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Comparison of the Adsorption of Different Charge Density Polyelectrolytes: A Quartz Crystal Microbalance and X-ray Photoelectron Spectroscopy Study

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The adsorption of a series of six cationic polyelectrolytes onto a gold surface was monitored via a quartz crystal microbalance with dissipation (QCM-D). The series of polyelectrolytes were chemically similar but differing in the ratio of two randomly ordered constituent monomers, one of which was charged, the other neutral. Thus the series of polyelectrolytes differed systematically in their charge densities, ranging from a high charge density (100% of monomers charged) to a low charge density (1% charged). It was determined that high charge density polyelectrolytes adsorbed in a relatively flat and rigid layer, while the low charge density polyelectrolyte, as expected, adsorbed in a much more extended structure that coupled strongly to the bulk solvent. By comparison to X-ray photoelectron spectroscopy results, we have also calculated the relative solvent mass hydrodynamically coupled to the adsorbed polymer, which ranges from almost 80% solvent for the 1% charged case down to close to zero for the 100% charged case. Since the QCM-D results are measured relative to uncoated gold in aqueous solution, the latter results should be interpreted as showing that the amount of water hydrodynamically coupled to gold and that coupled to gold coated with the 100% charged polyelectrolyte is very similar. It is believed that this systematic study on the effect of polyelectrolyte structure on the measured dissipation change in the QCM-D may serve as a first guide when inferring structural and viscoelastic information based solely on the QCM-D technique for other similar systems. In addition, a preliminary study on the ability of one polymer to replace another preadsorbed polymer layer was conducted that showed that a steric layer was able to prevent the adsorption of a thermodynamically more favorable polymer. In the reverse case, greater exchange was possible.

Introduction

Polyelectrolytes are used in a large range of industrial and technical situations.^{1–8} From medical to mining and paper making to pharmaceuticals, the list of applications is seemingly endless, though in most cases polyelectrolytes are used as either rheology or surface modifiers. Thus, in many cases the adsorption of these materials to different substrates, in terms of amount, kinetics, and layer structure, defines their application. For this reason, much effort has gone into characterizing these types of systems.

The adsorbed amount can be experimentally determined in a number of ways, providing information on the extent and possibly the dynamics of the adsorption process. For more detailed information on layer structure, additional experiments need to be carried out which often make the entire procedure lengthy and difficult. In this study, we employ the quartz crystal microbalance with dissipation (QCM-D) to study the adsorption characteristics of a series

of similar polyelectrolytes that differ mainly in their charge densities. This not only allows a comparison of the effect of the charge density on the adsorption of polyelectrolytes but also serves as a model system to demonstrate the range and accuracy of the technique, and in particular how the dimensionless so-called dissipation factor depends on the layer structure.

An advantage of the QCM-D technique is its ability to give some insight into the viscoelastic behavior of the adsorbed materials, which is achieved by monitoring the dissipation factor. The problem is that interpretation of this dimensionless number is difficult and thus it is mainly useful when comparing values either within a system undergoing changes⁸ or between two different systems.⁹ For example, it allows differentiation between two materials with different viscoelastic properties since the material with the more rigid structure would have a lower dissipation value. Additionally, as shown previously¹⁰ the technique can be used to monitor adsorption (or similar) processes and differentiate separate adsorption regimes within that kinetic process.

An inherent feature of the QCM-D technique when used in liquids is that the mass detected by the change in frequency includes contributions from both the adsorbed species and the solvent, which can be seen as either an advantage or a disadvantage. We have however previously shown that by combining QCM and X-ray photoelectron spectroscopy (XPS) results it is possible to determine both the polymer and solvent contributions to the sensed

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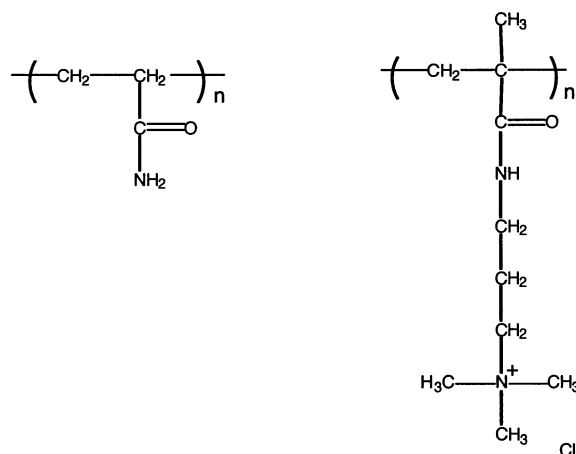


Figure 1. Schematic illustrations of AM (left) and MAPTAC (right) monomers.

mass.¹⁰ Thus, as will be shown here, it is possible to obtain the concentration of solvent within the polymer matrix as a function of the polyelectrolyte charge density and relate this to the measured dissipation values. To achieve this, we used the AM-MAPTAC (a random copolymer of uncharged acrylamide and positively charged [3-(2-methylpropionamide)propyl]trimethylammonium chloride) polyelectrolyte series and combined the QCM-D results with XPS measurements and also utilized previous data for these polyelectrolytes. This strategy helps us to overcome some of the difficulties of interpreting the QCM-D results.

An additional complication in adsorption studies occurs when the bulk contains more than one single adsorbing species, or even a single species with a high polydispersity. The equilibrium situation favors the lowest free energy; however, in many cases the equilibrium situation is never met and dynamic factors may determine the outcome of the adsorption process. In fact, the system may be arrested in a kinetically trapped state and true equilibrium never reached. As a consequence, the order in which the components are added may affect the structure of the adsorbed layer.^{19,26} In this case, it is not always so obvious what the final result will be. Kinetic aspects are also important when considering desorption phenomena with application to many processes, for example, cleaning. We have thus also attempted a small, preliminary study on competitive desorption between the highest and lowest charge density polyelectrolytes in an attempt to showcase the ability of the QCM-D and XPS to investigate such phenomena.

