Measuring Desorption Rates from Self-Assembled Monolayers at the Solution-Solid Interface.

K W Hipps and Ashish Bhattarai

Department of Chemistry, Washington State University, Pullman, WA 99164-4630

hipps@wsu.edu and ashish.bhattarai@email.wsu.edu

Nomenclature

1. $k_d$: Desorption rate constant
2. $\Delta S^\dagger$: Entropy of activation
3. $\Delta H^\dagger$: Activation enthalpy
4. $E_{a_i}$: Activation energy of adsorption by process i
5. $E_{d_i}$: Activation energy of desorption by process i
6. SAM: Self-assembled monolayers
7. Tecton: A molecular component that self-assembles into a 2-d or 3-d structure.
8. QCM: Quartz Crystal Microbalance
9. SPR: Surface Plasmon Resonance
10. PFD: Perfluorodecalin
11. SPM: Scanning Probe Microscopy
12. HOPG: Highly oriented pyrolytic graphite
13. AFM: Atomic Force Microscopy
14. STM: Scanning Tunneling Microscopy
15. OD: Octadecanol
16. TC: Tetracosanol
17. TUP: 5,10,15,20-tetraundecylporphyrinato
18. OEP: Octaethylporphyrin
19. MOEP: octaethylporphyrin complex where M is a transition metal or H$_2$.

Key words

1. Self-assembled monolayers
2. Adsorption
3. Desorption
4. Solution-solid
5. Single molecule
Abstract

The focus of this article is on the measurement of desorption rates of tectons that form self-assembled monolayers (SAMs) at the interface between a conductor surface and a solution. In an effort to make the physics and chemistry as simple as possible, only low surface area substrates are considered. Examples are separated into methods that provide ensemble averages and those that provide measurements at the single molecule level. SAMs with and without covalent linkage to the substrate will be considered. Of primary interest are techniques utilizing quartz crystal microbalance, surface plasmon resonance, and scanning probe microscopy.

Introduction

The focus of this article is on the measurement of desorption rates of tectons that form self-assembled monolayers (SAMs) at the interface between a conductor surface and a solution. In an effort to make the physics and chemistry as simple as possible, only low surface area substrates are considered. A self-assembled monolayer (SAM) is a 2-dimensional monolayer with periodic ordering in which the component molecules (tectons) have a structure that is defined both by the tecton-surface interaction and the tecton-tecton interaction. The best known example of such a SAM is the ordered structure that results when alkanethiols [(H₃C(CH₂)ₓSH where x ≳ 8] are adsorbed on gold, silver, or copper. In this case, adsorption commences with a sulfur-Au bond and alkane chains that are disordered and oriented more parallel than perpendicular to the surface. At low coverage the low barrier to diffusion generally results in a 2-d fluid like adlayer. As the surface concentration rises several different steps can eventually (sometimes hours in contact with solvent) produce a dense well-ordered system with alkane chains nearly perpendicular to the surface maximizing the van der Walls interactions between chains. Depending upon the exposure time, solution concentration, and temperature there may be different phases present on the surface. Less well studied, but of great current interest, are planar molecules that adsorb without covalent attachment to the solid substrate and then (eventually) form an ordered structure through tecton-tecton interactions such as H-bonding, dipole dipole, or van der Waals interactions.
Using a potential energy cartoon (Figure 1) we can visualize at least some of the kinetic steps involved in the adsorption and subsequent desorption processes. Starting from the left side of the diagram we can follow a molecule adsorbing at coverage well below one monolayer. A molecule in solution that approaches (through diffusion) a nearly tecton free surface sees a barrier to adsorption associated with loss of solvent from the surface and decrease in solvation of the tecton.8-11 The associated activation energy is $E_{a1}$. This barrier does not generally exist for vapor phase adsorption onto a clean substrate surface. Those tectons that have sufficient energy to surmount the barrier find themselves (at low coverage) on the substrate surrounded by solvent. These molecules can diffuse across the surface but must surmount a small barrier associated with both the periodicity of the substrate-tecton interaction and the displacement of solvent from its next site on the surface.12-16 These low density tectons can desorb from the surface by surmounting an activation barrier $E_{d1}$. $E_{d1}$ will be greater than $E_{a1}$ so long as surface assembly is energetically favorable since the thermodynamic desorption energy (for very low coverage) is $(E_{d1} - E_{a1})$. Conceptually, it is possible for the energy of desorption to be negative, but this can only occur in cases where multiple well-ordered solvent molecules are displaced per adsorbed tecton, That is when $\Delta S_{ads} > 0$.

