A Voltage-Modulation QCM-D Applied to the Study the Adsorption of Proteins and Particles

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Soft layers at interface are conveniently studied with the quartz crystal microbalance with dissipation monitoring (QCM-D). The QCM-D outputs sets of frequency shifts, $D f_n$, and shifts in the half bandwidth, DG_n, on a few different acoustic resonances. These parameters are turned into information on the layer much beyond gravimetry. In particular, the softness often is available in addition to the adsorbed amount.

The depth of information can be further increased by letting the adsorption occur while the electrode potential is periodically switched between two states ('high' and 'low'), thereby probing the sample's *electro-responsivity.* Mechanisms contributing to electro-responsivity are charge reversal in the diffuse double layer, adsorption and desorption, electrochemical reactions, pH effects, and effects of reversed polarity in the Helmholtz layer. Because the time resolution is two milliseconds, kinetics on the millisecond time scale aids the interpretation. Data obtained on two types of proteins and on latex spheres are shown.

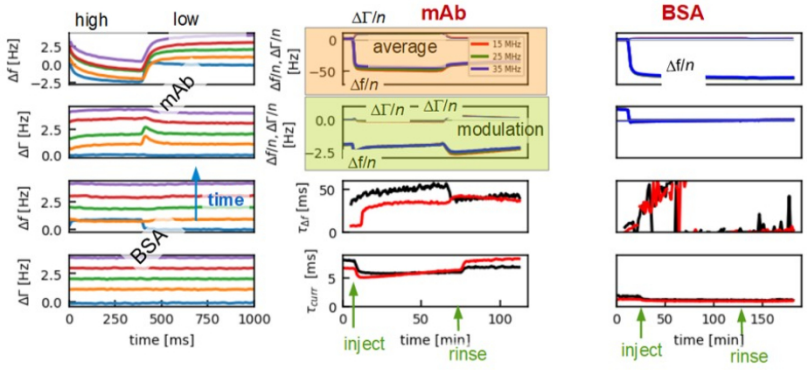
The figure compares data obtained on a monoclonal antibody (mAb, supplied by Boehringer Ingelheim) and on a reference system (BSA). The left hand side shows the short-time electro-responsivity, which is large for mAb and small for BSA. The bandwidth shows a transient maximum upon switching to "low". Time constants of the switching kinetics can be derived from such plots.

The graph overlaid in yellow shows shifts of frequency and bandwidth averaged over one modulation period. This information is equivalent to what the conventional QCM-D reports. Frequency decreases when the sample is injected. It slightly increase after the rinse. The graph overlaid in green shows the difference between "high" and "low" (the "modulation signal"). The modulation signal reports the electro-responsivity averaged over the two plateaus of the volage trace. The electro-responsivity of mAb sample is substantial, while it just about vanishes for BSA. The modulation signal is the novel information provided by this instrument.

The time constants (shown at the bottom) are much larger for the frequency shift than for the current. Clearly, the electro-responsivity in this case is not caused by charge reversal in the diffuse double layer.

Analogous data can be obtained by replacing the square profiles with linear ramps (as employed in cyclic voltammetry). The ramps evidence events at specific potentials, often linked to redox processes at the electrode.

Keywords:
QCM-D, Proteins, Adsorption, Viscoelasticity, Electroresponsivity



A data set obtained with the voltage modulation QCM, comparing the mAb to BSA

References:

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