J Mater Sci (2010) 45:4970–4976
DOI 10.1007/s10853-010-4341-7

ICAM 2009

Selective removal of hybrid di-block polyelectrolyte multilayers by means of quaternary ammonium surfactants

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Received: 13 November 2009 / Accepted: 22 February 2010 / Published online: 30 March 2010

Abstract The stability of polyelectrolyte multilayers (PEMs), fabricated by the layer-by-layer (LBL) assembly, upon treatment with the tetradecyl trimethyl ammonium bromide (TTAB) surfactant, was studied for multilayers composed of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) or poly(diallyldimethylammonium chloride) (PDADMAC) and PSS, and for hybrid PEMs formed by two blocks: a PEM of PAH/PSS with a PDADMAC/PSS PEM on top. The assembly of the PEMs was followed by means of the quartz crystal microbalance with dissipation technique (QCM-D). Also, QCM-D either alone or in combination with spectroscopic ellipsometry was used to study the interaction of the PEMs with TTAB at concentrations below and over the critical micellar concentration (CMC). While sole PDADMAC/PSS multilayers were completely removed with TTAB at concentrations over the CMC, PAH/PSS multilayers remained stable and adsorbed the surfactant. Nevertheless, for the combination of PAH/PSS with PDADMAC/PSS, the layers of PDADMAC/PSS on top were only partially removed. Increasing the number of PAH/PSS layers decreased the amount of PDADMAC/PSS that was removed.

Introduction

Polyelectrolyte multilayers (PEMs) fabricated by the layer-by-layer technique (LBL) are a good example of nanoscale-controlled self-assembly applied to the fabrication of supramolecular structures [1, 2]. Thickness and composition of PEMs can be controlled with nanometric precision in the vertical direction [3–6]. PEMs have potential applications as anticorrosive and antibacterial coatings, filtration membranes, or for surface modification without covalent binding [7–10]. The fabrication of PEMs by means of the LBL technique has also been extended to the colloidal domain. Colloidal structures can be coated, encapsulated, and protected from the environment using PEMs [11, 12]. PEMs are very stable either in time or during preparation steps, and generally once formed they resist high and low pH, environments of high ionic strength, and the action of surfactants [13, 14]. PEMs can be endowed with multiple components such as nanoparticles, DNA, proteins, lipids, etc. either by depositing them on top of the PEMs or inserting them during the assembly at the place of selected polyelectrolyte layers. The insertion of these molecules can be performed in the multilayer at different depths [15–18]. This flexibility in choosing the components of the multilayer makes the LBL technique a particularly versatile tool for noncovalent surface functionalization.

The interaction of surfactants with PEMs has been comparatively less studied than the interaction of PEMs with proteins, lipids, or even nanoparticles [19–23]. Recently, we have shown that depending on the choice of polyelectrolyte pairs, it is possible to employ the interaction of surfactants with the polyelectrolytes for a selective stripping off of the layers [24]. For instance, PEMs composed of poly(diallyldimethylammonium chloride) (PDADMAC) and poly (sodium 4-styrenesulfonate) (PSS) can be stripped off in the presence of *N*-tetradecyl trimethyl ammonium bromide (TTAB) surfactant. On the other hand, PEMs composed of poly(allylamine hydrochloride) (PAH) and PSS remain stable in the presence of this surfactant, which adsorbs to the PEMs. Since TTAB is positively charged it will be electrostatically attracted to PSS and not to the polycation.

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Nevertheless, the interaction of PSS with either PDADMAC or PAH will affect the interaction with TTAB. It is interesting to know how the PEMs will respond in the presence of TTAB when the PSS is facing PAH on one side and PDADMAC on the other side. This would be the case of a block of PAH/PSS with a block of PDADMAC/PSS on top, for example. The PAH/PSS layers below may affect the removal of PDADMAC/PSS block.

A PEM composed of two blocks, where the block on top could be removed, would also be an interesting system to fabricate due to the multiple possible applications. There are situations where only the top layers of the PEMs need to be removed: for instance, when protection and controlled de-protection of a surface is intended; when the walls of a polyelectrolyte capsule have to be decomposed to release its content; or when the surface coating is damaged and does no longer fulfill its function. In all these cases, controlled decomposition of the PEM under conditions not affecting the support or the core would be a desirable option, which could also be the case for filtration membranes based on PEMs [25–29].The combination of PAH/PSS and PDADMAC/PSS blocks could be extremely useful in those cases when the membrane is no longer functional due to foulants actions and has to be removed. The top layer could be removed without dismantling the whole membrane and hence the removed layers could be easily replaced by new and foulant-free layers of PDADMAC/PSS.