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**Figure 1:** Cartoon of potential energy surface seen by a single tecton as it moves from the solution to solid surface but is surrounded by solvent molecules. The tecton proceeds to the right where it surmounts a small activation barrier in order to attach to the edge of a growing island.
Once the tecton has been incorporated into a well-structured SAM, it can move back into solution by surmounting activation barrier $E_{d3}$.

As the surface concentration grows, nucleation of the self-assembled phase will occur and a few islands will form. A molecule that was diffusing across the surface can attach to the perimeter of such an island only by displacing solvent and there will be an activation barrier of $E_{a2}$ to surmount in order for the perimeter of the island to grow. $E_{a2}$ is the activation energy barrier for separation from the island perimeter and a return to diffusion across the surface. In order for a tecton on the perimeter of an island to return to solution, an energy of $(E_{d2} - E_{a2} + E_{d1} - E_{a1})$ is required. However, since the process of leaving the island edge and leaving the surface are probably not coordinated, the rate limiting step will likely be determined by the activation energy $E_{d1}$. Thus, unless $E_{d2} > E_{d1}$, desorption from island edges and "free" surface will appear to occur at the same rate. The very sharp increase in energy to the right of the edge attachment in Figure 1 is associated with a perimeter molecule attempting to burrow into the body of the dense and assembled monolayer island. The island grows through attachment of other tectons not shown in the diagram and the nucleation process is also not shown.

On the right side of the diagram is depicted the potential for a tecton in a stable position deep inside a self-assembled structure. Moving left we imagine the tecton attempting to force its way through the well-ordered 2-d structure. Moving right, the tecton is leaving the island by vertical desorption. The activation barrier for this process will generally be larger than for the previous processes since it involves both solvent reorganization and breaking the (presumed strong) inter-tecton bonding. These same factors make the energy of desorption $(E_{d3} - E_{a3})$ greater than the previous two desorption process energies.

Assuming that each of these desorption steps are first order in the appropriate species per unit area (number of diffusing tectons, number of perimeter tectons, number of tectons within islands) one can define a desorption rate constant for each process, $k_{di}$, $i=1-3$. Using the Eyring absolute rate theory, one can write equation 1 where $\Delta S_i^\ddagger$ is the entropy of activation and $\Delta H_i^\ddagger$ is the activation enthalpy, which for condensed phases is nearly the activation energy. With a further assumption of a not too wide temperature range, one has the familiar Arrhenius equation, equation 2.

\[
k_{di} = \frac{kT}{h} e^{\frac{\Delta S_i^\ddagger}{R}} e^{-\frac{\Delta H_i^\ddagger}{RT}} \approx k_{di} = \frac{kT}{h} e^{\frac{\Delta S_i^\ddagger}{R}} e^{-\frac{E_{dil}}{RT}} \quad \text{(eqn 1)}
\]

\[
k_{di} \approx k_{di}^0 e^{-\frac{E_{dil}}{RT}} \quad \text{(eqn 2)}
\]

At this point it is well to remind ourselves that the model in Figure 1 is perhaps the simplest possible case and that real systems can be even more complex. None the less, even with this simple model, there are clearly at least three desorption mechanisms with generally different rate constants. Moreover, the number of tectons that can utilize a particular mechanism will depend
upon the coverage. Thus, we should expect desorption rate expressions to depend on coverage in more than the trivial form of rate = -kaθ, where θ is the fraction of surface covered. If we are fortunate, there will be a single rate limiting step, or a narrow region of coverage where the dominant mechanism changes.

Because of this potential evolution in mechanism and rate with coverage, it can be extremely difficult to impossible to extract a detailed interpretation of data obtained from ensemble techniques (mass adsorbed, changes in index of refraction or absorbance, etc.). Ensemble methods do, however, often provide real time data as a function of concentration and temperature that can be difficult or impossible to obtain on a molecular scale. On the other hand, methods that allow direct tecton scale monitoring (such as scanning probe microscopy) can provide definitive mechanistic insights. Balance this positive against the fact that tecton scale events are difficult to measure with the statistical precision essential for extracting ensemble average data. These general issues should become clear as we discuss some of the common measurement methods in current use.

