KINETICS AND THERMODYNAMICS AT THE SOLUTION/SOLID INTERFACE: A SCANNING TUNNELING MICROSCOPY STUDY

By

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To the Faculty of Washington State University:

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I was always taught that Teachers ("guru") are the most important people in life. Without them and their teachings everything in the universe will always appear to be disordered and never make sense. I am fortunate to have teachers who have guided and supported me all the way through my doctoral degree process.

I would like to express my deepest appreciation to my committee chair, Professor Kerry W. Hipps, who is the most brilliant and genuine scientist I know. I am fortunate to have learned from him the skills to be a complete scientific researcher. His patience towards me to grow as an individual and a researcher has been immeasurable. Without his guidance and persistent help, this dissertation would have not been anywhere near possible. I will forever be indebted to him.

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A detailed investigation on the nature of stability of surface structures of octaethylporphyrins (OEP) on graphite and Au(111) has been performed using scanning tunneling microscopy (STM). In-situ temperature dependent studies on the monolayer of these porphyrins show that the surface structure is stable up to 70 °C and that the molecules do not exchange between the surface and solution. Hence, at temperatures lower than 70 °C the monolayer is controlled by kinetics and the rates of desorption are extremely slow. In order to extract kinetic parameters ex-situ annealing was performed at higher temperatures. Substrate effects are studied by measuring and comparing the rates of desorption of CoOEP from 1-phenyloctane/graphite and 1-phenyloctane/Au(111) interfaces. Significant desorption from Au(111) starts at 135 °C whereas that from graphite starts at 90 °C and the rate of desorption from graphite is 2 orders of magnitude greater than from Au(111). In a different study to understand the effects of the central metal of the porphyrin on the adsorption strength, it was shown that the metal-free and metallated OEP
adsorb on graphite with similar energy. This shows that the adsorption strength strongly depends on the interaction between the porphyrin core and the graphite surface and that the interaction between central metal and graphite is minimal. In any case, the adsorption energy for OEP on to graphite and Au(111) ranges from 100 – 130 kJ/mol.

Substrate effects on oxygen binding to CoOEP adsorbed on graphite and on Au(111) were also studied using STM. At temperatures close to room temperature oxygen binds to CoOEP on graphite whereas it does not bind on Au(111) even at -25 °C. It was shown that the binding of oxygen to CoOEP-graphite is a dynamic equilibrium process. Temperature and pressure dependent studies were performed to extract thermodynamic quantities such as ΔG, ΔH, and ΔS values for the oxygenation process.
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Dedication

This dissertation is dedicated to my mother and father who have sacrificed a lot and supported me throughout all these years.
Chapter 1. Introduction

The study of organic self-assembled molecules (SAMs) supported on an atomically flat surface has attracted an enormous amount of attention. Rightly so, due to its actual and potential applications in modern technology, molecular electronics, spintronics, solar cells, catalysis, sensors and various other areas. Temperature dependent studies of these SAMs can provide vast amounts of information. They can yield kinetic and/or thermodynamic parameters such as rate constants, activation energies, entropy and enthalpy of adsorption of adsorbed species and/or even guest molecules. There has been a significant amount of temperature dependent studies (significantly different than room temperature) of these SAMs, but mostly performed under Ultra High Vacuum (UHV) conditions where it is impossible to establish equilibrium. For a given solution-solid (here after denoted as SS) pair, temperature dependent studies can lead to the discovery of new materials and phases. SAMs can be constructed to mimic the biological environment and can provide insights into complicated biological processes.

Since the invention of Scanning Tunneling Microscopy (STM) in 1981 by Gerd Binning and Heinrich Rohrer it has been possible to investigate processes at molecular and even at atomic scale. It has to be acknowledged that much of the success of STM has been achieved under UHV conditions. Although STM studies at the SS interface have been around for more than two decades, they embody only a small fraction of total literature based on STM. Temperature dependent study of the SS interface has special prominence since it mostly eliminates the extreme conditions that come along with operating under UHV systems. More importantly, SS studies can be conducted under conditions where bi-directional exchange between the surface and surrounding medium is possible and where equilibrium can be established. Of course, this is compensated with various
problems that affect STM’s ability to perform at the SS interface which is discussed in more detail later. For example, at higher temperatures, evaporation of solvent results in multilayer deposition and crystallization of solute molecules which significantly hamper STM’s ability to image at that temperature.

Variable temperature UHV STM represents a large part of the total STM literature. It has been used to study molecular structures and processes below liquid helium temperatures\textsuperscript{10} to temperatures above 850 K.\textsuperscript{11} Low temperature facilitates probing and high resolution imaging of molecular orbitals\textsuperscript{12} and making spectroscopic measurements.\textsuperscript{12,13} Similarly, high temperature studies allow one to observe various surface structures and phases.\textsuperscript{14} Small guest molecules binding to the MP and MPc have been reported.\textsuperscript{3,15} Reaction products have been characterized using UHV-STM.\textsuperscript{12,13} Surface diffusion rates, activation energies, and mechanisms have been reported using UHV-STM.\textsuperscript{16,17} Manipulation by the STM tip to form various complexes and nano architectures on surface have been studied.\textsuperscript{13} But why has there been little attention given to solution-solid STM?

Unlike UHV-STM, SS-STM doesn’t allow ultra-high resolution imaging of molecules on an atomic scale. One has to be cautious about the solvent-solvent, solvent-adsorbate, solvent-substrate and adsorbate-substrate interactions. The continuous and random movement of solvent particles interfere with acquiring the atomic resolution images which STM is renowned for. The ability to image with the solution present at ambient conditions in itself was quite an achievement. Earlier SS-STM studies (until 1995) dealt mostly with corrosion related studies of various surfaces in aqueous solutions.\textsuperscript{18,19} There were only a handful of studies on self-assembled systems, mostly long chain hydrocarbons\textsuperscript{20-23} and very few based on porphyrins.\textsuperscript{24} One of the earliest temperature dependent studies was performed on long alkanes (C\textsubscript{24}H\textsubscript{50} to C\textsubscript{192}H\textsubscript{386}) by Askadskaya and Rabe.\textsuperscript{25}
For C₁₄H₅₀ they reported that at room temperature a highly ordered lamellae structure is formed. As the temperature was increased to 45 °C, the lamellae structure disappears and disorder appears. Whereas, for the C₁₉₂H₃₈₆, ordered structures were only observed at 65 °C. Even though this work was accomplished in the year 1992, temperature dependent studies have not received prominence until recently and only a handful of studies are known.²²,²⁶-³³ A recent development in a variable temperature STM where the whole STM body is contained in an enclosed chamber allows for in-situ temperature dependent studies even for volatile solvents.³⁴ This minimizes and to some extent eradicates the problems faced by conventional STM and are listed below:

1. Thermal drift that arises due to differences in temperature between the STM head and the sample in systems where only the sample is heated is minimized.
2. As temperature increases, solvent evaporation and resulting multilayer deposition and/or crystallization does not occur.
3. Solvent vapor that eventually coats all exposed areas during the heating process can be easily cleaned.
4. As opposed to a conventional "in air" STM designs that have preamplifiers permanently mounted to the STM head, are not designed for high temperature operation, this new STM uses the preamplifiers outside the STM chamber.

There are two other major ways in which temperature dependent studies have been performed at the solution-solid interface:

*In situ heating/cooling:* For this configuration, substrates are mounted on top of a variable temperature stage. Temperature is controlled in the form of an integrated circuit controlling a peltier stage (for cooling or heating) or resistive heater and measured using a thermocouple.³⁵ The
sample is heated and held at the desired temperature for some time to equilibrate (also settles the thermal drifts) and images are taken at the same temperature.27-29

*Ex situ heating:* There are two minor variations in this category. (a) The sample is deposited on the substrate first and then immersed into the respective solvent heated to the desired temperature for some time. The sample is taken out of the heated solvent and allowed to equilibrate to room temperature and imaged.29 (b) The second technique uses the heating stage as the heater. The sample is deposited and heated to the desired temperature for a specified time then it is allowed to equilibrate to room temperature and imaged.32,33

In order for SAMs to be effective in its use in modern electronics, one has to acquire a fundamental understanding of the interface between the SAMs and the surface. The driving force, whether it be kinetic, thermodynamic, or both has to be understood in detail and this requires temperature dependent studies of SAMs. Distinguishing these driving forces can be challenging and there have been reports where a kinetically controlled system is misinterpreted and treated as an equilibrium problem.36,37 Although, the authors later realized that their thermodynamic treatment was wrong and reanalyzed their work and showed that it was a kinetic system.38 A recent work by Jahanbeckam et al. has highlighted this importance where a kinetic product can easily be misinterpreted and treated as an equilibrium problem to deduce thermodynamic parameters.39

While solvents play a crucial role in the adsorption/desorption at the SS interface, one also has to consider solvent incorporation in determining the surface morphologies. Solvent molecules can integrate itself with the adsorbate to produce different phases at different concentrations and temperature.28,40 Blunt et al. showed that by varying the temperature and concentration one can achieve two equilibrium phases, linear and porous.28 The transition from linear (dense) to porous structures arises due to the co-adsorption of solvent molecules along with the adsorbates (DBA
molecules). Furthermore, thermodynamic treatment to measure the enthalpy and entropy changes for the phase transition was performed. For surface processes where more than one phase is present, this work is perhaps the most complete in terms of explaining and estimating thermodynamic parameters. Although, one can still question regarding the equilibrium status of both phases and it is possible that these phases are not in equilibrium between the surface and solution.