Materials and methods

Materials

Poly(sodium 4-styrene sulfonate) [$M_w \sim 70{,}000$], poly(allylamine hydrochloride) [$M_w \sim 15{,}000$], and poly(diallyldimethyl ammonium chloride) 20% in water [$M_w = 2 \times 10^5$–3.5×10^5] were purchased from Aldrich. *N*-Tetradecyl (myristyl) trimethyl ammonium bromide (TdTmAB), ≥98%, quaternary salt, was purchased from Fluka. All reagents were used without further purifications.

Methods

QCM-D

An E4 quartz crystal microbalance with dissipation (QCM-D) from Q-Sense, Göteborg, Sweden was employed for the characterization of planar multilayers [30–32]. SiO_2 (70 nm)-coated quartz crystals (5 MHz) from Q-Sense, previously treated by a UV–Ozone cleaning protocol, were used as substrates to be coated in situ in the chamber with PAH/PSS and PDADMAC/PSS films. The LBL technique was performed by passing with a peristaltic pump a 1 mg/mL polyelectrolyte solution in 0.5 M NaCl through the water-filled QCM-D chamber. The fundamental frequencies of the system are found in water to establish a reference zero value. Polyelectrolyte deposition can be followed by the decrease of the resonance frequency of the quartz crystal. When the frequency levels became stable, the polyelectrolyte solution was replaced by 0.5 M NaCl until a plateau in the frequency was reached. This procedure was repeated for the deposition of the desired number of layers. The resulting PEM was finally rinsed with water.

Polyelectrolyte multilayers (PEMs) were then exposed in the QCM-D chamber to increasing concentrations of aqueous TTAB solutions to study the interaction of the surfactant with the multilayer. After passing the surfactant solution the chamber was always rinsed with water.

The frequency changes monitored by QCM-D can then be transformed into wet mass values by application of the Sauerbrey equation (Eq. 1):

$$\Delta m_{\text{QCM-D}} = -C \cdot \Delta F \ \text{(Sauerbrey)}, \tag{1}$$

where ΔF is the frequency variation (Hz), $C = 18.06$ Hz cm^2 ng^{-1}, and $\Delta m_{\text{QCM-D}}$ is the film mass per surface unit (g cm^{-2}).

The application of the Sauerbrey model is limited by the rigidity of the sample and the amount of water incorporated. The measurement of the dissipation (ΔD) parameter with the QCM-D is a good way to characterize the nature of the film. Thus, systems showing a high viscoelasticity, which means high dissipation values, incorporate a huge amount of water and calculations would be far away from real mass. On the contrary, films showing a low ΔD, PEMs for instance, behave as a rigid block and are suitable for treatment by Sauerbrey equation.

QCM-D/ellipsometry

A spectroscopic M-2000V$^{\text{TM}}$ ellipsometer from J.A. Woollam Co., Inc (Nebraska, USA) was used to follow in realtime mass and thickness variations of the multilayer system [33, 34]. Measurements were done using a specially adapted QCM-D chamber connected to an E1 module from QSense. This combination allowed monitoring changes in the polarization state of light upon reflection at the QCM-D sensor surface simultaneously to changes in the vibrational behavior of the QCM-D sensor.

Data of the ellipsometric response at the wavelength range of 370–1000 nm were fitted by a block model, assuming the multilayer as a single block which followed a Cauchy equation [35, 36]. For these measurements, PEMs were assembled on top of 100/100-nm-thick titanium/silicon oxide wafers from Q-Sense and the assembly procedure was similar to that followed when performing single QCM-D measurements.

Critical micellar concentration (CMC)

The CMC value of TTAB surfactant, 4.2 mol/m^3, was determined by conductimetry, employing a CON 1500 Conductivity Meter (Eutech Instruments, Thermo Fisher Scientific) by measuring solutions of increasing quaternary salt concentrations. A pH of 6.3 was measured for the TTAB solution.

