Chemistry 160: The Determination of Water Content in Ultra-thin Polyelectrolyte Films at the Solid-Liquid Interface using a Quartz Crystal Microbalance

Objective

The fabrication of ultra-thin films with thicknesses in the nano-scale is important to a variety of fields such as microelectronics and biotechnology. In particular the issue of "trapped water" within such assemblies is a focus on-going research and is particularly important in biologically relevant assemblies. In this experiment you will fabricate a polyelectrolyte film with a thickness between 3 to 5 nm. You will monitor the growth of the film on a quartz crystal using a very sensitive microbalance known as a QCM (quartz crystal microbalance). The growth of the polyelectrolyte film occurs by the adsorption of the polyelectrolyte from an aqueous solution onto the surface of the crystal. Thus, the resulting film will be formed at the solid-aqueous interface and will contain an equilibrium amount of water. By studying the adsorption of the polyelectrolyte from H_2O and D_2O solvents, you will determine the percentage water content in the film.

Background

Reliable non-invasive measurements of binding events such as adsorption require techniques with nano-gram sensitivity with respect to measured masses. Recent developments in quartz crystal microbalance (QCM) technology have made it possible to extract this information *in situ*, making the technology suitable for the rapid characterization of chemical and biological interfaces. In short, the technique involves measuring the adsorption of material onto a functionalized quartz crystal. In this respect the QCM crystal serves as a mass sensor for mass up-take on pre-prepared surfaces, allowing direct measurement of equilibrium adsorbed amounts and adsorbate-adsorbent interactions.

A QCM sensor consists of a disk-shaped, AT-cut piezoelectric quartz crystal, usually coated with metallic electrodes on both sides. The crystal can be induced to oscillate at its fundamental resonant frequency by applying an rf voltage across the electrodes. If a small amount of mass adsorbs to the electrode surface, a reduction in the resonant frequency is observed. This reduction is proportional to the adsorbed mass, assuming that this mass is rigidly fixed to crystal surface, and the mass is much small than the mass of the QCM crystal. The resonant frequency (F) of the crystal depends on the total oscillating mass, including water coupled to the oscillation. When a thin film is attached to the sensor crystal the frequency decreases (Figure 1a). If the film is thin and rigid the decrease in frequency is proportional to the mass of the film. In this way, the QCM operates as a very sensitive balance. The mass of the adhering layer is calculated using the Sauerbrey relation [1], where ΔF is the frequency shift to due the adsorbed amount Δm, C is a constant characterizing the sensor crystal (C = 17.7 ng s^{-1} cm^{-1} for a 5 MHz quartz crystal), and n represents the overtone number.

$$\Delta F = -\frac{\Delta m}{nC}, \textbf{ [1]} \qquad D = \frac{E_{lost}}{2\pi E_{stored}}, \textbf{ [2]}$$

In many situations the adsorbed film is not rigid and the Sauerbrey relation becomes invalid. A film that is "soft" (viscoelastic) will not fully couple to the oscillation of the crystal which dampens the crystal's oscillation. The dissipation (D) of the crystal's oscillation is a measure of the film's softness (viscoelasticity) (equation [2]). E_{lost} is the energy lost (dissipated) during one oscillation cycle and

E_{stored} is the total energy stored in the oscillator. The dissipation of the crystal is measured by recording the response of a freely oscillating crystal that has been vibrated at its resonance frequency (Figure 1b). Thus, viscosity, elasticity and the correct thickness may be extracted even for soft films when certain assumptions are made.