For surface processes that occur in a reasonable time frame (few seconds to minutes), sequential STM imaging of the same area can be useful in determining whether the surface is a thermodynamic or a kinetic product. Using this sequential STM imaging technique, Friesen and co-workers successfully showed that oxygen binding to CoOEP at the 1-phenyloctane/HOPG interface is an equilibrium process.\textsuperscript{31} On the other hand, sequential STM imaging studies on porphyrins have shown that the monolayer formation on HOPG and Au(111) are predominantly kinetically controlled.\textsuperscript{32,33,41,42}

One of the difficulties in determining a thermodynamic and kinetic product with conviction is that, for a single component system the surface structures before and after the molecular desorption/adsorption remains unchanged. And thus, it is often assumed as a thermodynamic system. Other times, structures may not be accessible at temperatures and concentrations studied. For exchange processes that occur within a reasonable time frame of few seconds to few hours, one can use a two-component system comprised of two chemically very similar molecules that appear different under STM. This way one can analyze the sequential STM images of a mixed layer and track the changes if any in the monolayer with time. Thus, many two-component systems have been appearing in literature to address the relative stability of the adlayer at the SS interface.\textsuperscript{32,33,36-39,41,42}
When one incorporates solvent, the monolayer formation process becomes complicated by the interactions with solvent molecules. Song et al\textsuperscript{43} show that one can estimate the enthalpy change for the formation of monolayer by using an “adapted Born-Haber” cycle which is shown in Figure 1-1.

\textbf{Figure 1-1.} “Adapted Born-Haber” cycle for the monolayer formation.\textsuperscript{43}

Here, $\Delta H_{\text{sol-monolayer}} = \Delta H_{\text{sol-crystal}} + \Delta H_{\text{crystal-vacuum}} + \Delta H_{\text{vacuum-monolayer}} + \Delta H_{\text{wetting}}$. Several of enthalpy changes involved in this process can be determined using standard experimental techniques. $\Delta H_{\text{sol-crystal}}$ is determined as the enthalpy of dissolution ($\Delta H_{\text{crystal-sol}} = -\Delta H_{\text{sol-crystal}}$) that can be measured using temperature dependent UV-vis studies.\textsuperscript{43,44} $\Delta H_{\text{crystal-vacuum}}$ is the sublimation enthalpy and can be measured using temperature-dependent desorption experiments.\textsuperscript{43} $\Delta H_{\text{vacuum-monolayer}}$ is determined by the temperature programmed desorption (TPD) of monolayer to vacuum ($\Delta H_{\text{monolayer-vacuum}}$).\textsuperscript{43} $\Delta H_{\text{wetting}}$ consists of enthalpy changes due the solvation of the
adlayer and the bare surface. This enthalpy change is usually small and difficult to accurately measure experimentally and computational techniques are used to estimate this enthalpy change.\textsuperscript{43} In this dissertation, STM will be used to directly calculate $\Delta H_{\text{monolayer-sol}} (-\Delta H_{\text{sol-monolayer}})$ for octaethylporphyrins by performing temperature dependent desorption studies.

This study focuses on understanding the kinetics and thermodynamics and deducing rate and equilibrium parameters for adsorbates on HOPG, and Au(111) surfaces. SAMs of porphyrins are used as model systems to understand these phenomena. This work primarily focuses on the quantitative comparisons of rates of desorption and desorption energies of porphyrins from HOPG and Au(111) surfaces, and metalated versus non-metalated porphyrins from HOPG. These studies provide direct insights into the effect of substrates and the central metal ion of the porphyrin on the adsorption strength.

Porphyrins are highly versatile molecules that are found in nature and play a major role in photosynthesis and oxygen binding in hemoglobin. Hence, understanding small molecules binding to porphyrins will help us better understand life. Porphyrins are also capable of absorbing visible light which makes them great candidates for use as a sensitizer in solar cells.\textsuperscript{45-47} In a porphyrin, the metal center, eight beta, and four meso positions can be substituted and these modifications can be synthesized in almost any combination which could change the chemistry of the porphyrins and one can manipulate the adsorption/desorption phenomena as desired and/or required. In addition, the porphyrin core is nearly planar in geometry, symmetric, and is more likely to lie flat on surfaces. This allows one to minimize the variables and attribute the studied effects to either the porphyrin core or the substituent groups. These versatilities allow one to design SAMs on surfaces with a wide range of possibilities.
Cobalt(II) octaethylporphyrin (CoOEP), nickel(II) octaethylporphyrin (NiOEP), and octaethylporphyrin (H₂OEP) are used as adsorbates and 1-phenyloctane as solvent in this study. These OEP molecules are very similar in size and differ only in the occupation at the center of the porphyrin core. The choice of molecules and solvent are extremely important especially when two-component temperature dependent studies are performed. 1) If both molecules have similar rates of adsorption and desorption then the quantification of data is less complex and thus the results can be interpreted easily. 2) Both the molecules should appear distinctly different under STM. 3) The choice of solvent should be such that the solubility of each OEP is similar and the vapor pressure should be low in order to maintain the SS interface at higher temperatures. With similar solubility and heats of sublimation, the intermolecular interactions between solute and solvent can be approximated to be the same, thus minimizing any discrepancies in the measured rate parameters that arise due to solvent. Heats of sublimation, $\Delta H_{\text{sublimation}}$ for OEP’s are given in the range of $96 \pm 12 \text{ kJ/mol}^{48}$. Solubility of CoOEP, NiOEP, and H₂OEP in phenyloctane were measured and found to be 0.228, 0.319, and 0.06 g/L. Although the solubility values are different, the concentrations used are well below the solubility limit and thus the solvent-solute interactions can be approximated to be the same.

This dissertation focuses on using STM as a sole tool in determining quantitative rate and thermodynamic parameters. This work digresses from the traditional use of microscopy for qualitative analysis to quantitatively assessing single molecule level kinetics and thermodynamics, adding a new dimension to STM’s ability. Visualization of single molecule level chemistry of oxygen binding to CoOEP is achieved. Thus, this work provides not only a strong fundamental understanding of processes that occur at the solution/solid interface but also provides techniques that will form a foundation for future research studies.
Chapter 2. Theory of Techniques: Scanning Tunneling Microscopy

Majority of the experiments performed in this thesis are based on a technique called Scanning Tunneling Microscopy (STM). STM has been widely used to study surface structures, obtain spectroscopic signals, and to probe molecular orbitals. Due to its ability to resolve structures on an atomic scale, STM has become one of the most important tools for exploring the nano-scale world. When one considers nano-scale studies of the solution/solid interface, STM is perhaps the most used and informative instrument.

As the name suggests, STM works based on the tunneling phenomenon which is derived purely from Quantum Mechanics (QM). QM is the study of atomic and sub-atomic particles. It helps explain observables that cannot be explained by classical mechanics. According to QM, all particles have wave-like properties and hence can be described using a wave function, \( \Psi \). This wave function consists of all the information there is to know about the system and is described by the Schrödinger equation, the fundamental equation of QM and is given below:

\[
\hat{H} \Psi = E \Psi \quad \text{(eq 2-1)}
\]

where \( \hat{H} \) is the Hamiltonian operator, \( E \) is the total energy (kinetic and potential) of the system. It can be rewritten in one-dimension as,

\[
\hat{H} \Psi = -\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + V(x) \Psi = E \Psi \quad \text{(eq 2-2)}
\]

Here, we will use these equations to understand the origin of tunneling. In order to understand this, one has to have a basic knowledge regarding the famous “particle in a box” (PIB) problem.

In a PIB, a particle or in our case an electron is confined within two infinitely high potential walls in a one dimensional box and the potential energy within the box is zero. Figure 2-1 is a representation of this one dimensional PIB.
Figure 2-1: Pictorial representation of Particle in a box.