Results

The QCM-D technique can be used to follow the frequency changes after each polyelectrolyte layer is deposited during the LBL assembly process. The low dissipation values observed during the assembly allow for the application of the Sauerbrey equation (see "Methods") to obtain the mass variation occurring after each single layer is deposited. In Figs. 1a and 2a, the variations in frequency during PAH/PSS and PDADMAC/PSS assembly are shown. In both figures, the addition of a polyelectrolyte layer has been indicated with a number corresponding to its position in the multilayer. For both, the last layer was a polycation, either PAH or PDADMAC. The frequency variations upon multilayer assembly are shown as a reference to compare with the variations in frequency after surfactant treatment, represented in terms of the mass of the assembled PEM.

The PDADMAC/PSS and PAH/PSS PEMs were exposed to TTAB at increasing concentrations in the QCM-D chamber. The variations in frequency during the treatment are shown in Figs. 1b and 2b for the respective polyelectrolyte composition. Treatment of the PAH/PSS multilayer with increasing concentrations of TTAB resulted in a progressive decrease of the frequency signal. For the lowest TTAB concentration, 1 mM, the frequency remained almost invariable, while for the highest concentration, 20 mM, there was a decrease of about 50 Hz. This decrease was interpreted as a mass uptake resulting from the interaction of the surfactant molecules with the PEM. On the other hand, the PDADMAC/PSS multilayer with the same number of layers as the one composed of PAH/PSS showed a dramatic increase in the oscillation frequency once the multilayer is exposed to TTAB, even for very low surfactant concentrations applied. Indeed, at 1 mM TTAB, the frequency reached +200 Hz, while at 20 mM, TTAB frequency reached values close to +300 Hz after rinsing with water. This increase in the frequency is consistent with the almost complete removal of the multilayer.

The interaction of TTAB with the multilayer can be also studied by means of the recently developed QCM-D/ellipsometry combined technique. Single QCM-D measurements are known for considering the frequency changes occurring at the piezoelectric sensor due to the total mass adsorbed. However, the combined method also ensures in situ monitoring of variations in the optical parameters Psi and Delta of the sample, resulting from the change in polarization after reflection from the surface. These parameters can be translated into thickness and subsequently, by the De Feijter equation, into optical mass values [37]. The main difference between the mass values obtained by both techniques is based on the consideration of the adsorbed water. In the case of QCM-D, the water content results are critical, while it would be negligible for the optical measurements. Thus, the application of both techniques in parallel helps to set a comparative analysis between mass values calculated from either considering adsorbed water or not. Figure 3 shows the changes in thickness and dry mass for the PDADMAC/PSS multilayer when TTAB solutions are flushed through the chamber. It is clearly observed that even for the treatment with 1 mM surfactant thickness and dry mass of the film drop. This was observed in the QCM-D as a sudden frequency shift to high positive values.

Raman spectra of complexes with the same composition as the PEMs [38] revealed a stronger affinity between the PSS polyanion and the positively charged molecules of TTAB than with PDADMAC. This affinity leads to the replacement of PDADMAC by TTAB from the sulfonate binding groups of the negative polyelectrolyte as the