**Ensemble Desorption Rate Measurement Methods**

**Quartz Crystal Microbalance**

For many years shifts in the resonant frequency of quartz crystals have been used for measuring nanogram quantities of thin films produced by vacuum deposition. The use of these quartz crystal microbalances (QCM) in solution is more problematic. Thompson’s group thoroughly analyzed the problem in 1993 and provided a framework for interpreting the change in resonance frequency produced by changes in mass loading, surface stress, viscous damping, and nonshear coupling.18,19 Karpovich and Blanchard20-22 quickly took advantage of Thompson’s work and measured adsorption and desorption rates for alkanethiols on gold in the early (low density) adsorption regime. Because the quartz crystal resonance has a very strong temperature dependence it is important that the system be maintained at a well-controlled temperature. Further, the density and shear properties of the solvent have a dramatic effect on the resonance frequency. To correct for this, the crystal is first equilibrated in pure solvent and then a small volume (also thermally equilibrated) of a concentrated solution was rapidly mixed with the solvent in contact with the crystal. In performing their data analysis, Karpovich and Blanchard20 assumed that the QCM frequency shifts were proportional to the mass adsorbed and used a Langmuir adsorption isotherm and associated kinetics to analyze the resulting time dependent mass increase. Accordingly, if c is the concentration of alkanethiol in moles/L:

\[
\theta(t) = A[1 - \exp(-k_o t)] \quad \text{eqn 3}
\]

\[
k_o = ck_a + k_d \quad \text{eqn 4}
\]

\[
\Delta G_{ads} = -RT \ln(K) = -RT \ln \left(\frac{k_a}{k_d}\right) \quad \text{eqn 5}
\]
They found equation 3 to be applicable with $k_d \approx 0.3 \text{ s}^{-1}$ for both octadecanethiol and octanethiol in hexane and cyclohexane. While they are clear that their desorption rate constant is not $k_{d3}$, it is not clear if it is $k_{d1}$, $k_{d2}$, or a function of both. The adsorption rate constants, on the other hand, were very different for the C18 and C8 systems – 2000 M$^{-1}$s$^{-1}$ for the C18 system and only 800 M$^{-1}$s$^{-1}$ for octanethiol. All coverages were less than one monolayer at the single temperature studied (293 K). They used equation 5 to determine the equilibrium constant $K$, and from that $\Delta G_{\text{ads}}$. They found $\Delta G_{\text{ads}}$ to be -23 kJ/mole for the C18 system and -18 kJ/mole for octanethiol (both in hexane). In a later paper$^{22}$ they performed temperature dependent measurement on the C18 system in hexane on gold. From the temperature dependence of the equilibrium constant they determined that $\Delta H_{\text{ads}} = -83 \text{ kJ/mole}$ and $\Delta S_{\text{ads}} = -200 \text{ J/(mol K)}$.

These results should be contrasted against those found by Bain et al$^{5}$ who used ellipsometry to study fully formed SAMs composed of thiols with more than 10 carbons in the chain. They found that these were stable indefinitely at room temperature but that they would desorb if heated to 80°C in hexane. Bain also reported that desorption from a well-structured alkanethiol SAM was most rapid in organic solvents, slower in ethanol, and slowest in air. The difference in rates observed by Bain and by Karpovich may be due to the aggregation state of the surface thiol, with Karpovich’s results reflecting an as yet unorganized adlayer. It should also be noted that Bain’s ellipsometric time scale was on the order of minutes and that the adsorptions observed by Karpovich (initial low density phase) were completed in seconds. Thus the two experimental methods had completely different time scales.

An important note here is on the nature of the gold substrate in either experiment. The supports are coated with a vapor deposited film that is known to be Au(111) textured, but not single crystalline or defect free. This has two implications for data interpretation. First, one should not expect a perfect correlation between single crystal and deposited film results since the deposited gold has surface sites that are not (111) oriented and there are potentially many more defect sites. Second, Karpovich found that the observed extent of adsorption depended on the film roughness (as seen in electron microscopy). In interpreting their data they appear to have assumed that only the Au(111) sites were active for thiol adsorption.