For regions where $V = \infty$, the wave function, $\Psi = 0$. For $V = 0$, the Schrödinger equation becomes a simple differential equation as shown below,

$$\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = E\Psi \quad \text{(eq 2-3)}$$

and solving this gives us,

$$\Psi = \sqrt{\frac{2}{a}} \sin \left( \frac{n\pi x}{a} \right) \quad \text{(eq 2-4)}$$

Now, let us consider a slightly modified PIB. Here, we will introduce a finite potential barrier between the two infinite potential walls. Figure 2-2 represents this modified PIB problem.
Figure 2-2: Modified PIB. Region I and III represents $V = 0$, and region II represents $V > E$.

Regions I and III are similar to the PIB in a 1-D box as shown above in eq 2-3, whereas for region II, a different wave function is generated and can be written as follows:

Region I:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi_1}{dx^2} = E\Psi_1$$  \hspace{1cm} (eq 2-5)

Region II:

$$-\left(\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V\right)\Psi_2 = E\Psi_2$$  \hspace{1cm} (eq 2-6)

Region III:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi_3}{dx^2} = E\Psi_3$$  \hspace{1cm} (eq 2-7)

Solving these with appropriate boundary conditions, we get

Region I:

Boundary conditions: (i). $\Psi_1(-a)=0$ and (ii). $\Psi_1(0)=\Psi_1'(0)$

$$\Psi_1 = Ae^{\frac{2\pi x}{\hbar}} + Be^{-\frac{-2\pi x}{\hbar}}$$  \hspace{1cm} (eq 2-8)
Region II:

Boundary conditions: (i). $\Psi_I(0) = \Psi_{II}(0)$, (ii). $\Psi_I'(0) = \Psi_{II}'(0)$, (iii). $\Psi_{II}(d) = \Psi_{III}(d)$, and (iv). $\Psi_{II}'(d) = \Psi_{III}'(d)$

\[
\Psi_{II} = Ce^{\frac{2\pi \sqrt{2m(E-V)}}{\hbar}} + De^{-\frac{2\pi \sqrt{2m(E-V)}}{\hbar}} \tag{eq 2-9}
\]

Region III:

Boundary conditions: (i). $\Psi_{II}(d) = \Psi_{III}(d)$, (ii). $\Psi_{II}'(d) = \Psi_{III}'(d)$, (iii). $\Psi_{III}(a+d) = 0$

\[
\Psi_{III} = Ee^{\frac{2\pi \sqrt{2mE}}{\hbar}} + Fe^{-\frac{2\pi \sqrt{2mE}}{\hbar}} \tag{eq 2-10}
\]

The behavior of $\Psi_I$ and $\Psi_{III}$ are very similar but $\Psi_{II}$ represents an interesting problem. Classically, region II is forbidden and hence a particle can’t exist here whereas, in the above QM analysis the probability of finding the particle is non-zero and is exponentially dependent. This phenomena is known as “tunneling”. The probability distribution of the particle is given in figure 2-3.

![Box](image)

**Figure 2-3:** Probability distribution of the particle in the modified PIB.
The tunneling current, $I$ is proportional to the barrier width, $d$ and is given by,

$$I \propto e^{-2\kappa d} \quad (eq \ 2-11)$$

where $\kappa$ is related to the local work function. In an STM, region I and III in figure 2-3 represents the tip and sample, and $d$ represents the separation distance between the two. Due to the exponential dependence of the tunneling current with the distance of separation between the tip and sample, STM can resolve structures in an atomic scale if the tip ends in single atom as the greatest protrusion.

While 1-D PIB gives a decent approximation for the tunneling behavior, it is not sufficient to explain the workings of STM adequately. One has to consider the density of states for the sample, the STM tip, and the tunneling transmission probability of the electrons. Hence, all these factors are considered in the Wentzel-Kramers-Brillouin (WKB) approximation and can be explained as follows:

$$I = \int_0^{eV} \rho_s(r,E)\rho_t(r,\pm eV \mp E)T(E,eV,r)dE \quad (eq \ 2-12)$$

where $\rho_s(r,E)$ is the density of states of the sample, $\rho_t(r,\pm eV \mp E)$ is the density of states of the tip, $r$ is the position of the tip, $E$ is the energy with respect to the Fermi level, $eV$ is the applied bias voltage, and $T(E,eV,r)$ is the tunneling transmission probability function.

In an STM, a small bias voltage is applied between the tip and the sample to allow the electrons to tunnel. Without the applied bias, the fermi levels of the sample and tip are at the same energy and no net tunneling occurs. When a bias (positive or negative) is applied between the two surfaces, electrons tunnel from tip to sample or vice-versa. Depending on the applied bias one can probe HOMOs and LUMOs of the sample and study its spectroscopic characters.
Figure 2-4: Energy level diagrams of tip and sample for (a) $V = 0$, fermi levels are aligned for both the tip and the sample, (b) $V > 0$, electrons tunnel from HOMOs of sample to the tip, and (c) $V < 0$, electrons tunnel from tip to the LUMOs of the sample.

There are two major ways of operating an STM. 1) Constant height mode and 2) constant current mode and are represented in figure 2-5. In constant height mode, STM tip scans the surface by setting a constant voltage and the image represents the variation in tunneling current with position. In constant current mode, the tunneling current is set to a predetermined value and as the tip scans the surface the difference between the measured tunneling current and the desired current is adjusted by changing the height of the tip with a feedback loop. In this mode, the STM “height” is the change in z-voltage needed to maintain constant current corrected for the nm/V sensitivity of the height adjusting device. Among these methods, constant current is the most widely used for STM operation.
Figure 2-5: Representation of constant height and constant current modes in an STM.
Chapter 3. A Single Molecule Level Study of the Temperature-Dependent Kinetics for the Formation of Metal Porphyrin Monolayers on Au(111) from Solution

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3.1 Abstract

Scanning tunneling microscopy was used to make the first molecular scale measurements of the temperature dependence of composition of an adlayer at the solution–solid interface. We conclusively demonstrate that metal porphyrins adsorb very strongly on Au(111) at the solution solid interface such that the monolayer composition is entirely kinetically controlled below about 100 °C. The barrier for desorption is so great in fact that a temperature of 135 °C is required to induce desorption over a period of hours. Moreover, cobalt(II) octaethylporphyrin (CoOEP) and NiOEP desorb at different rates from different sites on the surface. We have measured the rate constant for desorption of CoOEP into phenyloctane to be $6.7 \times 10^{-5}$ /s at 135 °C. On the basis of these measurements, an upper bound can be set for the desorption rate of NiOEP into phenyloctane as $6.7 \times 10^{-4}$ /s at 135 °C. For solutions of the order of 100 μM in NiOEP or CoOEP, a dense monolayer is formed within seconds, and the adsorption rate constants fall within 40% of each other. The structures of NiOEP and CoOEP monolayers are essentially identical, and the molecular spacing for both can be described by $A = 1.42 \pm 0.02$ nm, $B = 1.32 \pm 0.02$ nm, and $\alpha = 57^\circ \pm 2^\circ$. The solubility of CoOEP and NiOEP in phenyloctane at room temperature was measured to be 0.228 and 0.319 g/L, respectively.
3.2 Introduction

The solution–solid interface is of growing importance to technology. While it has always been critical for processes such as catalysis, spin-casting, lubrication and wear, and crystallization, new demanding applications are appearing. A particularly contemporary example is inkjet printing of organic electronic components. To advance these technologies, science must provide an ever increasing understanding of the fundamental processes that occur at the solution–solid boundary.

Until the late 1980s, all molecular scale studies of the solid/solution interface were ex situ; surfaces were exposed to solution, the surface was dried (often put into ultra high vacuum), and then studied. With the advent of the scanning tunneling microscope (STM), it became possible to make molecular and even atomic scale measurements at the solution–solid interface at room temperature. Because of the STM, there has been a dramatic increase in our understanding of molecular process at the solution–solid interface at room temperature. As wonderful as these studies are, they are limited. They probe only a very narrow range of the possible processes but completely ignore what happens when the solution is hotter or colder than room temperature. The ability to see molecules ordering and reordering on a surface at different temperatures provides access to new materials, phases, reaction rates, reaction mechanisms, and the kinetics and thermodynamics of these surface processes. Studying the relative distribution and structure of bimolecular phases as a function of temperature allows one to determine relative adsorption energies and entropies. Temperature dependent imaging of film growth allows one to find the ideal temperature and time for a given commercial process. Unlike the case of STM in vacuum, where variable-temperature studies abound, there have only been a handful of variable-temperature STM studies at the solution–solid interface. There are both conceptual
and practical reasons why this has occurred. Conceptually, it was commonly believed that noncovalent ordering at the solution–solid interface is a dynamic process. It was thought that molecule level imaging of physisorbed species from solution was a marginal thing at room temperature because the thermal energy was close to the ordering and/or desorption energy. There is now evidence that STM can be used to image well-defined structures at the solid–solution interface at elevated temperatures. Detailed STM studies of surface structures and chemical processes at the solution–solid interface as a function of temperature are just becoming available.