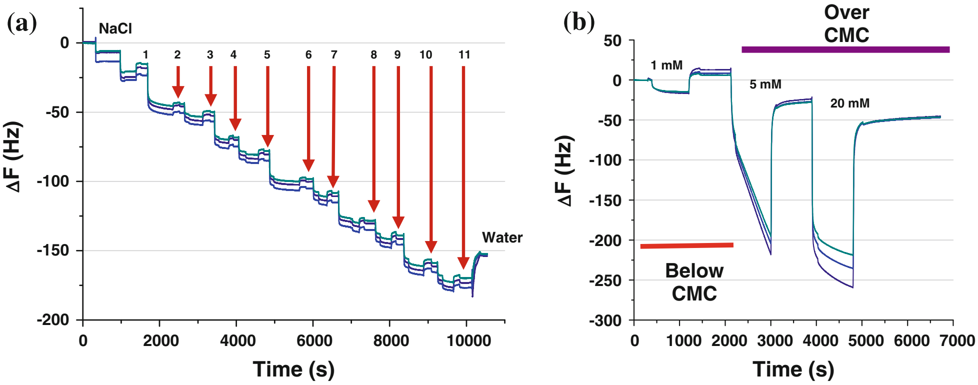
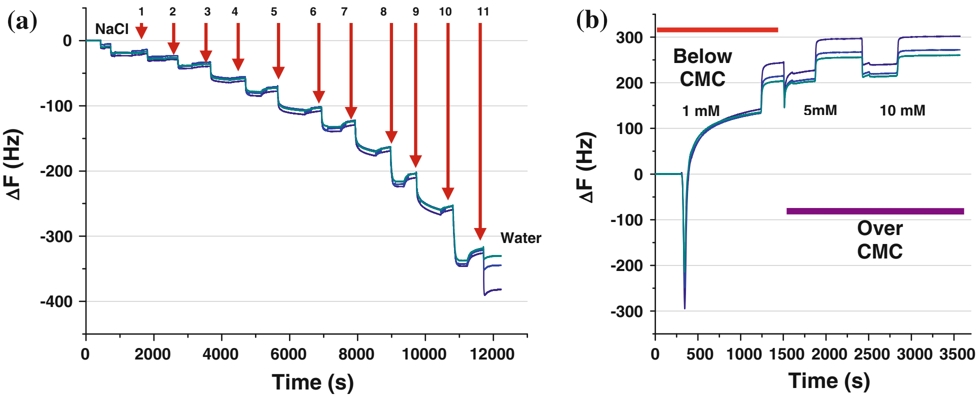


Fig. 1 Frequency curves measured with QCM-D showing the variation of the 3rd, 5th, and 7th overtones for a PAH/PSS PEM with 11 polyelectrolyte layers: **a** changes in frequency during assembly of PAH/PSS and **b** during treatment of the PEMs with TTAB at different concentrations

Fig. 2 Frequency curves measured with QCM-D showing the variation of the 3rd, 5th, and 7th overtones for a PDADMAC/PSS system with 11 polyelectrolyte layers: **a** changes in frequency during assembly of PDADMAC/PSS and **b** during treatment of the PEMs with TTAB at different concentrations



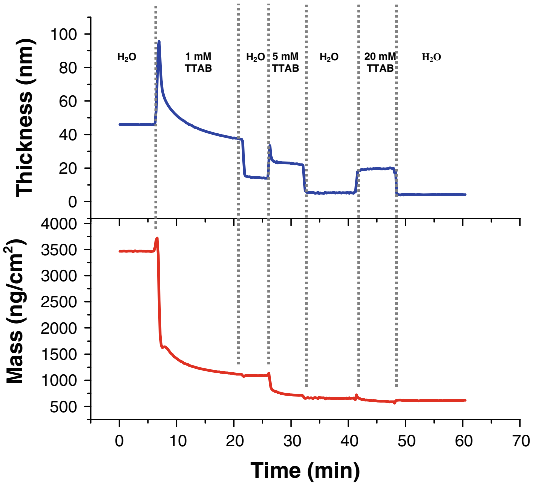


Fig. 3 In situ spectroscopic ellipsometry: variations in film thickness for 11 layers of PDADMAC/PSS treated with TTAB at increasing concentrations as a function of the time (*top*) and the corresponding variations in the dry mass also as function of the time for increasing concentration of TTAB (*bottom*)

surfactant concentration increases and, consequently, to the dismantlement of the multilayer. On the other hand, PAH/PSS complexes remained stable, although TTAB concentration was increased to values far over the CMC. The binding between the sulfonate groups in PSS and the primary amines of PAH is stronger than the binding with the quaternary amines of the surfactant. This is likely to be due to the presence of hydrogen bonding between the primary amines and the sulfonate groups, which provide extra stability to the complexes, the PAH/PSS multilayers. The presence of hydrogen bonding between the amine groups in PAH and the sulphonate groups of PSS has been hinted by Raman Spectroscopy and FT-IR [38]. Nevertheless, further experiments are required to probe the influence of hydrogen bonding in the PAH/PSS multilayer build-up.

We also assembled an initial block of (PAH/PSS) multilayers and a block of (PDADMAC/PSS) multilayers on top of PAH/PSS with the purpose of fabricating a PEM, which can be only partially removed (Fig. 4). PAH/PSS were assembled first to ensure resistance upon surfactant and thus a strong anchoring to the silicon surface. Hence the PDADMAC/PSS layer could be then removed with TTAB molecules as shown earlier. QCM-D was employed to follow in situ the assembly of two different PEMs composed of blocks of multilayer with different number of layers: one PEM based on a single PAH/PSS bilayer followed by deposition of PDADMAC/PSS layers and a second system where the build-up starts by assembling two PAH/PSS bilayers and then several PDADMAC/PSS layers.