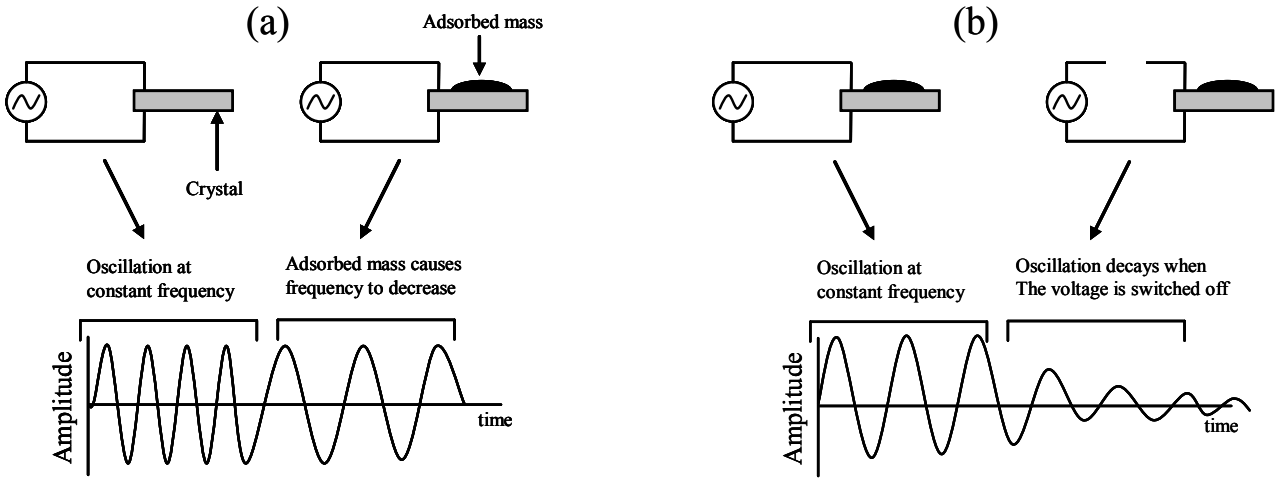

Figure 1. (a) The quartz crystal initially oscillates at constant frequency. In our case the exact frequency of oscillation is 4.95 MHz. When a small amount of mass, *m*, adsorbs from the bulk solution onto the surface of the crystal, the oscillation frequency decreases according to equation [1]. This frequency shift can be used to calculate *m*. (b) When the power source is disconnected, the amplitude of the oscillation decays, due to high energy loss in a viscoelastic film.

The Sensor Crystal and Flow Module

The QCM senor crystal (14 mm × 0.3 mm) operates at a frequency of 4.95 MHz ± 50 kHz. You will be using quartz crystals coated with a Au electrode (100 nm thick) on one side and the *active surface layer* (the counter electrode) on the other side. This *active* layer is SiO_2 (50 nm thick). The crystals are optically polished with a surface roughness of less than 3 nm (RMS). The active side is in contact with the aqueous polyelectrolyte solution.

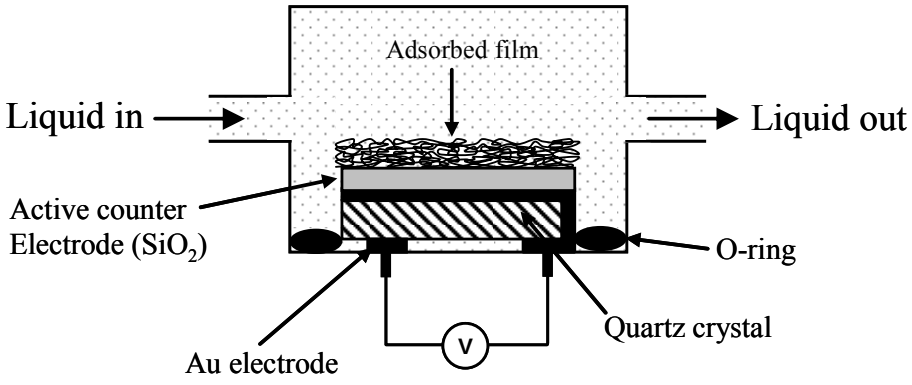

Figure 2. The measurement chamber (flow module) housing the sensor crystal. The active SiO_2 is deposited on Au which is wrapped around the edge of the quartz crystal. Only the active side of the electrode is in contact with the adsorbate solution. The counter electrode and the electrical contacts for the electrodes are on the backside of the crystal.

