other, which indicates that all samples could be protonated and deprotonated reversibly. In

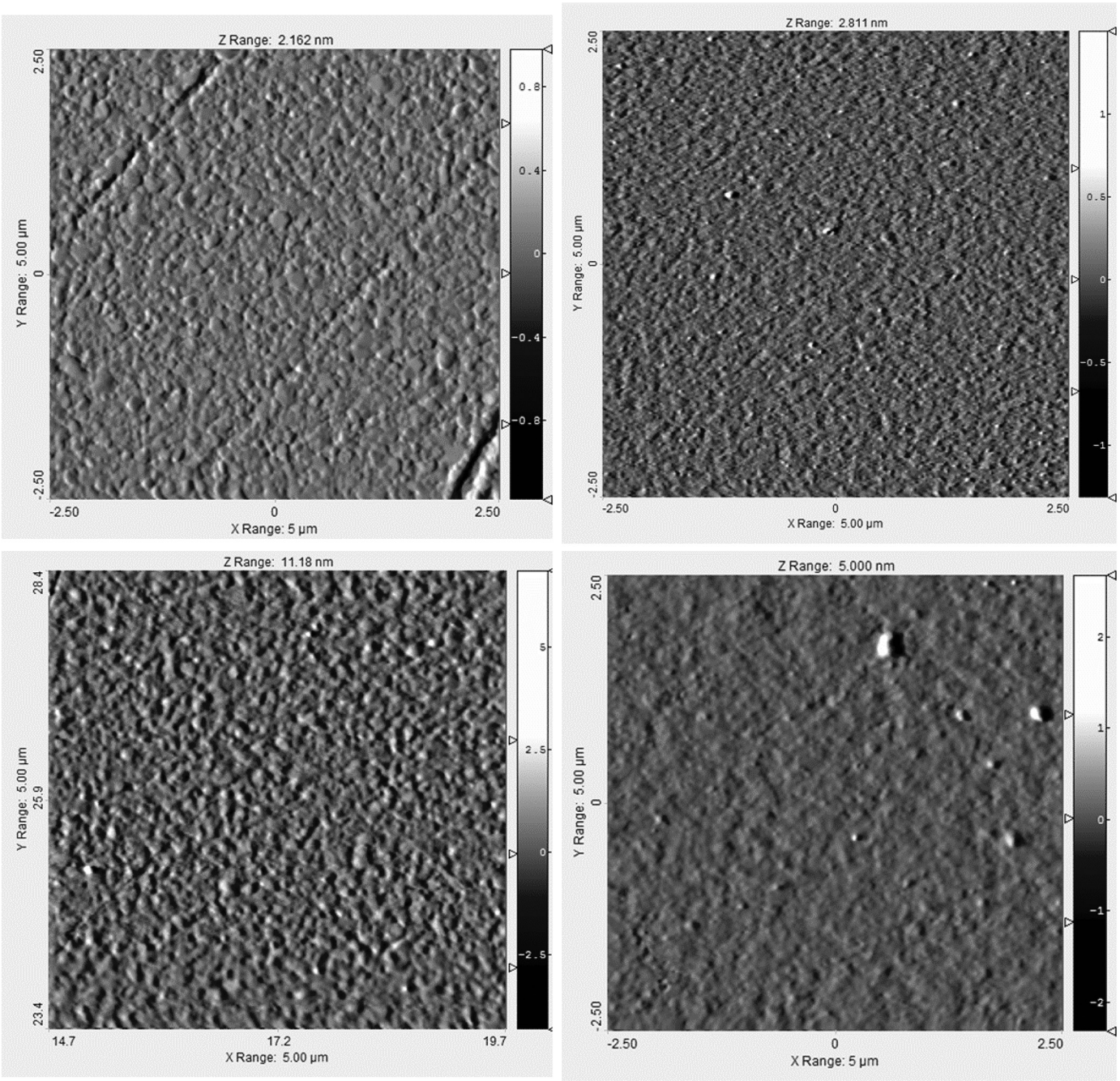

Fig. 3. AFM images of the ω-aminoethylcellulose carbamate films (coated at pH 7) on gold surface of QCM crystals: pure gold (top left, S_a 0.3 nm), **7a** (top right, S_a 3.1 nm), **7b** (bottom left, S_a 2.0 nm) and **7c** (bottom right, S_a 1.7 nm).

