REAL TIME THICKNESS MONITORING OF POLYELECTROLYTE MULTILAYER FORMATION IN SITU

INTRODUCTION

Polyelectrolyte multilayers have emerged as a method to build up well-defined coatings for several kinds of surface modifycations, ranging from photonics to biomaterials, membrane and sensor applications. QCM-D allows real-time monitoring of the layers' adsorption and build-up *in situ*, as well as giving structural information such as swelling. This study shows the successive build-up process of a two-component multilayer used for biomedical materials applications. The example also demonstrates the discrepancy between the Sauerbrey equation (assuming a rigid film) and the Voinova model (Voight-based, assuming a viscoelastic film) employed in QTools that appears when the adsorbed layer becomes significantly viscous upon swelling.

RESULTS

A two-component polymer system (Mw approx. 75,000) was coated on a SiO_2 surface. The anionic polymer A, and the cationic polymer B, were introduced alternately in the order A+B+A+B+A+B+A+B+A, 5 minutes each. After the last adsorption step, NaCl was introduced for 20 minutes.

Direct observations:

- Component A did not adsorb directly to the SiO_2 surface; component B was needed before A could adsorb.
- The dissipation, D, values and the difference between the overtones are fairly small in the adsorption phase before rinsing with NaCl, indicating a fairly rigid layer and that the Sauerbrey can be considered valid.
- The D values as well as the difference between the overtones increase drastically upon NaCl rinsing, showing the transition from a rigid to a soft layer upon swelling.

At first glance, when only looking at the frequency (as the Sauerbrey equation operates), it appears as there is a loss in mass upon NaCl and water rinsing. However, the dissipation showing a steady increase, as well as the difference between the overtones, tells us that there is a very significant transition from a rigid to soft layer (**Figure 1**). The appeared mass loss is nothing else but the underestimation of mass made by the Sauerbrey equation when applied to a soft film. Using the Voinonva viscoelastic model that take both parameters f and D into account at all three overtones shows how the film actually swells during the NaCl and repeated water rinsing (**Figure 2**).

CONCLUSIONS

QCM-D can be used for real time studies of polyelectrolyte multilayer formation *in situ*. By using modeling incorporated in Q-Sense analysis software QTools it becomes possible to extract correct thickness even for soft films that do not follow the linear Sauerbrey relation between change in frequency and change in mass.

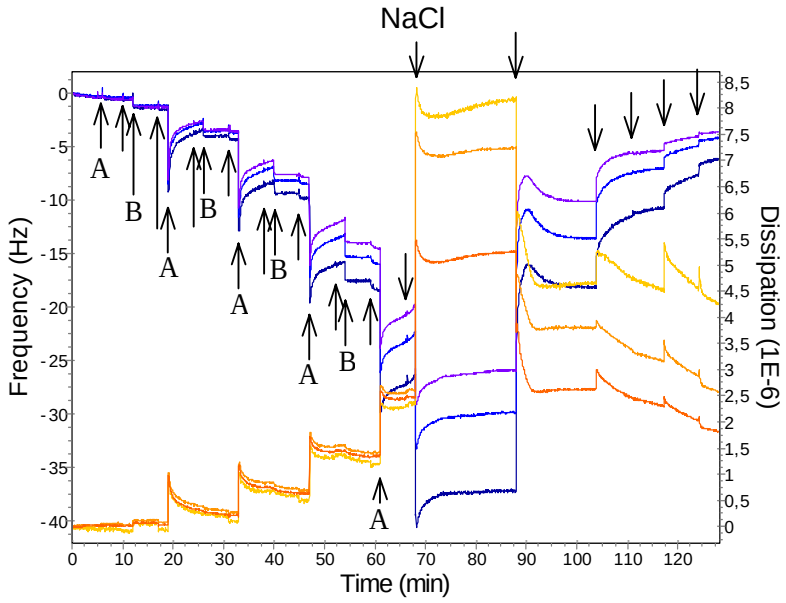

***Figure 1**. Frequency and dissipation responses followed simultaneously. At black arrows without letters, purified water was rinsed (the large buffer step was caused by the different liquid properties when going from water to NaCl and back).*

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REFERENCES

This example is taken from a pre-study performed by Hans Green, Q-Sense AB, for a medical device company that also provided the polymer samples.

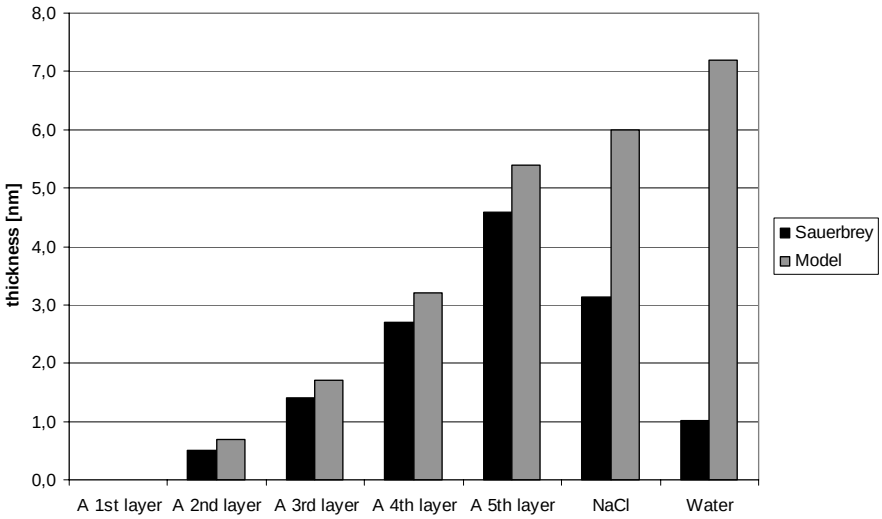

***Figure 2**. Thickness data taken after each of the 5 adsorptions of polymer A, followed by NaCl and water.*

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