Materials and Methods

Materials. In this study, a series of cationic polyelectrolytes were used. Each polyelectrolyte in the series is a random copolymer of uncharged acrylamide (AM) and positively charged [3-(2-methylpropionamide)propyl]trimethylammonium chloride (MAPTAC). The segment structures are shown in Figure 1. The different polyelectrolytes differ in the relative concentration of the two monomeric constituents, and hence the charge density. Thus, we henceforth refer to the polymers as AM-MAPTAC-*X*, where *X* is the percentage of charged MAPTAC monomer units. The samples used were obtained as a gift from Laboratoire de Physico-Chimie Macromoléculaire, Université Pierre et Marie Curie, Paris. The analysis of the AM-MAPTAC-*X* samples carried out there has given the MAPTAC fraction contained within each sample, in addition to the molecular weight, as tabulated in Table 1.

The QCM-D. The instrument used in these experiments was the commercial Q-Sense (Göteborg, Sweden) quartz crystal microbalance with built-in dissipation measurement (QCM-D),

Table 1

nominal	% MAPTAC			molecular weight	degree of polymerization
	elemental analysis	potentiometry	NMR		
1	0.5	0.98		900 000	12 200
5	4	4.8	4.6–4.7	1 000 000	12 600
10	10	9	8.8–9.5	1 000 000	11 600
30	31	31	24.2–25.6	780 000	6 600
60	59	66	57–69	340 000	2 100
100	99	95		248 000	2 200

which is fully described elsewhere.¹¹ This instrument uses a disk-shaped 14 mm AT-cut quartz crystal with a fundamental frequency around 5 MHz (third overtone around 15 MHz). The active surface was an evaporated gold electrode (around 100 nm thick) attached onto the quartz oscillator via a 5 nm thick chromium adherent layer. During operation, the crystal (plus adsorbed layers) is excited to oscillate in the thickness shear mode (approximately 1 nm amplitude¹²). The resonant frequencies are related to the total oscillating mass, and adsorption, which results in an increase in mass, leads to a decrease in the resonance frequency. When the Sauerbrey relation¹³ holds, the change in frequency is directly proportional to the adsorbed mass and is given by

$$\Delta f = -\frac{2f^2}{\rho_q \nu_q} m = -\frac{f}{\rho_q t_q} m = -Cm \quad (1)$$

where *f* is the frequency, ρ_q and ν_q are the specific density and the shear wave velocity in quartz, respectively, *t_q* is the thickness of the quartz plate, *m* is the adsorbed mass per unit area, and *C* is the calibration constant for the crystal. In this way, monitoring the resonance frequencies gives an apparent adsorbed mass. In the case of the current set of experiments, data from the third overtone was used since it was found to be most reliable as a result of so-called “energy trapping”¹⁴ concerns for the fundamental. The calibration factor for the third overtone is *C* = 171 cm² μg⁻¹ s⁻¹.

In liquid, the Sauerbrey relation (eq 1) is not necessarily valid, even for thin adsorbed layers. One reason is that the coupling between the oscillating crystal and the bulk liquid may change, due to changes in density or viscosity, when the bulk composition is varied. In the current work, however, these effects are minimal. It should be noted that solvent associated with the adsorbed layer is included in the measured mass. Hence, the adsorbed amount registered by the QCM-D device is expected to be larger than that registered by other means, for example XPS,¹⁰ optical waveguide lightmode spectroscopy (OWLS),¹⁵ or ellipsometry.¹⁶ Even for adsorbed surfactant layers the amount of water included in the measured mass is in many cases significant,¹⁷ and for more complex adsorbed layers such as those formed by proteins¹⁸ or polyelectrolytes¹⁰ the sensed mass may be dominated by hydrodynamically coupled water. (By hydrodynamically coupled water, we mean water that oscillates with the crystal.) Finally, any viscoelastic response from the adsorbed layer may result in less than 100% of the mass being registered, which invalidates the Sauerbrey equation.¹³ With measurement of the dissipation factor (*D*), information on the layer viscoelastic response provides additional information on the layer structure, and it also provides

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a means for judging the applicability of the Sauerbrey equation. The Q-Sense instrument operates on the ring-down principle where the crystal is first oscillated at the resonance frequency and then the driving alternating current (ac) voltage is removed and the decay of the oscillations in the crystal is monitored. The dissipation factor is found from the rate of this decay and is defined as a modified ratio between the energy dissipated and the energy stored during a single crystal oscillation¹¹ as shown in eq 2,

$$D = \frac{E_{\text{Dissipated}}}{2\pi E_{\text{Stored}}} \quad (2)$$

Experimental Procedure. Prior to experiments, the gold surface of the crystal was cleaned with bichromic acid to remove contamination, and thereafter the crystal was stored under ethanol in a sealed container. The crystal was then dried under filtered nitrogen gas in a laminar flow cabinet before being mounted in the cell. The experiment was initiated by exposing the cleaned gold-coated quartz oscillator to an aqueous 0.1 mM KBr solution, thus establishing a baseline for the frequency and energy dissipation. In the case of these experiments, the frequency and dissipation results are reported as changes from the measured baselines rather than actual magnitudes, since it is these variations that contain the required information. Next, a polyelectrolyte solution, containing the same type and concentration of inorganic electrolyte, was introduced in the measurement chamber. In all cases, the polyelectrolyte concentration was kept constant (20 ppm), variation only being in the charge density of the particular polyelectrolyte used. The adsorption process was followed by monitoring the change in frequency and dissipation as a function of time. It should be emphasized that these measurements were carried out in a cell where the liquid is introduced normal to the surface, and hence the initial adsorption is flow assisted and not diffusion controlled. This is different to a previous publication¹⁰ where diffusion-controlled adsorption occurred.

For the competitive adsorption studies, the first polyelectrolyte was adsorbed in the manner described above. Then a second polyelectrolyte was added to the bulk (replacing the first), and the resulting changes were measured. In the case of the XPS measurements, the surfaces were placed in the second polymer solution (after passing through a polymer-free 10^{-4} M KBr salt solution) for 2 h before being dried under nitrogen gas.