For the hybrid PEM containing a single bilayer of PAH/PSS (Fig. 5a), the total frequency variation measured after the assembly was −440 Hz, which corresponds to a total mass, including the mass of trapped water, of 7.9 μg/cm^2 as obtained by Sauerbrey equation. Figure 5b shows the response of this multilayer when flushing through the chamber TTAB solutions of concentrations going from below to over the CMC. While the treatment with 1 mM TTAB did not show any specific response, exposure to 5 mM TTAB induced a sudden frequency increase of about 290 Hz due to a mass loss on the surface. Increasing TTAB concentration led to a final shift of +310 Hz, which corresponds to a mass desorption of 5.7 ± 0.1 μg/cm^2. This meant that all the layers from the 7th to the 11th are completely erased or, in other words, that two-thirds of the mass deposited during the assembly were removed from the PEM.

The mass of the remaining layers corresponds to the initial PAH/PSS bilayer and a PDADMAC/PSS polyelectrolyte bilayer. If we compare this result to that from sole PDADMAC/PSS layers, we can see how the presence of PAH/PSS bilayer below the removable layers makes them more stable than in the previous case. If, instead of nine layers of PDADMAC/PSS, the assembly proceeded until two, four, or six layers, the amount of polyelectrolyte removed was none, or just a bilayer or two bilayers, respectively. The PDADMAC/PSS layer directly on top of PAH/PSS seems not to be removable in any case.

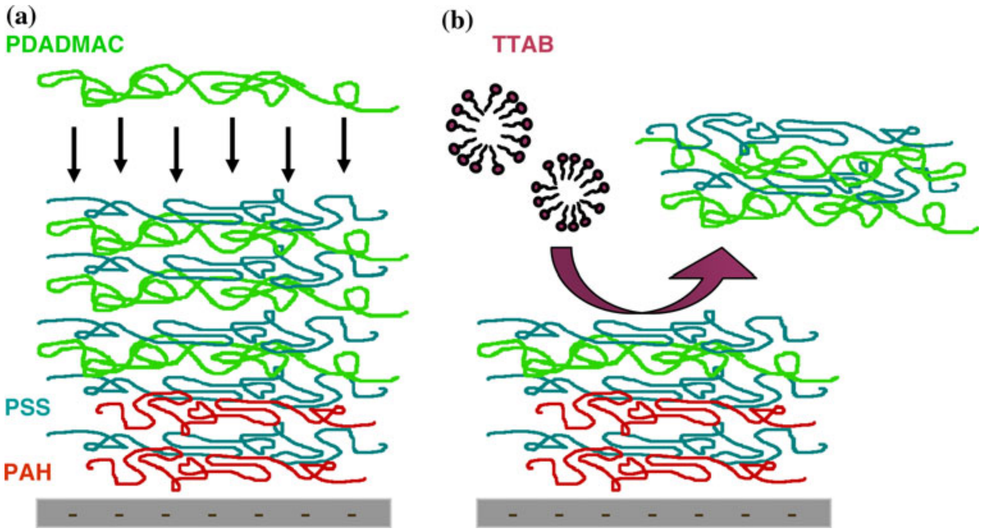


Fig. 4 Diagram of the two blocks PEM. **a** Formation of a two-block PEM by means of the LBL technique. **b** Surfactant removal of the upper block of the PEM