In this Article, we use solution phase STM to investigate the temperature dependence of the rate constants that determine the formation of an ordered monolayer of cobalt(II) octaethylporphyrin (CoOEP) on Au(111) when deposited from a subsaturation solution in phenyloctane. It is critical to note here that these studies are occurring at the unsaturated solution–solid interface, not just the liquid–solid interface. There have been numerous studies of porphyrins adsorbed on metal or HOPG surfaces from organic solvents, and then studied in aqueous electrochemical environments. In aqueous environments, the porphyrins studied here and by Itaya are totally insoluble. Thus, there is no possibility of desorption from the surface unless the chemical nature or oxidation state of the porphyrin is changed during the electrochemical process.

To study the solution–surface equilibrium, we will use the replacement of CoOEP with NiOEP as a tracer for the desorption process. Thus, we will focus on the kinetics and process of adsorption and desorption of these two metal porphyrins on Au(111). Prior to this study, the porphyrins and their close relative, the phthalocyanines, were extensively investigated as adsorbates on metal surfaces in UHV. Mixture of cobalt and nickel complexes have also been
studied in UHV, and it is now well-known that they can be easily differentiated in the STM image. There have also been a number of reports on porphyrins or phthalocyanines adsorbed on Au and HOPG from solution at room temperature. Mixtures of porphyrins and phthalocyanines adsorbed from solution have been studied on HOPG at room temperature, with the most relevant reports being those of Miyake and co-workers.

In their early reports, Miyake and co-workers measured the ratio of metalated porphyrins and free base porphyrin both on the HOPG surface and in solution at room temperature. They found a nonlinear relationship between the solution and surface concentrations. They assumed equilibrium between the surface and solution and used the concentration variation to derive the difference in free energies of adsorption of the metalated and free porphyrins; they called the resulting value $\Delta\Delta G$. In 2008, they performed a similar experiment with a Zn porphyrin complex and free base, and also found a nonlinear relationship between fraction in solution and fraction on the surface of HOPG. In that paper, however, they realized that the assumption of equilibrium was not justified by any data, and they refrained from associating the preferential adsorption with a $\Delta\Delta G$ value. They clearly stated that both kinetics and thermodynamics could be playing a role and that kinetics might be dominating.

Here, we will consider the solution phase adsorption of two very similar metalated porphyrins on Au(111). At room temperature, the adsorptive formation of a monolayer occurs very quickly and is consistent with either similar rates of adsorption or similar free energies of adsorption, or both. By observing the detailed atomic distribution of NiOEP and CoOEP on the surface with time, we find that the concentration of the monolayer is entirely controlled by kinetics. We will show that the desorption rate is almost nonexistent at room temperature, and even at 135 °C the rate is much slower than for many covalently bound thiols. The temperature-dependent
experiments reported here make it possible to conclusively show that noncovalent interactions can lead to extremely tight binding of adsorbates at the solution–solid interface.

### 3.3 Experimental Section

2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine cobalt(II) [CoOEP] and 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine nickel(II) [NiOEP] were purchased from Aldrich and Frontier Scientific, respectively. Phenyloctane (98%) was purchased variously from Aldrich, Alfa Aesar, and Fisher Scientific. All of the phenyloctane purchased from the above three companies was subjected to further purification. UV–vis spectra of solutions of CoOEP in undistilled phenyloctane provided as above had two Soret bands at 392 and 420 nm instead of a single expected 392 nm band. To get rid of the impurity complexing with CoOEP, phenyloctane was distilled over Al2O3 (90% Al2O3, 9% H2O; Alfa products). After several distillations, the UV–vis spectra of CoOEP in this solvent indicated that the impurity had been reduced to less than 10 ppm.

UV–vis studies were carried out using a Perkin-Elmer model 330 spectrophotometer with 0.1578 cm path length cuvettes. UV–visible spectroscopy on saturated and filtered solutions of porphyrins in phenyloctane was used to determine solubility at room temperature. The measured solubility of CoOEP in phenyloctane was 3.9 × 10\(^{-4}\) M or 0.228 g/L, and that of NiOEP was 5.4 × 10\(^{-4}\) M or 0.319 g/L. The highest concentration solution used in these experiments was 1.2 × 10\(^{-4}\) M, and most were less than 1.1 × 10\(^{-4}\) M.

Au(111) substrates were prepared by epitaxial growth of Au on mica using the vapor deposition technique. Au (99.999%) and mica were purchased from Cerac Inc. and Ted Pella Inc., respectively. Freshly made Au substrates were hydrogen flame annealed and imaged under STM
to ensure that surface reconstruction lines could be seen. Samples were deposited only on Au substrates, which had distinct reconstruction lines as observed in the STM images. STM images were recorded using a Molecular Imaging (now Agilent) Pico 5 STM equipped with a scanner capable of imaging a maximum area of 1 μm² and having an overall current sensitivity of 1 nA/V. The Agilent environmental chamber was used for all experiments, and an argon atmosphere was maintained. STM tips were primarily prepared by cutting and sometimes (about 15%) electrochemically etching the Pt₀.₈Ir₀.₂ wire bought from California Fine Wire Company. The best etched and cut tips gave similar results, but the cutting process yielded more high-quality images faster. Images were typically obtained in constant current mode at a sample potential of −0.7 V and a tunneling current of 20 pA. Images of sizes ranging from 20 × 20 to 40 × 40 nm² were collected at a scan rate of 4.7 lines/s, giving a total image time of just under 2 min. Images larger than 40 × 40 nm² were scanned at a slower scan rate of 3.3–3.9 lines/s, giving a total image time of roughly 2.5 min. The temperature of the sample was controlled by a variable-temperature hot stage using a Lakeshore 330 autotuning temperature controller. The Agilent supplied environmental chamber was purged with 99.996% Ar at all times. Before imaging, samples were allowed to sit for 30 min to an hour inside the environmental chamber purged with Ar at 2.5 standard cubic feet per hour (scfh). During imaging, Ar was continuously purged at 0.5 scfh.

Solutions of CoOEP and NiOEP were prepared by dissolving sufficient amount of the respective compounds in phenyloctane. Solution concentrations of 1.2 × 10⁻⁴ M CoOEP and 1.1 × 10⁻⁴ M NiOEP were prepared separately. The same stock solutions were used for all of the experiments performed by STM. A custom-made solution cell sample holder was used to accommodate large volumes of solution in contact with the Au surface (up to 100 μL sample). Large volumes of solution with low surface area were crucial to minimize evaporation during
multiple heating operations on the same sample at 135 °C. During the sample heating process for the kinetic experiments, the temperature of the sample was ramped from room temperature at a rate of 5 °C per minute, allowing the sample to reach 135 °C in 30 min. The sample then was held at 135 °C for the desired time period. After the desired period at 135 °C, samples were allowed to cool to room temperature by turning the heater off and were then allowed to equilibrate for at least 90 min prior to recording any images. All STM images were background subtracted using SPIP image processing software.

3.4 Results and Discussion

Figure 3-1: Constant current STM images of the interface formed between a solution of a pure MOEP complex in phenyloctane and the Au(111) surface. The left image is of CoOEP and the right is of NiOEP. Cross sectional apparent height data is also shown.
Figure 3-1 contrasts the constant current STM images seen from a monolayer of CoOEP (120 μM) and of NiOEP (110 μM) on Au(111) formed at the solution–solid interface with a solution of the appropriate porphyrins in phenyl octane at 25 °C. Also shown in the figure are cross sections and the structure of the complex. Note that the solutions had been deoxygenated and that all data were acquired under argon. As is expected from studies in UHV, the cobalt center of the CoOEP appears very high at the bias voltage used, while the nickel atom appears as a depression. It should be noted that the localization of the central peak (or depression) depends upon tip sharpness, so the CoOEP sometimes appears as a wider bright region. The NiOEP always appears shorter (dimer) than CoOEP for all tips used.

Figure 3-2: Effect of relative CoOEP to NiOEP solution concentration on the constant current STM images obtained. STM images obtained under set point conditions of -0.7 V sample bias and 20 pA.
When a Au(111) surface is exposed to a solution containing a mixture of CoOEP and NiOEP in phenyloctane, the monolayer formed contains a mixture of the two species. For example, Figure 3-2 contrasts the STM images seen with three different relative concentrations at 25 °C. As can be seen from both the images and the cross sections, NiOEP is easily distinguished from CoOEP, and the surface concentration of CoOEP diminishes as its relative solution concentration decreases. The experiments depicted in Figure 3-2 were repeated for five different concentrations, and many images were collected to ensure statistical significance. The ratio of NiOEP molecules on the surface to the total number of porphyrin molecules is defined either as $\Theta_{\text{NiOEP}}$, or just as $\Theta_N$ for brevity in later equations. $X_{\text{NiOEP}}$ (or $X_N$) is the ratio of molar concentration of NiOEP to the total molar concentration of both CoOEP and NiOEP in solution. Using these variables, the adsorption isotherm at 25 °C was obtained and plotted in Figure 3-3. Note that $\Theta_{\text{NiOEP}}$ and $X_{\text{NiOEP}}$ are essentially equal, suggesting that there might be a simple ideal equilibrium between surface and solution with the free energies of CoOEP and NiOEP being the same in each phase. This interpretation is wrong.