XPS. In the current work, we have used the method of Rojas et al.¹⁹ to determine the adsorbed amounts of polyelectrolyte on both mica and gold, in the same way as in a previous paper.¹⁰ XPS measurements were made using a Kratos (AXIS-HS) spectrometer equipped with a monochromator, Al X-ray source, and slotM lens. Adsorption was carried out on freshly prepared and cleaned substrates immersed in 20 ppm AM-MAPTAC-X solutions containing 0.1 mM KBr for 12 h. The samples were then passed through Milli-Q water before being blow-dried under a filtered nitrogen gas source and then stored in sealed containers prior to being inserted into the XPS instrument. The strong affinity between the polyelectrolyte and the surface allows the removal of the substrate from the solution without appreciable loss of material as discussed in a previous report.²⁰

By comparison of results from the two different substrates (mica and gold), the effect of the surface on the adsorbed amounts can be determined. The adsorption study on mica was also used as a reference for calculating both the reduced thickness for the particular polyelectrolyte layer and the absolute adsorbed amount on gold. Comparison between the adsorbed amount on gold and mica was achieved via the intensity of the nitrogen 1s peak, while the total adsorbed amount on mica was found from comparison between the nitrogen 1s peak and the potassium 2p peak in the mica sample. Since the number of exchangeable potassium ions on the mica surface is known, it is straightforward to calculate the total polyelectrolyte adsorbed amount on mica and thus also on gold. For further details, readers are referred to the work of Rojas et al.¹⁹

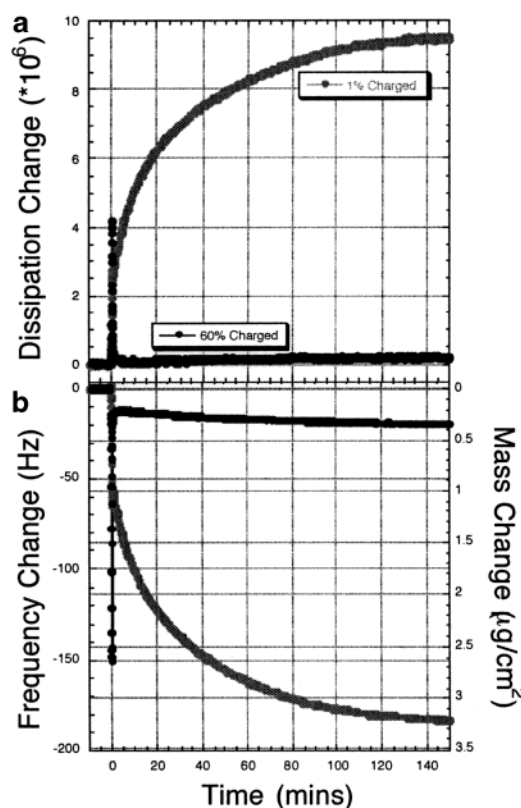


Figure 2. QCM-D results for comparison of the adsorption of AM-MAPTAC-1 and AM-MAPTAC-60. The top figure (a) shows the comparison of the dissipation, while the lower (b) compares the changes in frequency and mass (calculated assuming the Sauerbrey relation).

Table 2

% MAPTAC	gold (mono) (mg/m ²)	mica (mono) (mg/m ²)
1	2.5–2.7	2.3–2.5
5	2.2–2.4	1.8–1.9
10	1.6–1.7	1.5–1.7
30	1.3–1.4	1.1–1.2
60	1.1–1.2	0.8–0.9
100	0.8–0.9	0.7–0.8
1 then 100	2.2–2.8	2.3–2.6
100 then 1	1.0–1.2	1.4–1.5

Results

XPS. The adsorbed amounts obtained by XPS, on both mica and gold, are tabulated in Table 2. These results are used as an absolute measure of the mass of polyelectrolyte adsorbed on the surfaces, which can be compared to the mass sensed by QCM-D that includes contributions from both the polyelectrolyte and hydrodynamically coupled water. Also included in the table are the results for the competitive adsorption studies. The adsorbed amount, as expected, increases with decreasing polyelectrolyte charge density. The adsorbed amount is slightly larger on gold than on mica, which is remarkable considering the high negative charge density of the mica basal plane. Finally, we note already here that it is considerably easier to exchange the preadsorbed highly charged AM-MAPTAC-100 for AM-MAPTAC-1 on mica than on gold. On the other hand, the adsorbed amount does not change significantly when AM-MAPTAC-100 is added to a solution in contact with an AM-MAPTAC-1 coated mica or gold surface.

QCM-D. The polyelectrolyte was introduced into the measuring chamber after first determining the baseline in the 0.1 mM KBr solution. Figure 2 is included as an example of the raw results and to illustrate differences in

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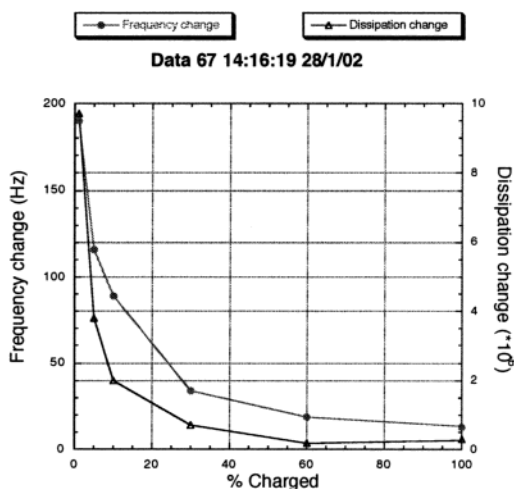


Figure 3. QCM frequency and dissipation changes as a function of the polyelectrolyte charge density.

the adsorption of two of the different charge density polyelectrolytes, the 60% and 1% charged AM-MAPTAC. Figure 2a shows the dissipation changes, while Figure 2b shows the frequency and apparent mass changes (calculated using the Sauerbrey relation, eq 1). Although the adsorption is not diffusion controlled (since there is initially flow-assisted adsorption),¹⁰ we can nonetheless see a large difference in the adsorption kinetics, the 60% charged polyelectrolyte being 80% adsorbed during the injection process and taking about 80 min to reach its final adsorbed amount while the 1% charged polyelectrolyte was less than 25% adsorbed during the injection and took over 4 h to reach adsorption equilibrium. In general, it was observed that adsorption equilibrium was reached more slowly the lower the charge density of the polyelectrolyte. This can be easily rationalized as follows: the increased adsorbed mass and the more extended layer configuration in the 1% charge case means that slow conformational changes are needed to accommodate the molecules that arrive at the surface at the later stages of the adsorption process.