Colavita and coworkers used the QCM to study the adsorption kinetics of 4-nitrobenzenediazonium salt on gold from aqueous solution.$^{23}$ In this reaction there is chemisorption with elimination of N2 to produce a Au-C bonded nitrobenzene group. Their experimental setup is similar to that used by Karpovich, but was of commercial manufacture. While they acknowledge the work of Thompson on solution induced QCM frequency shifts, they ultimately use the simplified Sauerbrey equation$^{24}$

$$\Delta f = -\Delta m \frac{2f_0^2}{A \sqrt{\mu \rho}} \quad \text{eqn 6}$$
Where \( f_0 \) is the resonance frequency in the pure solvent, \( A \) is the effective area of the electrodes on the crystal, \( \mu \) and \( \rho \) are the shear modulus and the density, respectively. \( \Delta m \) is the increase in mass due to adsorption and \( \Delta f \) is the change in resonant frequency upon adsorption. They considered the possibility that the rate of adsorption might be limited by the rate of diffusion to the surface; but, concluded that their results were not diffusion limited and followed Langmuir kinetics and Langmuir isotherm. Based on their analysis, and using equations 3 to 5, they found \( k_a = 10^2 \text{ M}^{-1} \text{ s}^{-1} \), \( k_d = 2 \times 10^{-3} \text{ s}^{-1} \), and \( \Delta G_{\text{ads}} = -27 \text{ kJ/mol} \).

G. A. Campbell used millimeter sized cantilever sensors to measure the adsorption kinetics of 1-hexadecanethiol on gold from ethanol over six orders in concentration. They found Langmuir adsorption with \( k_a = 0.061 \text{ M}^{-1} \text{ s}^{-1} \) and \( k_d = 3.61 \times 10^{-4} \text{ s}^{-1} \). Using these values they found that \( \Delta G_{\text{ads}} = -13 \text{ kJ/mol} \).

Most QCM instruments have a noise floor of about 1 Hz and are capable of providing a few measurements per second. For a 10 MHz crystal \((f_0)\), \( \Delta m/\Delta f \sim 4 \text{ ng/cm}^2 \text{ Hz} \). Further, the weight of adsorbate per unit area is \( w_a = \text{MW}/(A_m N_0) \), where \( \text{MW} \) is the molecular weight, \( A_m \) is the area/molecule, and \( N_0 \) is Avagadro’s number. Thus, a signal to noise ratio of 1 results when the adsorbate weight is 4 ng/cm\(^2\) and that corresponds to \( \text{MW}/A_m = 2.4 \times 10^{15} \text{ g-molecule/cm}^2 \). C18 alkanethiol on gold, for example has \( \text{MW} = 386 \text{ g} \) and an area/molecule of about \( 2 \times 10^{-15} \text{ cm}^2/\text{molecule} \) giving \( \text{MW}/A_m = 193 \times 10^{15} \) so that the signal to noise at one monolayer is about 80. On the other hand, the self-assembled “chicken wire” structure of trimesic acid has \( \text{MW}/A_m = 1.7 \times 10^{16} \) resulting in the monolayer adsorption providing a signal to noise ratio of only 7. Thus, QCM would be too insensitive for accurate adsorption desorption methods for a low surface density film like trimesic acid. For low density monolayers, there is a more advanced technique in which both the resonance and the Q factor of the QCM are considered, called QCM-D. While we could find no evidence it has been used for measuring desorption rates on SAMs, it has been used to study SAMs systems. The sensitivity of QCM-D is better than 10 times that of conventional QCM and makes studies of lower density monolayers possible.

### Surface Plasmon Resonance (SPR)

Surface plasmon resonance techniques are based on changes in optical reflectivity of a transparent metal film (often Au) when a species attaches to the metal surface. Campbell has identified two distinct forms – SPR spectroscopy (SPRS) and SPR imaging (SPRI). Reference to Figure 2 should be helpful for the discussion that follows. In SPRS, the incident light is broad band and the reflected light is analyzed by a diode array spectrometer (or equivalent). In the spectroscopy, one either measures the reflected intensity at a given angle as a function of wavelength, or the reflected intensity as a function of angle at a given wavelength. Adsorption of tectons on the upper metal surface causes a shift in the resonance frequency because of a change in the refractive index in the evanescent field near the metal surface. Through calibration
of the resonance shifts with known index solvents one can convert the shifts in the reflectance minimum into mean layer thickness.\textsuperscript{31}