**Figure 3-3:** Mole Fraction of NiOEP on Au(111) versus in solution at 25 °C.
Our first indication that this was not an equilibrium system at 25 °C came as we counted molecules in sequential STM images. For example, images (Figure 2-4) taken at t, t + 150 s, and t + 300 s are shown with two points of relative reference marked. The red circle surrounds a vertical dimer, and the white circle identifies a vacancy in the monolayer. Taking these two reference points, it is very clear that no CoOEP molecule moves on or off the surface in the full time frame of the experiment. In viewing all of our data taken at 25 °C, at many concentrations, and at different times, we never saw any indication of any MOEP molecule leaving a monolayer once it was formed. Experiments were then conducted with the sample heated to various temperatures and image at those temperatures. Representative images for 25, 50, and 70 °C are shown in Figure 3-5. Over the entire temperature range, all of the images could be described by \( \Theta_N = 0.82 \pm 0.03 \). It should be noted that \( X_N = 0.79 \pm 0.04 \) for this data set.

**Figure 3-4:** Sequential STM images taken from a monolayer formed from contact with a solution having \( X_N = 0.79 \). Images are taken about 2.5 minutes apart in time. Set point was -0.7 V and 20 pA.
Figure 3-5: Constant current STM images taken from monolayers formed from contact with a solution having $X_N = 0.79$ at different temperatures. These are in situ images acquired at the temperatures indicated. Set point was -0.7 V and 20 pA.

Clearly, in the temperature range up to 70 °C, the adlayer is either not in chemical equilibrium with the solution, or both the $\Delta G$ and the $\Delta S$ of adsorption (and thus the $\Delta H$) are all the same for CoOEP and for NiOEP. This latter possibility seems unlikely, and the fact that no change is seen in the detailed positions of molecules in the adsorbed layer with time at 25 through 70 °C also argues against an equilibrium model. To be certain, however, we modified our experimental procedure to allow us to observe the rates of desorption of the MOEP species and to perform our measurements reliably on a time scale much longer than is possible to image one particular region on a surface.

A dense monolayer of a single MOEP was first created. The solution above it then was changed to a mixture of both CoOEP and NiOEP with the species NOT present in the original monolayer in excess in solution. If any exchange occurs between solution and surface, it will become apparent because of the change in molecular contrast. Because we are looking for any
change on a statistical basis, there is no need to monitor the same area with time, and long periods of time can be used. An example of the low temperature results is given in Figure 3-6 where some of the 25 °C images are shown. At 25 °C it is very clear that, even on a time scale of hours, no exchange is occurring, and therefore no desorption is occurring from the surface once a monolayer forms. Similar results were obtained at temperatures approaching 100 °C. Obvious exchange in a 1 h period was not seen until about 120 °C. On the other end of the time scale, following a pure solution with a mixture after only a few seconds exposure yielded exactly the same results, a single species monolayer. Thus, the monolayer is formed in about 1–10 s. At 135 °C, the rate of desorption was such that significant changes in the monolayer composition could be seen in about 2 h. We therefore focused on this temperature to determine the rate of desorption. We initially thought the measurements would be symmetrical. That is, we thought that the CoOEP desorption in the presence of excess NiOEP would be qualitatively similar to the desorption of NiOEP in the presence of CoOEP. This was not correct. As can be seen in Figure 3-7, when NiOEP is initially replaced by CoOEP at 135 °C, the nickel species preferentially desorbs from the step edges and along reconstruction lines. On the other hand, at the same temperature, the CoOEP desorption does not appear to be site specific. The remainder of this Article will focus on the simpler CoOEP desorption problem and leave analysis of the NiOEP desorption for a subsequent study.
Figure 3-6: STM images obtained at 25 °C. a) Solution of NiOEP in phenyloctane in equilibrium with Au(111); b) monolayer from a exposed to a solution having $X_N = 0.31$ for a period of 2 hours. c) Solution of CoOEP in phenyloctane in equilibrium with Au(111); b) monolayer from c exposed to a solution having $X_N = 0.88$ for a period of 24 hours. Set point was -0.70 V sample bias and 20 pA tunneling current.
Figure 3-7: STM image of the MOEP in phenyloctane / Au(111) interface after 30 minutes exposure to mixed composition solution at 135°C. a) Initially full monolayer of NiOEP exposed to $X_N = 0.31$ solution for 30 min. b) Initially full monolayer of CoOEP exposed to $X_N = 0.88$ solution for 30 min. $[\text{CoOEP}] = 1.4 \times 10^{-5}$ M and $[\text{NiOEP}] = 9.7 \times 10^{-5}$ M. Set point was -0.70 V sample bias and 20 pA.

Monolayer samples of CoOEP were prepared and imaged by STM. They were then exposed to a solution of NiOEP and CoOEP in phenyloctane ($X_N = 0.88$) at 135 °C for varying lengths of time. After each time interval, the sample was cooled quickly to room temperature and repeatedly measured to obtain statistically significant values for the relative NiOEP coverage. Figure 3-8 displays the results of measurements ranging from 0 to 180 min. We would expect to see the greatest systematic error associated with insufficient time at temperature in the short time sample, and we do see such a trend.
What is immediately apparent in Figure 3-8 is that even after 3 h of exposure to a solution at 135 °C, $\Theta_{\text{NiOEP}}/X_{\text{NiOEP}}$ is only about 0.5. Thus, the desorption of CoOEP from Au(111) is a very sluggish process even at this high temperature. To make quantitative statements about the rates, a model is required. In the next section, we introduce such a model.

It is clear from the data presented above that the rate of formation of a monolayer is many orders of magnitude faster than the rate of desorption. Thus, our model will be based on the severability of these two problems. Let us first define the probability that a particular vacant site in the monolayer will be filled by a NiOEP from solution; call this $P_N$. Define it as:

$$P_N = \left[ \frac{d\theta_N}{dt} \frac{d\theta_N}{dt} + \frac{d\theta_C}{dt} \frac{d\theta_C}{dt} \right]$$

(eq 3-1)
where the measurements are made during the formation phase of the monolayer and reflect the high speed adsorption kinetics.

\[
\frac{d\theta_N}{dt} = k_N^a X_N^a M (1 - \theta)
\]

where \(k_N^a\) is the rate constant for the adsorption of NiOEP, \(X_N\) is the mole fraction of NiOEP in solution, \(M\) is the total molarity of porphyrins in the solution, and \(\theta_N\) is the fractional coverage by NiOEP. Similarly, \(\frac{d\theta_C}{dt} = k_C^a X_C^a M (1 - \theta)\), for CoOEP, and \(\theta = \theta_N + \theta_C\). Combining these, we find that \(\theta = (1 - e^{-kt})\), where \(\overline{k} = (k_N^a X_N^a + k_C^a X_C^a) = k_N^a X_N + k_C^a (1 - X_N)\). Substituting this back into the rate equation of NiOEP adsorption, we find that

\[
\theta_N = (1 - e^{-\overline{k} M t}) \left( \frac{k_N^a X_N}{\overline{k}} \right) \quad \text{(eq 3-2)}
\]

Let us digress for a moment to consider the application of eq 2-2 to the adsorption isotherm shown in Figure 3-3. Equation 3-2 can be used to predict the relative coverage observed at low temperatures where the desorption rate is very slow because at long times, \(\theta_N = \left( \frac{k_N^a X_N}{\overline{k}} \right)\). Note that at low temperatures and for a complete monolayer, \(\theta_N\) depends only upon the ratio of the adsorption rates and upon the mole fraction in solution. We have applied this equation to the data at 25 °C to determine an envelope in which the rates of adsorption must lie. Defining \(\kappa^a\) as the ratio of the adsorption rates, and observing the plots in Figure 3-3, it is clear that the rates of adsorption of NiOEP and of CoOEP are within 40% of each other. It is important to take a moment here and to realize that the above rates are the effective overall rates for formation of a monolayer.
These need not be the correct rates for early stages of adsorption where there is little, if any, intermolecular interaction.

Returning to our original problem, we can combine the above results to find that:

\[ P_N = \left[ \frac{d\theta_N}{dt} \right] = \frac{k^d_N X_N}{k^c_C X_C + k^d_N X_N} = \frac{k^d_N X_N}{k} \quad \text{(eq 3-3)} \]

We now turn to the much slower desorption process. The rate of appearance of NiOEP on a full monolayer containing both Ni and Co sites will be equal to: (the rate of disappearance of Co times the probability that the site will be filled by Ni) − (the rate of disappearance of Ni times the probability that it will be replaced by Co). Thus:

\[ \frac{d\vartheta}{dt} = k^d_C (1 - \vartheta) P_N - k^d_N \vartheta (1 - P_N) \]
\[ = k^d_C P_N + \vartheta (k^d_N P_N - k^d_C P_N - k^d_N) \quad \text{(eq 3-4)} \]

Assuming that the rates of adsorption for NiOEP and CoOEP are the same (a good assumption based on Figure 3-3), \( P_N = X_N \), and eq 2-4 can be written as \( \frac{d\vartheta}{dt} = k^d_C X_N (1 + a \vartheta) \), where

\[ a = \left[ \frac{k^d_N}{k^d_C X_N} \right] (X_N - 1) - 1 \]

Integrating from time 0 where \( \Theta_N = 0 \) to time \( t \) where \( \Theta_N \) takes on its observed value

\[ \int \frac{d\vartheta}{1 + a \vartheta} = k^d_C X_N t \]

The result of this integration is:

\[ \Theta_N (t) = \left( \frac{1}{b} \right) (1 - e^{-b k^d_C X_N t}) = \frac{k^d_C X_N}{k^d_C X_N + k^d_N (1 - X_N)} \left[ 1 - e^{-b X_N k^d_N t} \right] \quad \text{(eq 3-5)} \]

and
\[
\begin{align*}
    b &= \left\{ 1 + \left[ (1 - X_N) \left( \frac{k_{N}^{d}}{k_{C}^{d} X_{N}} \right) \right] \right\} \\
    \quad \text{(eq 3-6)}
\end{align*}
\]

We have used eqs 2-5 and 2-6 to estimate the possible values of \(k_{C}^{d}\) and \(k^{d}\). Given the value of \(X_{N} = 0.88\) used in the experiment, curves for \(\theta(t)\) are plotted in Figure 3-8. On the basis of this figure, it is clear that the desorption rate for CoOEP must be close to 0.004/min or \(6.7 \times 10^{-5}/s\). Comparing the blue trace to the data in Figure 3-8, it is clear that the desorption rate for NiOEP is not 10 times faster than that for CoOEP. On the other hand, the NiOEP desorption rate might be very much slower than for CoOEP. A much more precise evaluation of \(k_{N}^{d}\) can be extracted from measurements made at other values of \(X_{N}\), and those experiments are underway.

It is valuable to contrast the size of \(k^{d}\) for these large molecules bound by weak forces to that for a smaller molecule attached by a covalent bond. Karpovich and Blanchard determined that the desorption rate for 1-octanethiol from Au(111) in n-hexane at 25 °C was 25 /min. This is over 6000 times faster than that for CoOEP desorbing from gold at 135 °C! Thiols bonded to gold are often discussed in terms of surface modifying agents. The fact that porphyrins are so much more resistant to solvent removal should lay to rest any expectation that the solution solid interface is always fragile.

Finally, we report on the molecular spacing observed for the pure CoOEP and NiOEP monolayers. For CoOEP, \(A = 1.42 \pm 0.02\) nm, \(B = 1.32 \pm 0.02\) nm, and \(\alpha = 57° \pm 1°\). For NiOEP, \(A = 1.41 \pm 0.01\) nm, \(B = 1.33 \pm 0.01\) nm, and \(\alpha = 58° \pm 1°\). We note that because we could not resolve the individual ethyl groups, it was impossible to determine the true unit cell parameters. The values given here assume a single molecule per unit cell, but this may be incorrect because it
is known from high-resolution UHV STM studies that NiOEP vapor deposited on Au(111) prefers a cell with 2 molecules slightly rotated relative to each other.\textsuperscript{74}

Given the precision of the above measured molecular spacing, we must conclude that the CoOEP and NiOEP occupy identical environments and area in the monolayer. Thus, it is very likely that the adsorbate−adsorbate interactions are nearly identical and differences in behavior must arise from adsorbate−substrate and adsorbate solvent differences. Because the solubilities are similar (3.9 × 10\textsuperscript{−4} and 5.4 × 10\textsuperscript{−4} M), it also seems unlikely that adsorbate−solvent interactions are significantly different. Thus, differences in desorption may come primarily from adsorbate−gold interactions.

3.5 Conclusions

For the first time, scanning tunneling microscopy has been used to study the kinetics of molecular desorption at the solid−solution interface. The relative coverage of a binary mixture of porphyrins adsorbed from phenyloctane onto Au at room temperature is entirely kinetically controlled. For solutions of the order of 100 μM in NiOEP or CoOEP, a dense monolayer is formed within seconds. Contrary to conventional thinking, noncovalent adsorption can lead to exceedingly strong molecular binding such that solution−surface equilibration is extremely slow even above 100 °C. The rate of desorption of CoOEP from a Au(111) surface in contact with phenyloctane solution at 135 °C is only 6.7 × 10\textsuperscript{−5} /s and orders of magnitude slower than that for a covalently bound thiol at 25 °C.\textsuperscript{87} The structures of NiOEP and CoOEP monolayers are essentially identical, and the molecular spacing for both can be described by \( A = 1.42 \pm 0.02 \) nm, \( B = 1.32 \pm 0.02 \) nm, and \( \alpha = 57° \pm 2° \). NiOEP appears to desorb at different rates from step edges, reconstruction lines, and terraces. The CoOEP desorption rate seems to be more spatially uniform. We are in the process of extending these measurements to fully determine both the adsorption and
the desorption rate constants and the thermodynamic equilibrium values at high temperatures where equilibration occurs in finite times. We are also pursuing these studies on HOPG.
Chapter 4. Desorption Kinetics and Activation Energy for Cobalt Octaethylporphyrin from Graphite at the Phenyloctane Solution–Graphite Interface: An STM Study

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4.1 Abstract

Temperature-dependent desorption rates and desorption energies are determined from a monolayer assembly at the solution–solid (SS) interface. Scanning tunneling microscopy (STM) was used to measure molecular-scale temperature-dependent desorption of cobalt(II) octaethylporphyrin (CoOEP) at the phenyloctane solution–highly ordered pyrolytic graphite (HOPG) interface. At lower temperatures, monolayer formation of metal(II) octaethylporphyrin (MOEP) on HOPG from solution was found to be completely controlled by kinetics, and the adlayer formed was stable up to 70 °C. Significant desorption of CoOEP from the HOPG surface was observed above 80 °C on a time scale of hours. CoOEP desorbs from HOPG into phenyloctane at a rate of 0.0055 ± 0.0007 min⁻¹ at 90 °C, 0.013 ± 0.001 min⁻¹ at 100 °C, and 0.033 ± 0.003 min⁻¹ at 110 °C. From these temperature- and time-dependent measurements, assuming an Arrhenius rate law, the activation energy of molecular desorption at the SS interface was determined using studies solely based on STM. The desorption energy of CoOEP from HOPG into phenyloctane is determined to be $1.05 \times 10^2 \pm 0.03 \times 10^2$ kJ/mol. NiOEP desorption occurs at a slower rate and is homogeneous across HOPG terraces, unlike the inhomogeneous desorption observed on Au(111). A previous study performed on Au(111) reported that the rate of desorption of CoOEP is 0.004 min⁻¹ at 135 °C. The calculated desorption rate on HOPG in this work is 0.22 min⁻¹, making the rate of desorption of CoOEP from HOPG 2 orders of magnitude greater than from Au(111). On the other hand, for solution concentrations of the order of 100 μM, a dense monolayer is formed within seconds. For this fast adsorption process, where a full monolayer coverage occurs, the surface coverage of MOEP on both surfaces was determined by the relative concentration of each species in the phenyloctane solution. The rates of adsorption (for concentrations near 100 μM) are found to be within 20% of each other. The surface structures of
both the NiOEP and CoOEP on HOPG and Au(111) are very similar and can be described by $A = 1.30 \pm 0.04$ nm, $B = 1.40 \pm 0.04$ nm, and $\alpha = 57^\circ \pm 2^\circ$ with an area of $1.50 \pm 0.08$ nm$^2$/molecule.
4.2 Introduction

The study of organic self-assembled molecules (SAMs) supported on an atomically flat surface has attracted an enormous amount of attention. Rightly so, due to their actual and potential applications in modern technology, molecular electronics,1,2 spintronics,3 solar cells,4,5 catalysis,6 sensors7-9 and various other areas. Study of these SAMs at the solution-solid (SS) interface compared to vacuum-solid interface has a special prominence since it can be conducted under conditions where bi-directional exchange between the surface and surrounding medium is possible and equilibrium might be established. Unlike the vacuum-solid interface, at the SS interface solvent molecules play a critical role. In addition to the adsorbate-substrate interactions, one must consider solvent-solvent, solvent-adsorbate, and solvent-substrate interactions. These interactions are complex; but in the special case where equilibrium is established, important parameters can sometimes be estimated using various computational and experimental techniques.28,43,88. Of the very few instruments capable of investigating the SS boundary at the molecular scale, scanning tunneling microscopy (STM) is especially appropriate. STM has the ability to resolve structures on a molecular and even sub-molecular scale. It can perform these studies in various solution environments, at varying temperatures, pressures, and concentrations, and on various surfaces. These studies allow a direct single molecule level probe of surface structure, adsorption and reaction kinetics, and even molecular movies of the evolution of equilibrium. This last capability can provide experimental values for critical functions of state.