A comparison of the equilibrium results for the different charged polyelectrolytes is provided in Figure 3, which shows the associated dissipation changes and the negative frequency changes (proportional to the mass change via the Sauerbrey relation) versus the charge density of the adsorbing polyelectrolyte. It can easily be seen that there is a large increase in the adsorbed mass and the dissipation with decreasing polyelectrolyte charge density, suggesting very different adsorbed layer characteristics. This is further illustrated by plotting the dissipation versus the frequency (or $D-F$ plot) for the different polyelectrolytes as in Figure 4. $D-F$ plots are useful since they display the data independently of time and show the dissipation per unit of added mass (assuming the Sauerbrey relation). The mass increases with decreasing frequency, and hence the mass increases from right to left. Thus the time arrow also travels from right to left. Thus from the $D-F$ plots we can determine equilibrium results (the points furthest to the left in each data set). In addition, we can infer the relative conformational buildup of the layers from the slopes of the $D-F$ plot. There is a loss of information during the initial adsorption stages due to the flow-assisted adsorption that occurs during the injection spike, and this shows up as a loss of data in the lower magnitudes of dissipation and frequency. It is interesting to note that the intercept with the frequency axis always occurs at a negative frequency, indicating that at least some portion

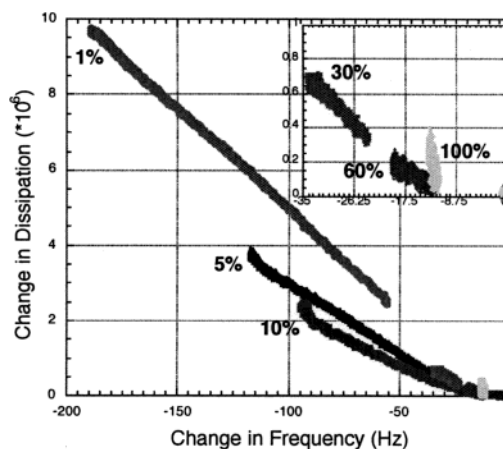


Figure 4. $D-F$ plot for the entire range of AM-MAPTAC charge densities. The inset is a blown-up region of the low frequency and dissipation area. The percentages on the figure relate to the percentage of charged monomers.

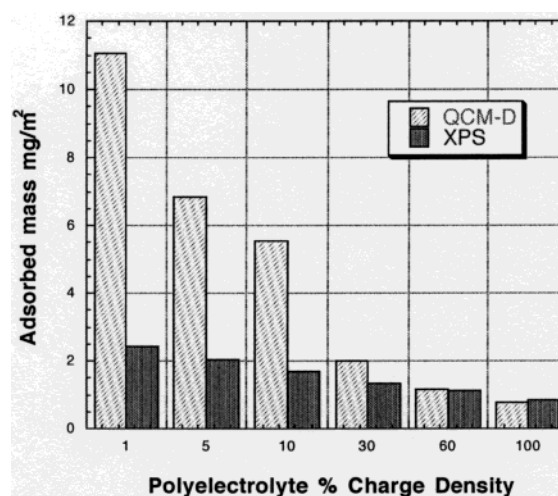


Figure 5. Comparison of the change in mass as detected from XPS and QCM-D.

of the adsorbed layer is flat and firmly attached. Hence, the molecules that arrive first to the surface adopt very flat conformations. It remains an open question whether the conformation of these molecules remains flat as the adsorption proceeds.

In addition to measuring the mass associated with the oscillating crystal in the QCM-D, we have independently quantified the polyelectrolyte adsorption employing XPS. A comparison between results found by the two techniques is shown in Figure 5. As we have discussed previously,¹⁰ this difference in the mass detected by the two techniques is due to the QCM-D measuring all mass which oscillates with the crystal rather than just the amount of adsorbed polyelectrolyte (which is what is measured with the XPS technique). It can be seen that the two techniques are in good agreement for the high charge density polyelectrolytes (lower adsorbed mass). Since the QCM-D technique measures the change in mass, this result indicates that the amount of water hydrodynamically coupled to bare gold and gold coated with a layer of AM-MAPTAC-100 or AM-MAPTAC-60 is very similar. This, in turn, indicates that the adsorbed layers are very flat. However, as the charge density decreases, there is progressively more solvent associated with the polyelectrolyte layer, up to the case of the 1% charged polyelectrolyte, where almost 80% of the detected mass is actually solvent.

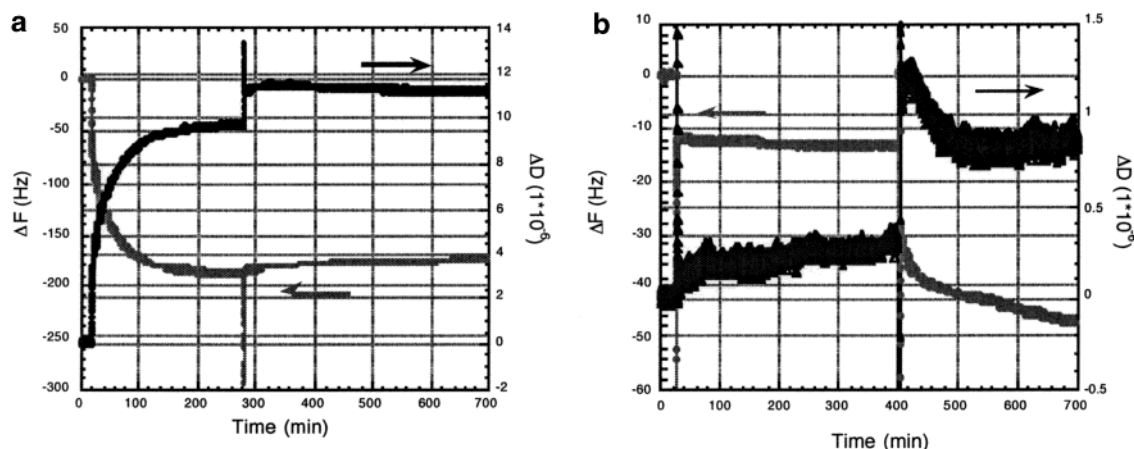


Figure 6. QCM-D results for changes in frequency and dissipation versus time. The plots are for the competitive adsorption of AM-MAPTAC-1 and AM-MAPTAC-100 onto gold. The plot to the left (a) is for adsorption of AM-MAPTAC-1 at 20 min and AM-MAPTAC-100 at 280 min. The plot to the right (b) is for AM-MAPTAC-100 adsorbed first (time = 12 min) followed by AM-MAPTAC-1 at 400 min.