In the case of SPRI, the input light is generally monochromatic and the reflected light is directed to a CCD camera (or equivalent). In this way, changes in reflectivity (at one wavelength and angle) can be collected with \( \sim 10 \) micron spatial resolution over the entire area of the sample. Figure 2 also illustrates how that is accomplished. By selecting the angle of incidence in the linear region of the SPR reflectance curve, small changes in index at the metal surface lead to linear changes in the observed intensity at the CCD. For the purposes of adsorption and desorption studies, the top of the prism-gold assembly would be covered by a small volume (very thin) flow cell and the intensity would be monitored as a function of time as first pure solvent and then solution flow through the cell. Modern commercial systems are designed around biochemical binding events and can monitor hundreds of different active sites simultaneously. If measuring adsorption and desorption kinetics for a single species on Au is the goal, the spatial resolution could be used to good advantage if a double flow cell was employed so that one part of the imaged surface always sees solvent while the second chamber has a time varying solute concentration. Absolute accuracy of SPRI is low (\( \sim 35\% \)) but the precision is often \( \leq 5\% \).\textsuperscript{30}

![Figure 2: Optical configuration for SPR, and angle selection for linear response of reflected intensity with index of refraction change. Figure inspired by reference 30.](image)

As in the case of both QCM and SPR kinetic measurements, the transport of solute from solution to the surface can play a significant role in the time dependence of the adsorption. Jung and Campbell addressed this problem in detail in order to apply SPR to the adsorption and desorption of alkanethiols on gold.\textsuperscript{32} The studied systems ranged from C2 to C18 in ethanol (note that
Karpovich and Blanchard studied C8 and C18 system in hexane). Campbell’s treatment of the role of diffusion makes interesting reading. By equating the sticking coefficient to the adsorption rate constant times the thermal velocity of tectons in solution, Jung and Campbell were able to report both sticking coefficients and adsorption rate constants. Unlike the case in UHV where the sticking coefficient is near unity for these alkane thiols, they found that the initial sticking probability ranged from about $10^{-8}$ to $10^{-6}$ as the number of carbons increased from 2 to 18. These very low but increasing sticking coefficients were associated with a chain length dependent activation energy of adsorption ($E_a$) that decreased by about 0.65 kJ/mole per CH$_2$ group. The corresponding adsorption rate constants ranged from 250 to 15,000 M$^{-1}$ s$^{-1}$ over the same series of compounds at 300 K. Over the period of several hours they saw no tendency towards desorption. This was consistent with Whitesides observation. Campbell also suggests that the value of $k_d$ reported by Karpovich$^{20,22}$ is too large and contrary to the known stability of alkenethiols in hexane at 298K.

Other Methods

Ellipsometry has been applied in several studies of adsorption and desorption of alkane thiols. Two examples are Whiteside’s early studies where the time interval between measurements was the order of minutes,$^5$ and the much more recent study by Yuan et al where the measurement interval was about 10 minutes.$^{33}$ In Yuan’s paper, SAMs composed of F(CF$_2$)$_x$(CH2)$_{11}$SH, where $x = 1$-10 and of F(CF$_2$)$_{10}$(CH2)$_y$SH, where $y = 2$-6, 11, were heated in decalin (DC) and perfluorodecalin (PFD) at 80 °C for various periods of time to monitor their thermal stability as a function of solvent. They note, as have others, two distinct desorption regimes. At 80 °C in hydrocarbon solvents the desorption constant for the fast regime is of the order of $2\times10^{-3}$ s$^{-1}$.

Other methods that have been used to at least qualitatively study desorption of thiol SAMs are infrared spectroscopy,$^{34}$ second harmonic generation,$^{35}$ mass spectroscopy,$^{6,36}$ chronoamperometry,$^{37}$ and reductive desorption.$^{38,39}$