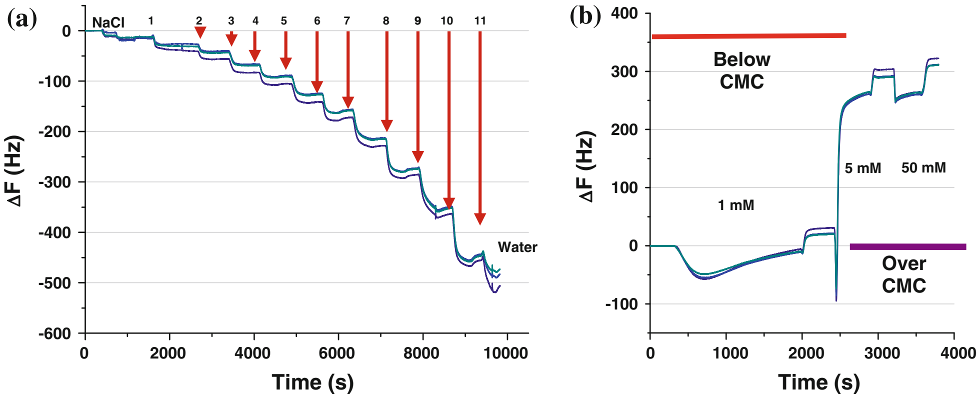


Fig. 5 Frequency changes as measured by QCM-D of the 3rd, 5th, and 7th frequency overtones for (PAH/PSS)/(PDADMAC/PSS)$_4$/PDADMAC multilayer system: **a** frequency changes during the assembly of the PEM. **b** Frequency changes during TTAB treatment

Then, to study how the thickness of the PAH/PSS multilayer affected the stability of the PDADMAC/PSS on top, a thicker initial block based on a double bilayer of PAH/PSS was assembled. A PDADMAC/PSS block was deposited again on top up to 11 layers. Figure 6 shows the response upon surfactant treatment measured by QCM-D. As shown in Fig. 6a, the build-up of this PEM resulted in a total frequency variation of 260 Hz or, after conversion by Sauerbrey, a deposited wet mass of 4.7 μg/cm^2. Since in this case a bilayer of PDADMAC/PSS has been replaced by another PAH/PSS, the PDADMAC/PSS multilayer was thinner and with almost a 40% less of wet mass than the value measured for the first PEM studied. This mass difference corresponds to the last PDMAC/PSS layers, which show a high water content. However, the main result came from the treatment with the surfactant solutions (Fig. 6b).

The treatment of this PEM with TTAB resulted in a smaller mass loss than the one observed for the system with a single bilayer of PAH/PSS. In this case, the change in frequency reached +20 Hz when the concentration employed is 1 mM TTAB, and for the maximum value over the CMC, 50 mM, the frequency measured reached +50 Hz. This shift corresponds to the loss of only the last two layers of the PEM. Conversion of this frequency by Sauerbrey to wet mass shows that 0.9 ± 0.1 μg/cm^2 were removed. It means that only 19.2% of the total mass was peeled off from the surface, while in the previously assembled PEM, there was a loss of around 65% of the mass. These thickness variations for both di-block PEMs after treatment with TTAB was studied by ellipsometry, as shown in Fig. 7.

Figure 7a clearly shows that working below the CMC causes only a loss in thickness of 5 nm for the system built on top of a (PAH/PSS) bilayer. Once the CMC is exceeded, this shrinkage becomes dramatic for the film and minimum thickness values below 10 nm are reached. For the second system studied, which is based on a double bilayer of PAH/PSS (Fig. 7b), a smaller decrease can be observed. Thickness changed from an initial thickness of 29 nm to a final value of around 22 nm after exposure to high concentration surfactant solutions.

Therefore, the assembly of PAH/PSS below the PDADMAC/PSS multilayer and the thickness of the PAH/PSS have a direct influence on the number of layers of

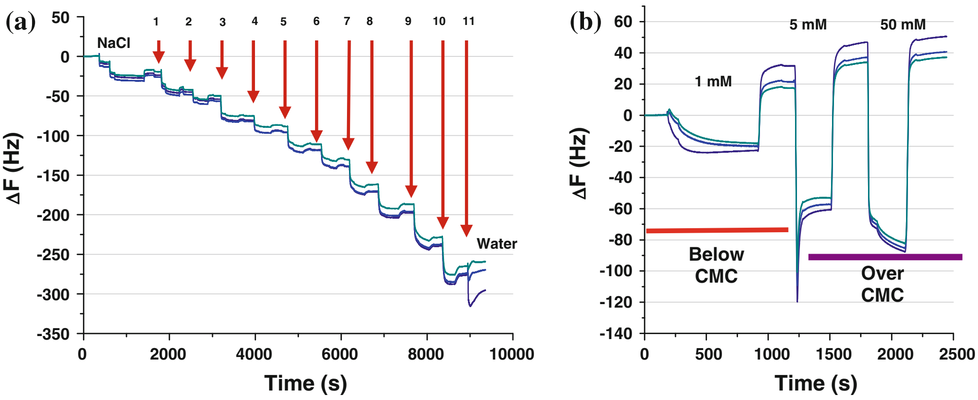


Fig. 6 Frequency changes as measured by QCM-D of the 3rd, 5th, and 7th frequency overtones for $(PAH/PSS)_2/(PDADMAC/PSS)_3/$PDADMAC multilayer system: **a** frequency changes during the assembly of the PEM. **b** Frequency changes during TTAB treatment