We have also taken preadsorbed layers of the highest and lowest charge density polyelectrolytes and then replaced the bulk with the other of these two polymers and used the QCM-D to monitor the changes in the adsorbed mass and the dissipation (see Figure 6). As seen in the figure, the change for the case with the preadsorbed AM-MAPTAC-1 is relatively small, while in the preadsorbed AM-MAPTAC-100 case, there is apparently a more significant change. However, it must be considered that the scales are significantly different and that it only takes a small amount of the low-charge polymer to increase the sensed mass and dissipation. The reason is that AM-MAPTAC-1 adopts conformations that extend far from the surface and thus traps a large amount of solvent. This will be discussed more fully later when adding in the XPS results for these systems. The dynamics of the process should however be noted in the QCM results, which indicate change over a time scale of hours.

Discussion

Forces between Adsorbed Polyelectrolyte Layers.

Surface force studies using mica surfaces and some of the polyelectrolytes employed in this work have previously been conducted.^{21–24} A summary of relevant surface force data is provided in Figure 7. AM-MAPTAC-100 forms a very thin layer (0.5–1 nm) on mica, and no steric repulsion is observed on approach. For AM-MAPTAC-30, thin (2.2–2.3 nm) and incompressible layers are also formed. The layer formed by AM-CMA-10 (structurally similar to AM-MAPTAC-10) is significantly larger, and the layer can be compressed considerably by applying a high force. In these cases, an attractive force pulls the surfaces into contact. The presence of a weak repulsive electrostatic double-layer force for the AM-MAPTAC-30 case makes this feature less obvious in Figure 7 for this polyelectrolyte. Finally, for AM-MAPTAC-1 very thick and compressible layers are formed and in this case a long-range repulsive steric force dominates the interaction. For further details, the reader is referred to the original reports. What is

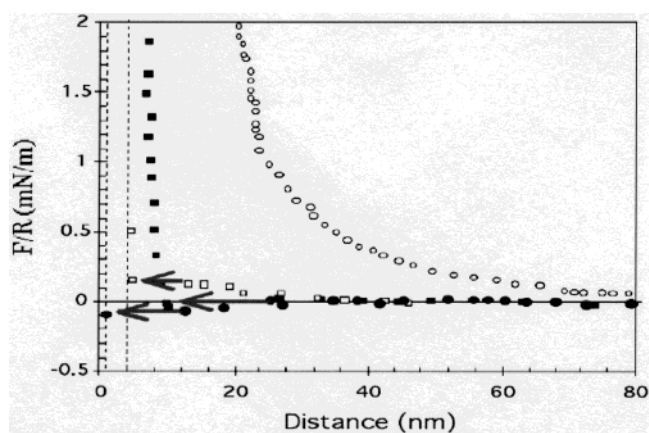


Figure 7. Force normalized by radius as a function of surface separation. The measurements were conducted using mica substrates in weak electrolyte solutions (0.1 mM or below). The data are for AM-MAPTAC-100 (filled circles), AM-MAPTAC-30 (unfilled squares), AM-CMA-10 (structurally similar to AM-MAPTAC-10) (filled squares), and AM-MAPTAC-1 (unfilled circles). Arrows indicate the onset of an attractive force that pulls the surfaces into contact. These results are from previous SFA experiments (refs 21–24).

important in the context of the present paper is that the thickness of the adsorbed layer and its compressibility increase with decreasing charge density of the polyelectrolyte.

Polyelectrolyte Adsorption on Mica and Gold. On mica, the adsorption is promoted by an electrostatic interaction between the negatively charged surface and the positively charged polyelectrolyte. There is also a negative charge on the gold substrate that aids the adsorption, but the adsorption onto this surface is primarily driven by image charge effects. Despite the differences in nature of the gold and mica surfaces, the adsorbed amounts on the two surfaces are rather similar and it is plausible that the layer structures formed on the two surfaces also are similar. The XPS spectra in Figure 8 allow not only the adsorbed amount to be determined, but also the ratio between charged and uncharged nitrogen to be estimated, Table 3. The polyelectrolytes used are polydisperse both in molecular weight and in charge density. Hence, we observe that the fraction of charged nitrogen groups in the adsorbed layer on mica is larger than expected for the low charge density polyelectrolytes (the quality of the spectra obtained for gold substrates

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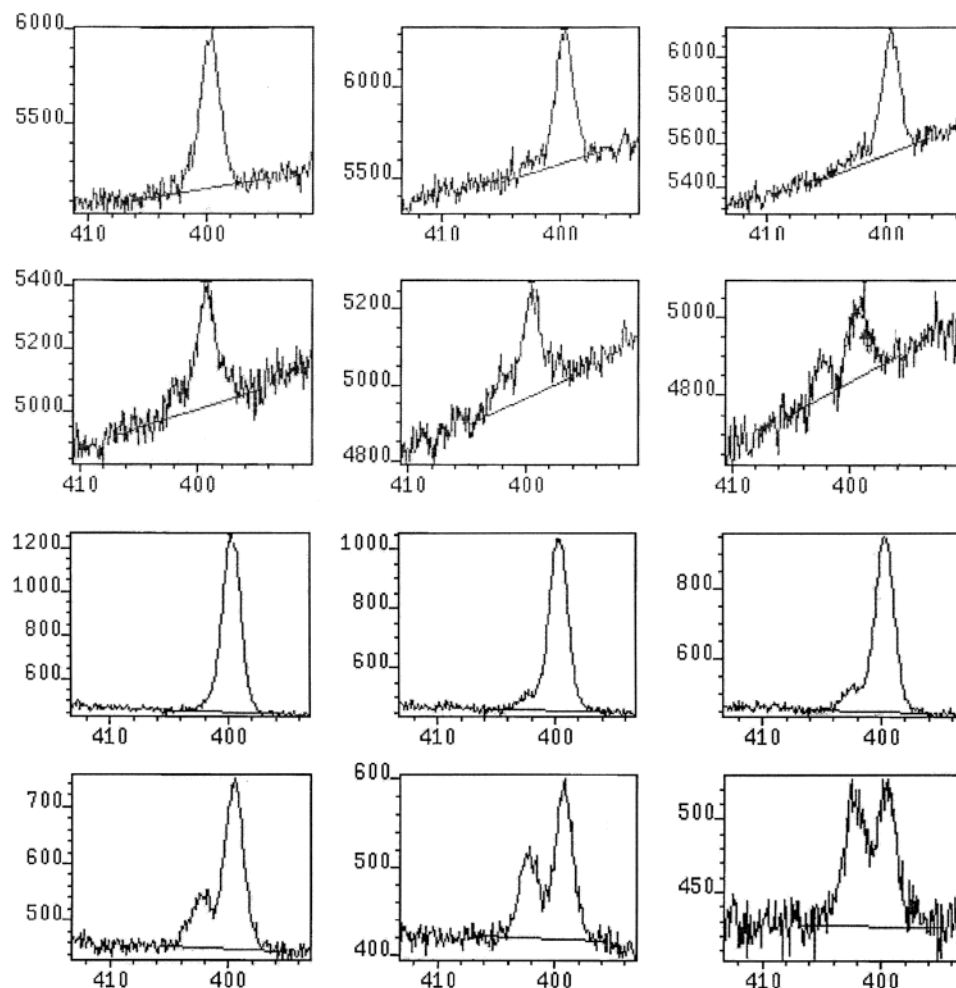


Figure 8. XPS curves for the adsorption of differently charged polyelectrolytes. The top six curves are on gold substrates, while the bottom six are on mica. The charge density of the polyelectrolytes is in both cases (from left to right) 1, 5, 10, 30, 60, and 100%.

Table 3. Percentage of the Nitrogen Peak Due to the Charged Nitrogen^a

sample (%)	theoretical	Au	mica
1	1	n.d.	n.d.
5	5	n.d.	8.4
10	9	n.d.	12.8
30	23	17.2	24.1
60	37.5	24.9	36.6
100	50	35.3	50.3
1 and 100		n.d.	6.4
100 and 1		25.2	13.8

^a The first column includes the charge density of the AM-MAPTAC polymer used. The last two cases include the results. The notation n.d. means "not determined".

did not allow accurate determination of the fraction of charged nitrogen). This indicates a surface fractionation with a preferential adsorption of the more highly charged polyelectrolytes. A similar result has previously been noted.¹⁹ At higher charge densities, the agreement between theoretical and measured fractions of charged groups is excellent on mica. However, as noted previously,¹⁰ the fraction of charged groups detected on the gold surfaces is lower than theoretically expected. This is due to the intimate contact between the charged nitrogen in direct contact with the gold surfaces and their image charges. (Note that for AM-MAPTAC-100 there is no charge polydispersity so a preferential adsorption of less charged polyelectrolytes cannot explain this result.)

Adsorbed Mass and Sensed Mass. An advantage of studying a series of adsorbing materials, which differ in

a well-characterized way, is that it allows us to understand more fully the frequency and dissipation shifts recorded in the QCM-D instrument. For determination of equilibrium adsorbed amounts, XPS is more appropriate than the QCM-D method. It has however a disadvantage that the sample must be analyzed in a vacuum, and as such XPS can never give information about the structure of the adsorbed layer in contact with solvent. Hence, there is an advantage of combining XPS and QCM-D results. First, we can see in Figure 5 that the total adsorbed amount, as obtained by either QCM-D or XPS, is higher as we decrease the charge density of the polyelectrolyte. Second, from Figure 5, we observe that the QCM-D overestimates the mass found by the XPS, except for the highest charge density polyelectrolytes, which is a direct result of the QCM-D technique sensing the incorporation of solvent within the polyelectrolyte layer. Thus, by using results obtained with the two techniques we are able to calculate the relative concentration of polyelectrolyte and solvent within the adsorbed layer. Clearly, as the polyelectrolyte charge density decreases, the total amount of adsorbed polyelectrolyte increases and so does the relative concentration of hydrodynamically coupled solvent within the adsorbed layer. This is a result of the more extended structure of the adsorbed layer; see the surface force data in Figure 7. Hence, in general the QCM-D technique overestimates the adsorbed amount if the frequency shift is misinterpreted as being due to the adsorbing species only. Further, it is expected to be a general phenomenon

that a more extended and compressible adsorbed layer will have a larger contribution from hydrodynamically coupled water than a thinner, more compact layer.

The Energy Dissipation Factor. The other information obtained from the QCM-D experiments is the rate of energy dissipation, which is expressed in the change in the dissipation term and contains information on the changes in coupling between the adsorbed layer and the bulk solution as well as dissipative processes occurring within the adsorbed layer. The relation between the changes in energy dissipation with frequency (sensed mass) for each polyelectrolyte is displayed in Figure 4. A significant portion of each curve is linear and may appear to suggest a linear relation between sensed mass and energy dissipation for each polyelectrolyte (but not the same proportionality constant for different polyelectrolytes). However, a closer inspection shows that this is a too simplistic interpretation. The initial decrease in frequency, due to the first adsorbing polyelectrolytes, gives rise to a lower than average dissipation increase. On the other hand, as equilibrium is approached the increase in dissipation increases rapidly even though the change in sensed mass is rather small. The interpretation of these findings is that the first adsorbing polyelectrolytes adopt very flat conformations whereas the last adsorbing polyelectrolytes give rise to formation of extended loops and tails. Further, we note that when the polyelectrolyte charge density decreases from 10% to 5% and further to 1% the slope of the D - F plots increases. This is a result of the more extended layers formed for lower charge density polyelectrolytes during the buildup process (which also is reflected in the equilibrium data, Figures 3 and 7). For the polyelectrolytes with higher charge density, a too large fraction of the data is lost during the injection period to allow a similar discussion of the buildup process.