**Single Molecule Desorption Rate Measurements**

The presence of site dependent desorption rates (Figure 1) makes single molecule based studies of adsorption and desorption especially valuable. Unlike bulk measurements which require the deconvolution of several rates and only inferentially identify their origin, single molecule measurements allow direct determination of each rate and certain identification of its origin. Scanning probe microscopy (SPM) is the technique of choice for molecular level studies of high density assemblies at the solid-solution interface. While some may argue that there are optical techniques that allow monitoring single molecules, these only apply when the density of the photoactive species is quite low (< 1 molecule /150 nm$^2$). An additional important feature of
scanning probe studies is that they lend themselves naturally to single crystal surface studies. Thus, it is possible to take advantage of the simplification that results when one has a single type of surface [e.g.; C(0001), highly oriented pyrolytic graphite (HOPG)] with a limited number of defect and step edge types. One potential negative that must be considered when using scanning probe techniques is that excessive feedback settings can result in tip induced changes in the surface.\textsuperscript{40-43} Another potential issue is the time required to perform SPM measurement. If $\tau = 1/k_d$, and $\tau$ is much smaller than the imaging time, desorption rates will be unmeasurable. Reviewing the rate constants reported above, and realizing that imaging in solution at a rate of greater than 1 image s\textsuperscript{-1} has been multiply demonstrated, it should be clear that many (if not most) of the desorption rates from SAMs are compatible with SPM techniques. To date, most of the scanning probe based desorption studies have been qualitative in nature with only a very few providing both mechanism and kinetic parameters.

In order to use scanning probe methods to study desorption, we must have some way to separate adsorption and desorption events. If molecule A is replaced by molecule A in a time short compared to the imaging time, no desorption event is recorded. There are basically two general approaches that have been used. In the first, the ordered monolayer is transported to pure solvent and (assuming readsorption events are rare in pure solvent) the loss of tectons from the surface per unit time is used to determine desorption kinetics. In the second method, a second species is introduced to the solution layer above the sample (a tracer) and the replacement of the original species is used (with appropriate kinetic equations such as in reference 42) to determine the desorption rate. The second method works best when the tecton and tracer are physically and chemically identical, but distinguishable in the scanning probe microscope.

**Alkane Thiols**

Of the scanning probe methods, atomic force microscopy (AFM) lacks molecular resolution but can provide information about island growth, phase segregation, and desorption from defects and grain boundaries. For example, Liu and co-workers\textsuperscript{43} used the AFM tip to produce mechanical displacement of a small patch of alkanethiols from the center of a well-structured SAM and then monitored the rate of regrowth. They found that the rate of formation of the SAM within the confined region was 10 times faster than on unconfined bare gold surface. Combining STM and AFM allowed Liu’s group\textsuperscript{44} to demonstrate that degradation of alkanethiol SAMs mainly initiates at defect sites and that it occurs both by direct desorption and by oxidation.

The Weiss group used scanning tunneling microscopy (STM) to study the replacement of pre-formed 1-adamantanethiolate self-assembled monolayers on Au(111) by n-dodecanethiol molecules on both the ensemble (infrared spectroscopy) and molecular (STM) scales.\textsuperscript{34} While they make time dependent measurements and show that half the original monolayer is replaced in 30 minutes, they do not perform a kinetic analysis. This system is not simple to analyze because of the observed nucleation and growth associated with the replacement.
SAMs non-covalently bound

A topic of great interest in the early days of non-covalent SAM formation was the nature of monolayers formed by terminally functionalized alkanes at the graphite-solution interface. Long range well-ordered structures of parallel zig-zag alkane chains were easily observed at room temperature by STM. In the case of alcohol and carboxylate terminated alkanes, H bonding causes the tectons to organize in double rows, often with a herringbone like structure. Elbel and coworkers were one of the first to question the time stability of individual molecules in these monolayers. Using a mixed solution of octadecanol (OD) and tetracosanol (TC) in phenyloctane (on HOPG), they used STM to image the surface with a rate of 10 s per frame. Because of the difference in length in OD and TC, replacement of one with the other was apparent as a change in the spacing of the rows. They suggested that hydrogen bonded pairs of molecules (rather than single tectons) exchanged between surface and solution. They could not rule out tip effects being responsible for the observed changes. Later, Beebe studied mixtures of alkane alcohols, thiols, and acids. The S end of the thiol appeared bright in the STM image allowing it to act as a tracer. Based on the time-position variation of bright spots in the monolayer, Beebe suggested that the residence time for a typical thiol in an alcohol monolayer was between 0.2 and 20 seconds. Their result is a bit confusing since they assert rapid exchange with solution yet there is only a small amount of thiol present in the monolayer even when there is a 20:1 excess in the solution. De Feyter and coworkers used fluoridation to create a tracer to follow desorption. They studied mixtures of H20- and F12H6-isophthalic acid. Using STM they imaged fluorinated acid in a protonated monolayer and observed residence times ranging from several seconds to several minutes. They did not report a numerical value for k_d. While I note that this time spread might be consistent with a k_d of roughly 0.006 s^{-1}; no such simple analysis works because it does not take into account the “like to like” molecular exchanges that were not observable by STM.
Self-assembly can occur even without covalent bonding to the surface or long alkyl chains. Coronene in heptanoic acid solution adsorbs on Au(111) in one of three possible polymorphs depending upon concentration and temperature. At low concentration or high temperature, coronene exist in a hexagonal structure co-adsorbed with heptanol. If the surface is quickly washed with heptane at 298 K, no loss of adlayer is observed.