While UHV studies allow for improved understanding of adsorbate-substrate interactions and of surface localized transformations, they are extremely limited for studying systems driven by thermodynamic and/or kinetic processes where molecular exchange occurs on and off the surface. When a SS pair is present, these phase exchange processes can be addressed. Although
the SS pair provides a foundation for studying these adsorption-desorption processes, it is often difficult to distinguish between those that are thermodynamically driven, kinetically driven, or where both processes are active. A few early studies of long chain substitute alkanes on graphite indicated that exchange between solution and surface could be fast on the order of seconds.\textsuperscript{89,90} Intuitively, one may think of temperature dependent studies to identify and separate these processes.\textsuperscript{28} Hence, there has been a recent dramatic increase in temperature dependent STM studies at the SS interface.\textsuperscript{26-28,30,31,35,91-93} Outside of temperature dependent studies, there have been only a few successful attempts to separate kinetically driven from thermodynamically controlled processes at the SS interface. It was shown that the addition of a species different than the one at the surface can yield both thermodynamic and kinetic products.\textsuperscript{94} Similarly, concentration\textsuperscript{28,40} dependent and two component\textsuperscript{36-38,41,42} studies can also yield useful information about driving forces. Unfortunately, not all surface structures are stable and accessible at higher temperatures, allowing only a small temperature range for studying these processes. Hence, very little quantitative information regarding the thermodynamics and kinetics at the SS boundary is known.\textsuperscript{95} Furthermore, most of the quantitative analysis found in the literature deals with phase transition processes.\textsuperscript{95}

Very few SS interface STM studies deal with the actual adsorption strength of molecules on surfaces. One such study is the adsorption/desorption kinetics of cobalt(II)octaethylporphyrin (CoOEP) at phenyloctane-Au(111) interface.\textsuperscript{33} It was shown that the CoOEP desorbs extremely slowly from the Au(111) surface and the rate of desorption was determined to be 0.004 min\textsuperscript{-1} at 135 °C. This showcased how strongly porphyrins can adsorb on a surface even though no covalent or ionic bonds are involved. While there have been a handful of adsorption studies of metal porphyrins on highly ordered pyrolytic graphite (HOPG) in the past, these studies at most
qualitatively suggested that the surface structures observed near room temperature were kinetically controlled. The study by Bhattarai et al\textsuperscript{33} was the first to provide an imaging based quantitative measure of the desorption rate at the SS interface for any substrate.

It is well known that the substrate can play an important role in the assembly of organic molecules. Self-Assembly of an adlayer can be heavily influenced either by the electronic coupling between the adsorbate and substrate or by the arrangement/packing of atoms in the underlying substrate. For example, under ultra-high vacuum (UHV) conditions, coronene adsorbs face down on Ag(111),\textsuperscript{96} and has a slightly different lattice constant compared to coronene on HOPG,\textsuperscript{97} and MoS\textsubscript{2}.\textsuperscript{97} More recently, it was shown that coronene on Ge(001) adsorbs in an upright configuration, contrary to the previously mentioned studies.\textsuperscript{98} The authors argued that while the electron density on the metal surface enhances the adsorbate-substrate interactions, the semiconducting behavior of Ge(001) allows for the π-π interactions between the adsorbates to outweigh the adsorbate-substrate interactions. Another such surface induced interaction is of vanadyl phthalocyanine (VOPc) adsorbed on Si(111)-(7x7) and on Ag(111).\textsuperscript{99} It was shown that VOPc adsorbs with oxygen-up configuration on Ag(111), whereas on Si(111) it prefers oxygen-down configuration. Although the underlying surface can play a strong role in monolayer formation, these interactions are poorly explored. A deeper knowledge and understanding of the assembly of organic molecules on various surfaces is required.

In this work we will go far beyond the study reported by Bhattarai and coworkers.\textsuperscript{33} We will make desorption rate measurements at different temperatures in order to extract the energy of activation for the desorption process – the first such determination for any system by STM at the SS interface. We also will explore the effects of changing the substrate from Au(111) to HOPG.
This will allow a quantitative evaluation of the relative desorption kinetics associated with changing only the substrate.

NiOEP will be used as a tracer for desorbed CoOEP from the HOPG surface. It is well known that cobalt and nickel porphyrins or phthalocyanines at the solution-solid and vacuum-solid interface can be well distinguished in an STM image.\cite{33,76,100,101} Thus, the loss of a CoOEP from the surface and the subsequent replacement by NiOEP can be separately distinguished and easily measured. Using this tracer methodology, we will demonstrate that monolayer formation at temperatures close to room temperature is very fast and dominated by kinetics. We will demonstrate that the rate of desorption of CoOEP at the phenyloctane-HOPG interface is almost non-existent at room temperature and is very slow even at temperatures up to 70 °C. Whereas, at 90, 100, and 110 °C desorption occurs on a time scale of hours. By comparing these measured desorption rates to those determined for CoOEP desorption from the phenyloctane-Au(111) interface,\cite{33} valuable quantitative insights into the role of the substrate at the SS interface will be provided.

4.3 Experimental Section

The experimental procedures used in this work are similar to those in Bhattarai et al.\cite{33} There are, however a number of differences such as temperatures studied, solution concentration determinations, and substrates used. Moreover, for the metal octaethylporphyrin (MOEP)/HOPG system, unlike the MOEP/Au system, tip induced changes must be considered.

2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine cobalt(II) [CoOEP] and 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine nickel(II) [NiOEP] were purchased from Aldrich and Frontier Scientific respectively. The structure of a MOEP can be seen in Figure 1.
Phenyloctane (98%) was purchased from Aldrich and was subjected to further purification as described in reference 33. HOPG of grade-I and II were purchased from SPI Supplies and were freshly cleaved using scotch tape before the sample was deposited.

UV Visible spectroscopy on saturated and filtered solutions of porphyrins in phenyloctane was used to determine solubility at room temperature. The measured solubility of CoOEP in phenyloctane was 3.9×10^{-4} M or 0.23 g/L and that of NiOEP was 5.4×10^{-4} M or 0.32 g/L. The highest concentration solutions used in these experiments was 1.5×10^{-4} M and most were less than 1.1×10^{-4} M. Thus, all solutions were below the solubility limit.

STM images were recorded using a Molecular Imaging (now Agilent) Pico 5 STM equipped with a scanner capable of imaging a maximum area of 1 µm^2 and having an overall current sensitivity of 1 nA/V. The Agilent environmental chamber was used for all experiments and argon atmosphere was maintained. STM tips were primarily prepared by cutting and sometimes electrochemically etching the Pt_{0.8}Ir_{0.2} wire purchased from California Fine Wire Company. An exception to this occurred while examining tip effects (described in the supplemental materials) in which case both etched and cut tips were used equally. Images were typically obtained in constant current mode at a sample potential of +0.5 to +0.7 V and a tunneling current of 20 to 50 pA. Images of sizes ranging from 30 × 30 nm^2 to 50 × 50 nm^2 were collected at a scan rate of 4.7 lines/sec, giving a total image time of just under 2 min. Images larger than 50 × 50 nm^2 were scanned at a slower scan rate of 3.3 to 3.9 lines/sec, giving a total image time of roughly 2.5 min. The temperature of the sample was controlled by a variable-temperature hot stage using a Lakeshore 330 auto-tuning temperature controller. The environmental chamber was purged with 99.996% Ar (A-L Compressed Gases, Inc., Spokane, WA) at all times. Before imaging, samples were allowed to sit for 30 minutes to one hour inside the environmental chamber purged with Ar
at 2.5 standard cubic feet per hour (scfh). During imaging, Ar was continuously purged at 0.5 scfh into the environmental chamber.

Solutions of CoOEP and NiOEP were prepared by dissolving solid porphyrin compounds in phenyloctane. Concentrations were measured using a UV-visible spectrophotometer where the extinction coefficient of each species had been previously measured by applying Beer’s law to a series of dilutions of a known concentration solution. Stock solutions of 1.1×10⁻⁴ M CoOEP and 1.5×10⁻⁴ M NiOEP were prepared separately. A custom made solution cell STM sample holder was used to accommodate large volumes (up to 100 µL) of solution in contact with the HOPG surface.