In Figure 3, the change in dissipation as a function of the polyelectrolyte charge density at equilibrium is displayed. It is found that in general the change in dissipation increases as the charge density of the polyelectrolyte decreases. The change in dissipation is affected mainly by the amount of material adsorbed, the layer thickness, and the viscoelastic properties of the layer. The polyelectrolytes of highest charge density (AM-MAPTAC-100 and AM-MAPTAC-60) have a significantly lower molecular weight than the other polyelectrolytes. However, due to the flat layers formed by these polyelectrolytes in low ionic strength solutions, the effect of the molecular weight on the structure of the adsorbed layer is small.²⁶ For the other polyelectrolytes, the molecular weights are more similar, particularly for the three lowest charge densities, and thus the effects discussed above and below are primarily due to differences in polyelectrolyte charge density rather than a molecular weight effect. It is of interest to plot the change in dissipation as normalized by the corresponding change in frequency. This is done in Figure 9 and shows that the polyelectrolyte charge density also affects the dissipation normalized by the change in frequency (i.e., sensed mass), demonstrating that the average viscoelastic properties of the adsorbed layer change as a function of the charge density of the polyelectrolyte. Clearly, the coupling between the layer and the solvent increases as the charge density of the polyelectrolyte decreases. This is a consequence of the fact that the adsorbed layer becomes more extended and compressible as the charge density decreases; see for

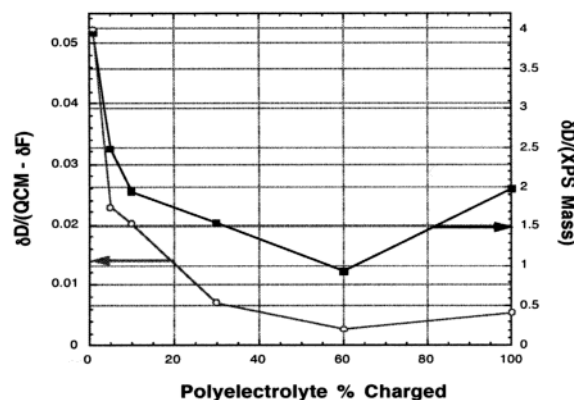


Figure 9. The change in dissipation normalized by the change in frequency (QCM response which is proportional to mass) or normalized by the change in mass detected by XPS.

example the surface force data in Figure 7. However, the energy dissipation change does not scale with true adsorbed mass, sensed mass (i.e., frequency change), or layer thickness but depends in a complex way on the structure of the adsorbed layer. It is, however, known that the energy dissipation rate increases with the extension of the layer and with decreasing rigidity of the layer, a result that is confirmed in the present investigation. The interpretation of the dissipation value in more quantitative terms remains a theoretical challenge even though some attempts in this direction have been made.^{27,28}

An exception to the general behavior discussed above is found when comparing AM-MAPTAC-100 and AM-MAPTAC-60. Although the adsorbed amount and the relative concentration of hydrodynamically trapped solvent in the layer are smaller for AM-MAPTAC-100 than for AM-MAPTAC-60, the change in normalized dissipation is higher. This is also seen in Figure 4 as the slope of the D - F plot is much greater for AM-MAPTAC-100. With the magnitudes of both frequency and dissipation being low in the AM-MAPTAC-100 case, the contributions due to experimental errors were considered. However, after numerous additional repeats for the high charge density polyelectrolytes, the errors for the QCM-D (± 1 Hz in frequency and $\pm 0.1 \times 10^{-6}$ for dissipation) were found to be reasonable, and hence the effects noted for the 100% charged polyelectrolyte were found to be significant. We suggest that the unexpectedly large dissipation per unit adsorbed mass for the AM-MAPTAC-100 can be explained by the existence of small numbers of highly extended loops or tails, which are highly efficient at energy dissipation but not at trapping solvent. This notion is consistent with the XPS results, Figure 8, demonstrating that not all charged nitrogen is in direct contact with the gold surface. In fact, evidence for the existence of some loops and tails for AM-MAPTAC-100 on mica has been found also from surface force measurements.²⁴ The existence of these relatively few loops and tails for the most highly charged polyelectrolyte can be explained by the high degree of electrostatic repulsion that makes it difficult for the last arriving molecules to attach with all charged segments to the surface. It is conceivable that the lowest free energy corresponds to essentially all the molecules being adsorbed in a flat conformation.²⁵ However, once the polyelectrolyte adsorbs rearrangements within the layer are slow²⁶ and

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it is difficult to reach the true equilibrium structure within experimentally accessible time scales.

Previously we have been able to use the dissipation change in a relative manner, for example, to infer the adsorbed conformation as a function of adsorbed amount, and to study surfactant-assisted swelling of preadsorbed polyelectrolyte layers.¹⁰ The systematic approach in this study, where we have changed the layer structure by varying the polyelectrolyte charge density and monitored the change in energy dissipation, provides some new insight, particularly when also considering data from surface force and XPS studies. The existence of a small number of extended loops (as for AM-MAPTAC-100) results in a significant increase in energy dissipation but does not affect the sensed mass significantly. Further, even though we do not find any straightforward relation between layer thickness (obtained from surface force measurements) and the change in dissipation (obtained with QCM-D) we find that the ratio between the onset of the steric force (in nanometers) and the energy dissipation is between 5×10^6 and 9×10^6 for the studied systems. These numbers may be used as a rough guide to estimate the layer thickness in water for other adsorbed polyelectrolytes from dissipation values determined with the QCM-D. For instance, from the dissipation value for AM-MAPTAC-5, we may estimate the onset of the steric force to be at a surface separation between 30 and 50 nm. Of course, much more accurate information can be obtained by conducting surface force experiments.

Events Occurring during the Injection Period. At this point, we discuss the spikes that accompany the exchange of fluid in the cell during an experiment and the accompanying rapid changes to both the frequency and dissipation. When an adsorption experiment starts, the bulk fluid is exchanged from pure solvent to the same solvent with additional adsorbing species. When this occurs, there is a large spike noted in both the frequency and dissipation data, which contains no information about the adsorption process. These spikes occur due to changes in the pressure and temperature of the bulk fluid. In particular, changes in the pressure affect the crystal since the flow of fluid is directed normal to its surface, which also leads to flow-assisted adsorption during the bulk fluid exchange. The cell is designed to maximize the exchange of fluid within the cell; however, that means that the adsorption that occurs during the solvent exchange process (which can be very significant) cannot be monitored, except as a final amount. For this reason, we cannot monitor the initial dynamics of the adsorption process, which is evident from the lack of data points at low frequency and dissipation changes in the D - F plots, Figure 4. We note, however, that an experiment with a cell that allowed horizontal injection of the solvent gave very similar results in terms of dissipation versus frequency plots at longer times. Hence, the vertical injection of the solvent did not affect the buildup of the adsorbed layer, except initially, to any significant degree.

The magnitude of the adsorption that occurs during the exchange process is affected by the rate of flow, which, although similar for all experiments, is not strictly controlled. The adsorbed amount is also affected by the affinity for the surface, which is why a greater percentage of data is lost for the more highly charged polyelectrolytes.