In order to observe desorption, the newly prepared monolayer was heated in hot heptane for a fixed period of time, cooled to room temperature, imaged by STM, and then the process was repeated. A new sample was made for each temperature-time data set. As can be seen in Figure 3, desorption does not occur randomly but instead starts at defects and grows as the perimeter of the defect grows. Moreover, the coronene tectons do not immediately leave the surface but some remain in the interior of the defects in a disordered state. At elevated temperature they are probably diffusing across the low density region of the surface. Thus, just as in a well ordered alkanethiol SAM, coronene has distinctly different binding energies in an island, at the surface of an island, and in the low density region on the surface. The authors explained the differences in
delay for the start of desorption as due to different amounts and types of defects in the original monolayer.

In 2011 Coenen and coworkers studied the surface phase transformation of copper (5,10,15,20-tetraundecylporphyrinato) [(TUP)Cu] in 1-octanoic acid on HOPG.49 Based on STM imaging of the transforming adlayer, they concluded that it required specific surface defects to nucleate the transformation and that exchange between the surface and solution only occurred at these defects. To prove this they used (TUP)Co as a tracer in solution added above the existing (TUP)Cu monolayer. The cobalt complex was chosen because the Hipps group had demonstrated that Co ion in porphyrin and phthalocyanine complexes at negative bias appears very tall while replacing Co with Ni or Cu results in an apparent depression.42,50-52 In the absence of desorption of (TUP)Cu during the transformation process, only one (TUP)Co adsorbate is expected to be incorporated in every annihilated row. This was the case for the vast majority of rows. They concluded that desorption of (TUP)Cu within an island (kd3) occurs very rarely at 298 K.

In a series of recent papers, the Hipps group set out to use STM to make quantitative measurements of desorption rate and activation energy (Ed3) for the ordered monolayer of various forms of octaethylporphyrin (OEP) on gold and HOPG.42,42,53 Using the strong STM image contrast between CoOEP and either NiOEP or H2OEP, they were able to make tracer type measurements over temperatures up to 135°C. They first took real time movies of the surface of a mixed adlayer of CoOEP with NiOEP in contact with a phenyloctane solution containing both species in the same concentration as the relative surface coverage. Up to a temperature of 70 °C they saw no evidence for CoOEP being replaced by NiOEP, or vice versa. At temperatures up to 70 °C the surface composition was controlled by adsorption kinetics. Thus, quantitative determination of desorption kinetics required heating to well above 70 °C.

Desorption experiments between 90 and 135 °C were conducted by heating samples for a fixed time interval (usually 30 minutes) and then quickly cooling them to room temperature for STM imaging. Once a statistically significant number of images were obtained to allow determination of the change in surface concentration, the heating/cooling/imaging cycle was repeated. All of these operations were carried out in a heated STM solution cell, so the sample was always in physical contact with exactly the same solution. In order to extract rates from the coverage versus time data, one must account for MOEP replacing MOEP during the exchange process. They developed a kinetic rate expression that included like replacing like terms.53 In this model, the rate of appearance of YOEP on a complete monolayer covered by both XOEP and YOEP is equal to: \{the rate of disappearance of XOEP \times the probability that this vacant site will be filled by YOEP\} \text{–} \{the rate of disappearance of YOEP \times the probability that this vacant site will be replace by XOEP\}. This model assumes that the rates of adsorption are many orders in magnitude faster than the rates of desorption. The model also contains the assumption that the
probability of replenishing a vacant site with a particular tecton is the same as the mole fraction of that tecton in solution. The following equations result from the above model:

\[ \Theta_y(t) = \frac{X_x}{X_x + K_y^d (1 - X_x)} \left[ 1 - e^{-bX_k^X t \frac{X_x}{d}} \right] \]