Table 2 the amount of amino groups, the resulting DS and the pK_a values are summarized. The DS values of ω-aminoethylcellulose carbamates (**7a–c**) determined by titration and elemental analysis are in good agreement. Moreover, the pK_a is 8.6 and independent of the DP. The longer spacer (butylene, sample **8**) reduces the electron withdrawing effect of the carbamate moiety while the +I-effect of the alkyl chain is increased. Thus, the nitrogen atom of the amine group becomes more basic and the pK_a increases to 9.7. In case of the 2,2′-(ethylenedioxy)bis(ethylene)-spacer (**9**) there is an influence of the oxygen atoms from ether moieties resulting in electron withdrawing effect and decreasing pK_a (9.0).

Considering the titration study, it becomes obvious that the difference in coating at pH 5 or pH 7 cannot be explained by degrees of protonation, because up to pH 7 nearly all amino groups of the polymer are protonated. Therefore, the kind of phosphate species could be an explanation. At pH 5 mainly hydrogen phosphate ions are present. At pH 7 an equimolar mixture (1:1) of hydrogen phosphate- and dihydrogen phosphate ions is existent. In this case double charged ions could form a further anchor surface on the first layer of ω-aminoalkylcellulose carbamate that lead to electrostatically stabilized multilayer formation or aggregation. At pH 10 dihydrogen phosphate ions are present but the polymer is not charged anymore. The electrostatic interaction

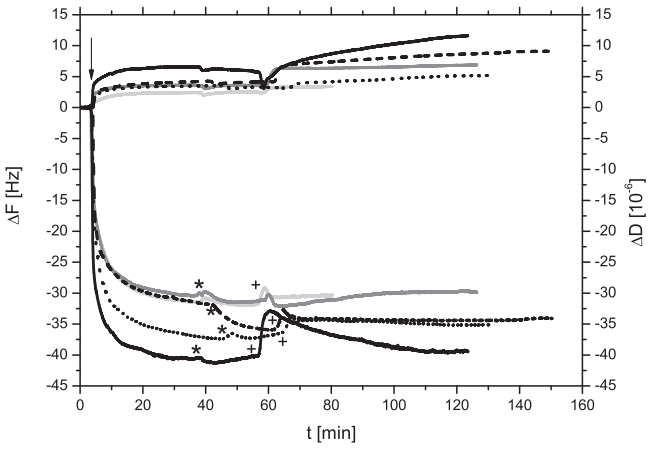

Fig. 4. Change in frequency and dissipation (third overtone) as function of time during adsorption of ω-aminoalkylcellulose carbamates **7a** (light gray), **7b** (gray), **7c** (black), **8** (dashed), **9** (dotted) at pH 10. Addition of sample (arrow) and start of rinsing (*buffer, +water) are marked.

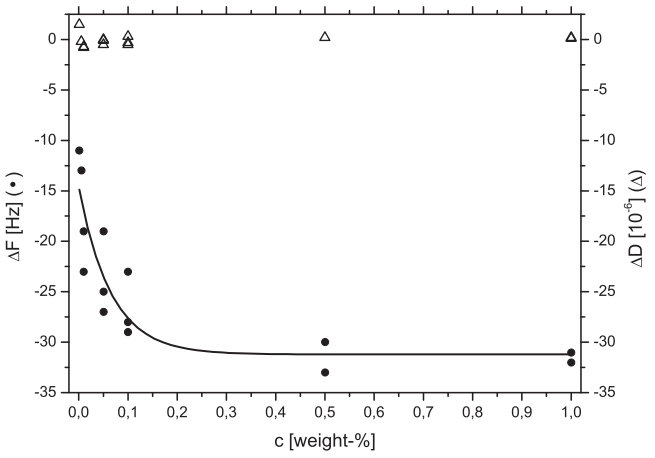

Fig. 5. Adsorption of ω-aminoethylcellulose carbamate **7a**: Change in frequency and dissipation (third overtone) at equilibrium of rinsing as function of polymer concentration.

decreases and the tendency to the formation of mulilayers is less pronounced.

3.4. Conlusions

The film formation of ω-aminoalkylcellulose carbamates on gold surface was investigated by means of quartz crystal microbalance with dissipation monitoring (QCM-D) and atomic force microscopy (AFM). The adsorption of the polymer in aqueous, buffered solution is highly dependent on the pH value. While at pH 5 no adsorption takes place, at pH 7 a multilayer and aggregates occur on the surface. However, at pH 10 a rigid and thin film is formed. The roughness of the layer and the adsorbed mass increase with increasing degree of polymerization. The spacer length of the substituent has almost no influence on the adsorbed mass. The pH dependent formation of bivalent ions causes different adsorption behavior. The pK_a values of the amino groups were determined by means of potentiometric titration. Within this work a procedure to yield rigid and thin films of ω-aminoalkylcellulose carbamates was developed that might be applied in sensor technology. Due to the biocompatibility and the high density of functional groups the composites obtained are promising materials for the immobilization of biomolecules.

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Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.04.101.

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