In cases where the dynamics of the adsorption is important, the flow rate may influence the results. This was in part noticed in some experiments for AM-MAPTAC-100. When the flow rate was larger than normal, the frequency change was not affected but an initially larger change in dissipation (0.6×10^{-6}) was observed. However,

the dissipation value decreased over time (30 min) to the same equilibrium value (0.3×10^{-6}) as obtained for the lower flow rate. It is believed that the initially higher dissipation after executing the injection at higher flow rates is due to an increase in the initial number of loops and tails formed upon adsorption. However, over the course of the experiment the layer relaxes to the same (quasi) equilibrium structure.

Polyelectrolyte Exchange. The study of polyelectrolyte exchange reported in Figure 6 and by the XPS data shows that the exchange process is very slow. This is due to the high affinity of the polymers to the surfaces and to the fact that the polyelectrolyte in solution first has to penetrate the preadsorbed layer before it can replace the polyelectrolytes adsorbed at the surface. The latter process is particularly slow when the layer is thick and explains why it is more difficult to replace AM-MAPTAC-1 by AM-MAPTAC-100 than it is to replace the preadsorbed highly charged polyelectrolyte with the low charge density one (even though the higher charged polyelectrolyte has the higher affinity for the surface). By monitoring the fraction of charged nitrogen on the surface after the exchange process and comparing the value with that for each type of polyelectrolyte on the same type of surface, we are able to determine the composition of the adsorbed layer. For preadsorbed AM-MAPTAC-100 exposed to a solution of AM-MAPTAC-1, the fraction of charged nitrogen decreases due to polyelectrolyte exchange, and after 2 h 80% of the polyelectrolyte on mica is due to AM-MAPTAC-1. The corresponding value on gold is about 30%. Thus, the exchange process occurs less readily on gold than on mica due to image charge interactions at the former surface. This result is consistent with the observation that it is more difficult to remove polyelectrolytes by addition of surfactant from gold than from mica.¹⁰ We also find that the fraction of charged nitrogen does not increase significantly when AM-MAPTAC-100 is added to a surface precoated with AM-MAPTAC-1. Thus, the thick preadsorbed AM-MAPTAC-1 layer induces an electrostatic hindrance to the diffusion of the higher charged polymer to the substrate and the exchange is very limited.

The QCM-D data, Figure 6, can provide some additional information. When AM-MAPTAC-100 is introduced above a gold surface precoated with AM-MAPTAC-1, Figure 6a, we find that the dissipation first increases and then slowly decreases whereas the sensed mass decreases slowly. This indicates that the first step is a limited adsorption of AM-MAPTAC-100 that results in formation of a number of tails and loops, which is efficient at dissipating energy but not in trapping solvent. Thus the sensed mass is hardly affected. As the process proceeds and the AM-MAPTAC-100 penetrates the layer, the layer becomes more compact and mass is also lost due to initiation of desorption of AM-MAPTAC-1.

When precoated layers of AM-MAPTAC-100 are exposed to an AM-MAPTAC-1 solution, we find a decrease in frequency, that is, an increase in sensed mass, which is easily understood as resulting from the adsorption of the low charge density polyelectrolyte. The interpretation of the changes in the dissipation factor is less obvious. There is an initial increase in dissipation followed by a time interval where the dissipation decreases even though it remains well above that prior to addition of AM-MAPTAC-1. At even longer times, the dissipation increases again. The initial increase in dissipation due to adsorption of AM-MAPTAC-1 indicates that some large loops and tails are formed at this stage. The decrease in dissipation at intermediate times can be interpreted as desorption of the AM-MAPTAC-100 forming the longest tails and

adaptation into flatter conformations of the adsorbing AM-MAPTAC-1 as it adopts to the surface that becomes available due to desorption of AM-MAPTAC-100. Finally, the slow increase in dissipation observed at longer time scales is simply a result of the incorporation of more AM-MAPTAC-1 in the adsorbed layer. Even at the conclusion of the monitoring of the exchange process, the exchange is far from complete and the dissipation value is significantly lower than for pure AM-MAPTAC-1. Clearly, the combination of data from XPS and QCM-D provides some insight into the polyelectrolyte exchange mechanism, which is worth exploring in more detail.

Conclusion

It has been shown how the QCM-D can be used to investigate the adsorption process for a series of polyelectrolytes and that the sensitivity of the instrument is adequate not only to determine the adsorbed amount (which includes contributions from solvent) but also to differentiate between the different viscoelastic properties of the adsorbed layers formed by the different polyelectrolytes. In addition, by combining information obtained with other techniques (in this case XPS) it is possible to calculate the relative solvent concentration within the adsorbed layers and thus approximate the layer thicknesses.

The adsorbed amount of polyelectrolyte increases from 0.8 mg/m² for the 100% charged polyelectrolyte on gold up to 2.5 mg/m² for the 1% charged case. At the same time, the relative solvent concentration increased from virtually 0% to nearly 80% in the respective cases. By monitoring the changes in the dissipation factor, we could follow structural changes with time in the adsorbed layer and characterize the effect of the polyelectrolyte charge density

on the coupling between the adsorbed layer and the solvent. For the most highly charged polyelectrolyte, we concluded that a small number of highly extended loops and tails were formed. This conclusion was supported by XPS, showing that not all charged segments were in contact with the gold substrate, and by previous surface force data. Further, by systematically varying the charge density of the polyelectrolyte we have changed the structure of the adsorbed layer and demonstrated how the energy dissipation factor increases with decreasing polyelectrolyte charge density and thus increasing extension of the adsorbed layer. When considering different polyelectrolytes, there is no simple relation between the energy dissipation factor and the adsorbed mass, sensed mass, or layer thickness. However, the energy dissipation allows rough estimates to be made about the extension of adsorbed polyelectrolyte layers. On the other hand, for a given polyelectrolyte there is, over a large range of the adsorption versus time curve, a simple proportionality between the change in sensed mass and the change in the energy dissipation value.

A preliminary study on the ability of one polyelectrolyte to replace another preadsorbed layer has been carried out. For the case of thick, extended preadsorbed polyelectrolyte layers, replacement is unlikely to occur due to the electrosterically imposed hindrance for the bulk polymer to diffuse to the surface. For a thin preadsorbed polyelectrolyte layer, exchange occurs more readily even when the replacing polyelectrolyte has a lower charge density than the preadsorbed one. The XPS results were used in order to determine the composition of the resulting mixed adsorbed layer.

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