Procedure

You will do the following:

(a) Prepare a solution of a polycation and a solution of a polyanion, in both H_2O and D_2O.
(b) Use QCM to monitor the deposition of the polyanion on top of a negatively charged crystal surface (SiO_2).
(c) Use QCM to monitor the deposition of the polycation on top of the polyanion.
(d) The steps above will be done for polyelectrolytes in both H_2O and D_2O.

Materials: You will need to prepare the following polyelectrolyte solutions (in both H_2O and D_2O) based on the molecular weight of the monomeric repeat unit. (1) 1 mM solution of the polyanion PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt]), and (2) 1 mM solution of the polycation PEI (poly(ethylenimine)). You will be provided with ultra-pure samples of H_2O and D_2O. A clean sensor crystal functionalized with SiO_2 will be provided.

Mounting the Crystal: Carefully holding the outer edge of the sensor crystal with tweezers rinse it with ultra-pure water (resistivity > 18 MΩcm), and then dry the sample with in a stream of dry N_2. Carefully mount the crystal with its active side down. Note that the anchor shaped electrode has to point towards the anchor shaped symbol on the module. Assemble the flow module, insert it into the measurement chamber platform, and close the latch.

Measurements. Switch on the instrument and run the QSoft software. The instructor will demonstrate the software. Through the software, set the temperature to 25 ^oC. Run the pump and fill the flow module with ultra-pure water. The flow rate will be pre-set at 300 μL/s. Wait 20 min before taking measurements. You will measure ΔF as a function of time with the sensor crystal under pure water. You need ensure that you have a stable baseline (i.e. $\Delta F = 0$ for $t = 5$ min). You are now ready to assemble the polyelectrolyte layers:

[1] Stop the pump and place the in-flow tube into the PEI solution. Start the pump. Monitor ΔF as a function of time.
[2] Once ΔF stops changing, stop the pump. Switch out the PEI solution with pure water and rinse the film for 5 min.
[3] After the water rinse, stop the pump. Switch out the pure water with the PAZO solution. Monitor the adsorption as a function of time.
[4] Once ΔF stops changing, stop the pump. Switch out the PAZO solution with pure water and rinse the film for 10 min.
[5] The above steps will be done for polyelectrolyte solutions prepared in both H_2O and D_2O. The H_2O and D_2O experiments will be done on two separate but identical crystals.

Note: If an air bubble is trapped in the tubing, stop the pump immediately. Reverse the direction of the pump until the air bubble is released into a waste beaker. Once you have completed the above steps, you will save your data in the folder Chem160. You can then shut off the instrument but keep the pump running with pure H_2O flowing through the chamber. The instructor will disassemble the module and clean the sensor crystal.

Analysis of Data

The instructor will demonstrate the QTools software used to analyze ΔF and D data. You will use QTools to determine the following:

[1] Convert ΔF values to adsorbed masses. Export the data to Excel and plot mass versus time.
[2] Determine binding constants for the adsorption of PEI and PAZO by fitting rate expressions to the mass verses time curves.
[3] Report the masses of the PEI/PAZO bilayers adsorbed from both H_2O and D_2O solvents.
[4] Determine the amount of water trapped in the PEI/PAZO bilayer when in equilibrium with a pure aqueous phase.

The data you will collect has not been obtained before. Thus, the work is original and your report must be written in this context. Your report will must be typed with all graphs (correctly labeled) prepared in an appropriate spreadsheet. Your report will contain the following sections: Abstract, Introduction, Results and Discussion, Conclusion. You are free to provide references. An excellent database of QCM literature can be found at http://www.q-sense.com/viewPublication.asp?linkto=35. Your final report should be between 4-7 pages (line spacing 1.5 and 12 pt font size).