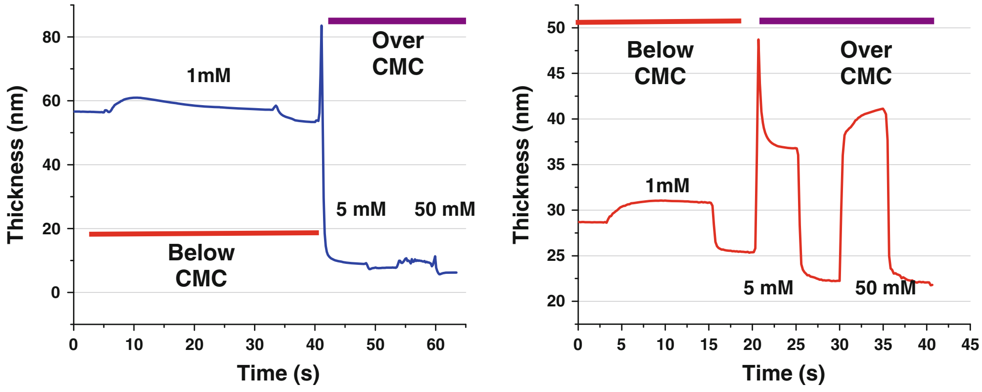


Fig. 7 Ellipsometric film thickness variations in realtime of PEMs containing a PAH/PSS bilayer (*left*) or a PAH/PSS double bilayer (*right*), when exposed to increasing concentrations of TTAB

PDADMAC/PSS that can be stripped off. Since the interaction with TTAB with PAH does not induce layer degradation, it is very likely that there is an intermixing of the layers of PAH and PDADMAC. This mixing of the layers must occur for the first layers assembled on top of the PAH/PSS. It is more pronounced when the PAH/PSS film is thicker since only the PDADMAC/PSS bilayer on the very top of the film is erased in those conditions. It is known that there could be a certain degree of mixing of the layers during polyelectrolyte assembly and that the PEMs are not as stratified as it could be expected [39, 40]. Our results with QCM-D hint that this is the case and also to what extent mixing could be happening. For the 4-layer PAH/PSS system, the mixing of the layer can be such that the next 4–5 layers of PDADMAC/PSS are stable against the action of TTAB. The intermixing of the layers must reinforce the stability of the PDADMAC/PSS film inducing a sort of crosslinking of the layers.

The combination of PAH/PSS and PDADMAC/PSS films of different thickness in one PEM can be used for the design of surfaces that could be only partially removed. The number of layers to be removed can be simply controlled by the thickness of the initial PAH/PSS multilayer. Such a coating could be useful, as mentioned in the “Introduction”, for filtration membranes based on PEMs, where foulants could be retained on the surface of the PEM. The last layers of the PEM with foulants could be then erased with TTAB and new layers could be assembled without causing significant changes in the membrane.

Conclusions

PEMs of PAH/PSS and PDADMAC/PSS sequentially assembled have been exposed to solutions of the quaternary ammonium surfactant TTAB below and over the CMC. QCM-D and spectroscopic ellipsometry have been employed to follow the sequential multilayer build-up and the exposure to TTAB. Results show that a single bilayer of PAH/PSS as basement reduces the removal of the PDADMAC/PSS layers assembled on top of PAH/PSS directly to that bilayer. When the initial PAH/PSS multilayer incorporates a second bilayer, the extent of the stabilization seen for the previous system reaches almost the entire multilayer and only those PDADMAC/PSS layers in the outermost positions can be erased.

Acknowledgements S.E. Moya is a Ramón and Cajal fellow and thanks this program and the grant MAT 2007-60458 from the Spanish Ministry of Science and Innovation for support.

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