(7)

Where, \( K_y^d = \frac{k_y^X}{k_y^Y} \) and \( b = \left[ 1 + \left( 1 - X_y \frac{K_y^d}{X_x} \right) \right] \)

Subscript or superscript \( x \) and \( y \) denote which porphyrin and, XOEP is assumed to be at 1 monolayer coverage at time = 0, \( \Theta_y(t) \) represents the surface coverage of the YOEP (tracer), \( k_y^Y \) denotes the desorption rate constant for YOEP, \( K_y^d \) is the relative rate of desorption of XOEP to YOEP, and \( X_x \) is the mole fraction of XOEP relative to total porphyrin in solution.

Assuming an Arrhenius type desorption, equation 7 can be expanded using \( k_y^X = k_y^O \frac{-\Delta E_y}{RT} \).

Thus, equation 3 can be re-written as follows:

\[ \Theta_y = \frac{1}{1 + \left( \frac{1 - X_y}{X_y} \right) \left( \frac{k_y^O}{k_y^X} \right) \left( \frac{\Delta E_y - \Delta E_x}{RT} \right) \left( 1 - X_y \right) e^{-\frac{\Delta E_y}{RT}} \left( 1 + \frac{\Delta E_y}{\Delta E_x} \right) + t} \]

(8)

Bhattarai learned that desorption of NiOEP from a fully covered Au(111) surface in phenyloctane depended upon the surface site, while CoOEP desorbed at about the same rate from everywhere on the Au(111).\(^{42}\) This is a good example of the advantage of using a molecular imaging technique since an ensemble average method would have missed the difference in mechanism for NiOEP relative to CoOEP. The desorption rate constant, \( k_{d3} \), for CoOEP on Au(111) was found to be \( 6.7 \times 10^{-5} \) s\(^{-1}\) at 135 °C. At 298 K the CoOEP monolayer on Au(111) would last years. By fitting equation 8 to the surface coverage versus temperature and time data for the CoOEP/H2OEP system, it was determined that \( k_{d3}(\text{CoOEP}) = 3.5 \times 10^{13} \) s\(^{-1}\), \( E_{d3}(\text{CoOEP}) = 126 \pm 5 \) kJ/mole, \( k_{d3}(\text{H2OEP}) = 3.5 \times 10^{13} \) s\(^{-1}\), and \( E_{d3}(\text{H2OEP}) = 126 \pm 5 \) kJ/mole.

Figure 4 shows the STM images of an initially CoOEP monolayer on HOPG after 30 minutes exposure to a phenyloctane solution having \( X_{\text{NiOEP}} = 0.80 \) at the indicated temperatures. Images of the inverse experiment (initial NiOEP monolayer exposed to \( X_{\text{CoOEP}} = 0.8 \) are similar but
inverted in contrast. While it will require statistical analysis to determine if there is cooperativity in these images, they do not show obvious positional preferences. The authors report no evidence of position dependent desorption of NiOEP from HOPG, although H$_2$OEP in phenyloctane on HOPG does show a preference for desorption from grain boundaries and step edges. Thus, the assumption of complete energetic equivalence of the three adsorbates cannot hold exactly. In fact, when CoOEP and NiOEP are paired on HOPG in phenyloctane, one finds $k^0_{d3}(\text{CoOEP}) = (7 \pm 6) \times 10^{12}$ s$^{-1}$ and $E_{d3}(\text{CoOEP}) = 1.05 \pm 0.3$ kJ/mole. Thus, a more accurate analysis would include cooperative adsorption in the rate expression. An alternative way to approach this would be to focus analysis in the regime where the coverage of tracer is less than about 0.2 so that there is small probability of a desorbing system being surrounded by tracers.

Figure 4. STM images (50 nm × 50 nm) of HOPG surfaces initially covered by CoOEP following a 30 min exposure to a solution of $X_{\text{NiOEP}} = 0.80$ at the indicated temperatures.

Acknowledgement

This material is based upon work supported by the National Science Foundation under CHE-1403989 and we gratefully acknowledge their support.

FURTHER READING:


