Quartz Crystal Microbalance (QCM) Gravimetry

Purpose

- To study *in situ* solution phase kinetics of adsorption/desorption of alkanethiols on gold.
- To determine the free energy, enthalpy, and entropy of adsorption of octadecanethiol on gold in an *n*-hexane solution.

Introduction

When a clean gold surface is immersed in an alkanethiol solution, the following net chemical reaction occurs:

$$\mathrm{Au + RSH \rightleftarrows Au\text{-}SR + \tfrac{1}{2}\,H_2}$$

This is a chemisorption reaction, which self-terminates at one monolayer under the conditions used in this experiment. Langmuir adsorption isotherm kinetics can be used to describe this reaction. This model assumes that adsorption is limited to one monolayer, that all surface sites are equivalent, and that adsorption to one site is independent of the occupancy condition of the adjacent sites. Although there are defects on the gold surface, the resultant modulation of surface site energies is apparently small enough so that the Langmuir approximation holds. The alkyl chains do interact with each other, however this interaction is only significant for nearly complete surface coverage because of the inherently short range nature of dispersive (van der Waals) forces. Thus, adsorption to one site can be considered independent of whether adjacent sites are filled for fractional coverage less than unity. The Langmuir adsorption isotherm model was derived initially for physisorption, not chemisorption, but the bond strength of the alkanethiol-gold bond is small enough that this condition is not violated seriously.

Assuming Langmuir adsorption kinetics, the rate of formation of the monolayers can be expressed as:

$$\frac{d\theta}{dt} = k_a(1-\theta)C - k_d\theta \qquad (1)$$

where θ is a unitless quantity which expresses the fraction of available sites that have reacted (or equivalently, the fraction of a monolayer formed), C is the thiol concentration in the solution, and k_a and k_d are the rate constants for the adsorption and desorption processes, respectively.

Integration of equation 1 leads to:

$$\theta(t) = \frac{C}{C + \frac{k_d}{k_a}}\left(1 - e^{-(k_aC + k_d)t}\right) \qquad (2)$$

Setting:

$$k_{obs} = k_a C + k_d \tag{3}$$

and

$$k' = \frac{C}{C + \frac{k_d}{k_a}} \tag{4}$$

results in the equation:

$$\theta(t) = k'(1 - e^{-k_{obs} t}) \tag{5}$$

If the fractional coverage θ is measured as a function of time t, k_{obs} and k' can be determined by fitting this experimental data to equation 5. The experiment is repeated at several different thiol concentrations and a plot of k_{obs} vs. C yields a line with slope k_a and y-intercept of k_d (equation 3).

The equilibrium constant for this reaction K_{eq} is equal to the ratio of k_a/k_d and the free energy of adsorption ΔG_{ads} at a given temperature is given by:

$$\Delta G_{ads} = -RT \ln K_{eq} \tag{6}$$

Since:

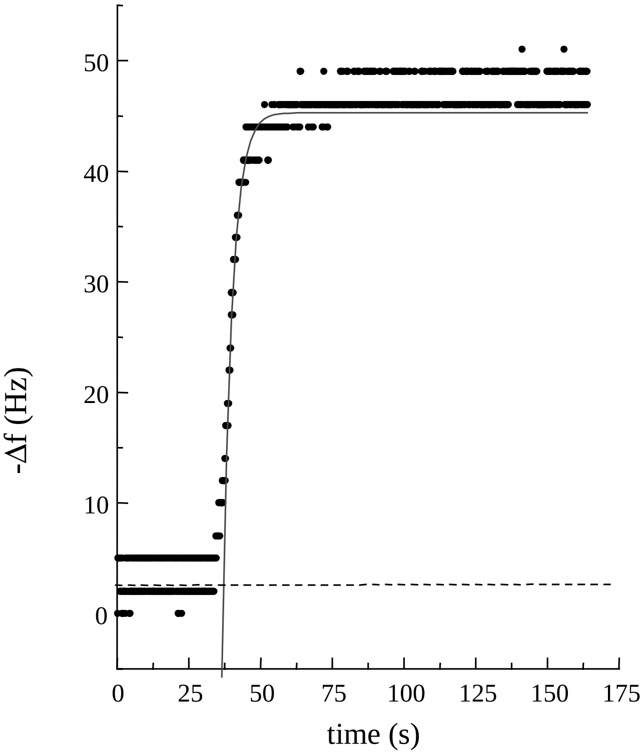
$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \tag{7}$$

both ΔH_{ads} and ΔS_{ads} can be determined by carrying out this experiment over a range of temperatures. ΔH_{ads} is the y-intercept and $-\Delta S_{ads}$ is the slope of a plot of ΔG_{ads} vs T.

Being able to make these determinations rests upon the ability to measure the fractional coverage θ as a function of time. In this experiment, this is accomplished by using a simple gold-coated mass sensor as the substrate: as the monolayer forms, the increase in mass reflects the change in fractional coverage of the surface.

The mass sensor is a gold-coated quartz crystal microbalance (QCM) and it is sensitive, in principle, to mass changes as small as several nanograms. The basis of the QCM is a piezoelectric quartz crystal which oscillates at a resonance frequency determined by several factors, including the mass of the crystal. Because we are concerned only with *rates* of mass change in this experiment, we do not need to determine the absolute mass change associated with the formation of the monolayer. A baseline oscillation frequency for the uncoated QCM is measured. The difference between this value and the oscillation frequency measured as the monolayer forms is directly proportional to θ, the fraction of the surface that has been covered.

An example of the raw QCM data and best-fit curve to equation 5 for 10 μM thiol solution at 288 K is shown below:



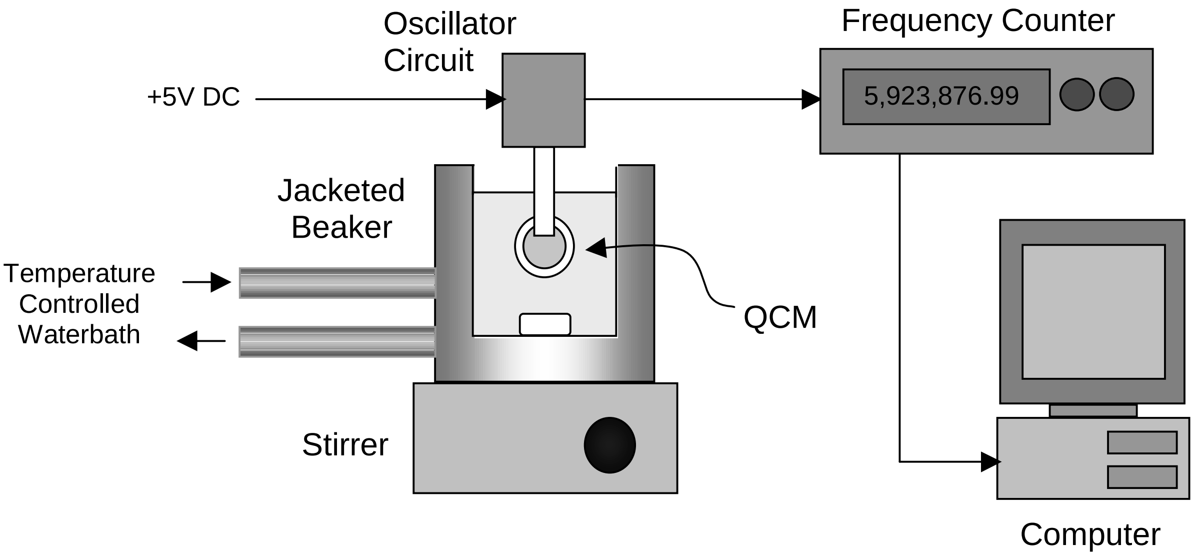
Notice that the the maximum initial rate of monolayer formation is not reached immediately upon injection. Depending on the volume and concentration of thiol aliquot injected, it may take up to several seconds to achieve the maximum adsorption rate because of limitations inherent to mixing of the solvent and the thiol aliquot. The aliquot mixing time is substantially shorter than the monolayer formation time and the smaller the amount injected, the more time is required for thorough mixing. The "roll-on" of the maximum initial rate is caused by the concentration gradient introduced by mixing. We can account for this mixing effect by modifying the variable t in Eq. 5 to t-t_o:

$$\theta(t-t_o) = k'(1-e^{-k_{obs}(t-t_o)}) \qquad (8)$$

Fitting the portion of the curve from the onset of the maximum rate through a significant portion of equilibrium yields the variable t_o which is the predicted time of injection if mixing were instantaneous.

If a slight frequency drift is present, it can be accounted for before curve fitting using the slope of the initial 10 sec baseline, or, if necessary, a longer baseline. A strong, positive, monotonic frequency drift may indicate that the gold electrode is lifting away from the substrate because of damage incurred during use or cleaning, and the crystal should be discarded.

Experimental Setup



Experimental Procedure

As with all of the experiments in this course, careful cleaning of all surfaces is essential if meaningful data is to be collected.

1. Cleaning the jacketed beaker:

   TURN OFF THE CHILLER! Carefully pour any solution in the jacketed beaker into a large beaker and empty the beaker into the waste container. Don't throw away the stirbar.

   Disconnect the jacketed beaker from the tubing by tipping it on its side and removing the upper hose. Allow the water to drain back into the chiller before removing the lower hose. Place the tubing connector in the line so that water from the chiller will not siphon out onto the floor.

   In the hood, fill the jacketed beaker (with the stirbar in it) with chromic acid cleaning solution. Wait at least 5 minutes before pouring the solution out. Rinse thoroughly with distilled water, followed by tetrahydrofuran (THF) to remove the water, and a hexane rinse to remove the THF. The cleaned beaker should be used shortly after cleaning to minimize the buildup of adventitious carbon contamination.

   Rinse the QCM holder carefully with clean *n*-hexane.

2. Cleaning the QCM:

   Immerse the QCM crystal in fresh piranha solution (3:1 conc. sulfuric acid: 30% hydrogen peroxide) for 5 min, then rinse with distilled water. Dry under a stream of nitrogen. Rinse with THF to remove any remaining water and rinse with n-hexane to remove the THF. Cleaned crystals should be used immediately.

3. Clamp the jacketed beaker to the ringstand, clip the hoses into the water line, and start the chiller. Make sure that there are no leaks. Check the setpoint on the chiller by pressing the “Next Enter” button. Make adjustments to the setpoint by pressing the ▲ or ▼ buttons to get the desired temperature. Push “Next Enter” to save the value and push it a second time to display the current temperature. NOTE: If you do not press “Next Enter” twice within 10 seconds, the controller will revert to the previous setpoint value.
4. Add the cleaned stirbar and 100.00 mL of *n*-hexane to the jacketed beaker. Put a clean watch glass on the top of the beaker and begin stirring. This will allow the hexane to reach the desire temperature with minimal evaporation.
5. Meanwhile, gently squeeze the “ears” of the QCM holder to open it *slightly* and carefully clip the QCM into the holder. The QCM should be held near its upper edge. Be sure that the pin is contacting the gold surface.
6. Turn on the 5 V power supply and the frequency meter. The oscillation frequency of the QCM should be approximately 6 MHz.
7. Start the Labview software and select the Mass Sensing VI from the Mass Sensing. llb library. The software will immediately begin monitoring the frequency of the crystal. Select the temperature of the run and the thiol concentration that you are using from the pull-down menus on the upper right-hand side of the screen. These values will be written at the beginning of your data file.
8. Once the temperature in the chiller has reached and sustained the desired temperature, remove the watchglass and lower the holder into the *n*-hexane. The hexane level should be just below the black insulation on the wire inside the holder. Check to make sure that there are no bubbles next to the QCM and that the vortex from the stirring is away from the crystal. Both will cause excessive noise in the frequency measurement. Changing the stirring rate will help to dislodge bubbles.
9. Wait until the oscillation frequency has stablized. The noise level should be ~ ±1 Hz and the frequency should not drift excessively. This will probably take several minutes. Press the green Start button on the screen to begin data collection. Wait at least 10 sec to establish a baseline and then inject the stock thiol solution using an Eppendorf pipette with a fresh tip. Injection should be done quickly, toward the base of the beaker and not directly on the QCM. Collect data long enough to ensure that the adsorption process has reached equilibrium. Press the red Stop button to end data collection. You will be prompted to give a file name so that the data can be saved.
10. The program will begin monitoring the frequency again. Stop the program by pressing the “Exit” button. It can be restarted for the next experiment by pressing the arrow button on the far left-hand side of the toolbar. **TURN OFF THE CHILLER!**
11. You will be provided with multiple QCM’s and two jacketed beakers so that cleaning preparations for the next run can be accomplished while carrying out an analysis.

Experiments

(1) In these experiments, the monolayers are assembled from octadecanethiol in *n*-hexane on the surface of gold-coated QCM's.

(2) The kinetics of the adsorption reaction at 293 K are studied for a range of solution concentrations: 300 to 3μM (Langmuir adsorption isotherm kinetics are followed over this concentration range). Solution concentrations to be used and the appropriate volumes of the 0.01 M stock thiol solution (provided) to inject into 100.00 mL of *n*-hexane are given in the table below:

Formal Alkanethiol Concentration (M)	Volume of 0.01 M Stock Solution
3.00×10^{-4}	3.09 mL
1.00×10^{-4}	1.03 mL
3.00×10^{-5}	309 μL
1.00×10^{-5}	103 μL
3.00×10^{-6}	30.9 μL

(3) Run the experiment in triplicate at a minimum of three concentrations. Start with the lowest concentration and work up to minimize contamination errors. For each run, fit the data to equation 8 and determine k_{obs}. Then plot k_{obs} vs. thiol concentration and determine the rate constants for adsorption and desorption. Use these values to determine the equilibrium constant K_{eq} and the free energy of adsorption ΔG_{ads} for this reaction at 293 K.

(4) Repeat this experiment at 288 K and either 298 K or 303 K. Plot ΔG_{ads} versus T, and determine ΔH_{ads} and ΔS_{ads} for this reaction.

References

D. S. Karpovich and G. J. Blanchard, "An Undergraduate Laboratory Experiment for the Direct Measurement of Monolayer Formation", *J. Chem. Ed.*, **72**, 466-470 (1995).

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