During the sample heating process, the temperature of the sample was ramped at a rate of 5 °C per minute, allowing the sample to reach the desired temperature (within the 90 - 110 °C range) in 20 min. The sample then was held at the desired final temperature for the desired time period. After this fixed time heating, samples were rapidly cooled to room temperature by turning the heater off. Samples were then allowed to equilibrate for at least 60 minutes prior to recording any images. All STM images were background subtracted using SPIP image processing software.

Tip induced desorption of porphyrins is known in the literature,¹⁰⁰,¹⁰² and we noted occasional tip induced local changes in our samples. These events were dealt with by moving to new areas to continue measurement. The role of tip induced defects in this study is discussed in the Supplemental Section.

4.4 Results and Discussion

Figure 4-1 presents separate STM images of CoOEP (110 µM in phenyloctane) and of NiOEP (150 µM in phenyloctane) at the solution-HOPG interface at 25 °C under Ar. As reported
in the literature, the center of CoOEP appears bright and the center of NiOEP appears dark.\(^{33,76,86}\) The cross-sectional profile of CoOEP in Figure 4-1 clearly shows a peak at the center of the molecule, whereas for NiOEP a depression is seen which gives rise to its dark appearance. It must be noted that the localization of the peak or depression is dependent on the tip sharpness and bias voltage. Hence, CoOEP sometimes appears as a wider bright region. In all cases where various tips are used, CoOEP always appears brighter, hence taller than the NiOEP at the voltages used in this study when both species are in the same image. We must proceed with caution while imaging CoOEP at the solution-HOPG interface, since it is well known to bind atmospheric O\(_2\) at room temperatures.\(^{31}\) This changes the appearance of oxygen bound CoOEP molecules (O\(_2\)-CoOEP appear dark) under STM and can be misinterpreted as NiOEP. Hence, prior to recording all STM images, Ar was flowed at 2.5 scfh for at least 15 minutes before deposition and 0.5 scfh at all times to ensure ambient air was replaced by Ar. Thus, any possibility of oxygen binding to CoOEP and oxidation of Co\(^{+2}\) ion was unlikely.
**Figure 4-1.** Constant current STM images of MOEP at the phenyloctane-HOPG interface. An image of CoOEP is shown on the left and of NiOEP on the right side in the Figure. The bottom portion of the Figure shows the cross-sectional apparent height of each of the MOEP. STM images were obtained under set point conditions of +0.7 V bias and 50 pA tunneling current. Scale bar is 5 nm.
When a mixture of CoOEP and NiOEP solutions of varying relative concentrations are deposited on HOPG, a mixed monolayer is formed consisting of bright (CoOEP) and dark (NiOEP) species as depicted in Figure 4-2. It can be seen in Figure 4-2 that the surface coverage of bright species decreases as the relative concentration of CoOEP in solution decreases. Similarly, the surface coverage of dark species increases as the relative concentration of NiOEP in solution is increased. In order to report surface concentrations, we define $\Theta_{\text{NiOEP}}$ as the number of NiOEP molecules in a given area divided by the total number of molecules in the same given area on HOPG. This notation works here because of the monolayer coverage observed in all images. For solution concentrations, we define $X_{\text{NiOEP}}$ as the number of moles of NiOEP divided by the total
number of moles of porphyrins in solution. Thus, it is a mole fraction of total porphyrins present, not of total moles present (solvent is excluded). Using this notation, four different mixtures of CoOEP and NiOEP were prepared, allowed to equilibrate on HOPG, and the resulting surface layers (still in contact with the solution) were then studied under STM. In order to ensure statistical significance, numerous (more than 10 per mixture) STM images of all the mixtures were analyzed. From these images, an average value of $\Theta_{\text{NiOEP}}$ was obtained for each value of $X_{\text{NiOEP}}$. Using these data, an adsorption isotherm can be created and it is plotted for data acquired at 25 °C in Figure 4-3. From this room temperature isotherm, it can be seen that $\Theta_{\text{NiOEP}}$ and $X_{\text{NiOEP}}$ are essentially equal.

![Figure 4-3](image)

**Figure 4-3.** Adsorption isotherm at 25 °C: Surface coverage of NiOEP relative to CoOEP on HOPG ($\Theta_{\text{NiOEP}}$) versus fractional concentration of NiOEP in phenyloctane solution ($X_{\text{NiOEP}}$).
In-situ imaging experiments were performed for various mixtures where the sample was heated at different temperatures. Figure 4-4 is a representation of the in-situ images taken at 25, 50, and 70 °C for $X_{\text{NiOEP}}= 0.38 \pm 0.04$. Averaged over all images acquired over the duration of six to ten hours at each temperature, $\Theta_{\text{NiOEP}} = 0.34 \pm 0.03$ at 25 °C, $\Theta_{\text{NiOEP}} = 0.34 \pm 0.02$ at 50 °C, and $\Theta_{\text{NiOEP}} = 0.33 \pm 0.02$ at 70 °C. Investigation of sequential images separated by a few minutes apart at various temperatures up to 60 °C shows an even more important feature. There is no sign of molecules exchanging between the surface and solution, clearly indicating that the rate of desorption is extremely slow even at elevated temperatures. That is, no bright site is seen to change to dark, or vice versa. Thus, the relative coverage was independent of temperature over the 25 to 70 °C range. Our only indication of in-situ molecular exchange was seen at 70 °C and is depicted in Figure 4-5. The red hexagon and oval shapes in Figure 4-5 are drawn as markers. With respect to these markers, only one site changes its appearance from image (b) to image (c). A dark site (circled white) is converted into a bright site, meaning that a NiOEP molecule on the surface is desorbed and the vacancy that is left behind is filled by a CoOEP molecule. It must be noted that no other sequential images obtained within a period of up to 15 min at 70 °C show any sign of molecular adsorption/desorption processes. Thus, even at 70 °C the rate of desorption of CoOEP and NiOEP is very slow. This parallels the behavior of CoOEP and NiOEP adsorbed from phenyloctane on Au(111). In order to record any quantitative desorption at 70 °C, we would have to monitor the same area on the surface on a time scale of hours.
**Figure 4-4.** *In-situ* temperature dependent STM images of monolayers formed from $X_{\text{NOE}} = 0.38$ where $\Theta_{\text{NOE}} = 0.34 \pm 0.03$ on HOPG at 25, 50, and 70 °C. Set point condition was +0.5 V bias and 50 pA tunneling current. Scale bar is 5 nm.

**Figure 4-5.** Sequential STM images of $X_{\text{NOE}} = 0.38$ at 70 °C. Each image is separated by 108 sec. Set point condition was +0.7 V bias and 50 pA tunneling current. Scale bar is 5 nm.

Knowing that the rate of desorption near 300 K is extremely slow, and that the monolayer forms in a matter of seconds, it is clear that the isothermal adsorption data displayed in Figure 4-3 resulted entirely from a kinetically controlled process. There is no equilibrium between solution
and surface. Thus, the data in Figure 4-3 may be understood through an analysis given in reference 33. Because the rate of formation of a monolayer is many orders of magnitude faster than the rate of desorption, \( \Theta_{\text{NiOEP}} \) or \( \Theta_N \) (for brevity) at steady state is given by,

\[
\Theta_N = (1 - e^{-\bar{k}M})(\frac{k_N^a X_N}{\bar{k}})
\]

(eq 4-1)

and,

\[
\bar{k} = \left( k_N^a X_N + k_C^a X_C \right) = k_N^a X_N + k_C^a (1 - X_N)
\]

(eq 4-2)

where, \( k_N^a \) and \( k_C^a \) are the rate constants for the adsorption of NiOEP and CoOEP, respectively. \( X_N \) and \( X_C \) are the mole fractions of NiOEP and CoOEP (relative to total porphyrin) in solution, respectively. \( M \) is the total molarity of porphyrins in the solution. At lower temperatures where the desorption rate is extremely slow or non-existent, \( \Theta_N = \left( \frac{k_N^a X_N}{\bar{k}} \right) \). Thus, \( \Theta_N \) depends only on the mole fraction and relative rates of adsorption of CoOEP and NiOEP. This relationship is represented in Figure 4-3 by the smooth curves. The black curve is for the case where \( k_N^a = k_C^a \), and the red curve is for the case where \( k_N^a = 0.8k_C^a \). Thus, the rates of adsorption of CoOEP and NiOEP are within 20% of each other and are probably the same.

A complete kinetic analysis of the monolayer formation requires accounting for monolayer nucleation and growth and for reorganization of molecules along the domain boundaries. Studying the domain sizes on both HOPG and Au(111) could provide valuable qualitative insights into the adsorption mechanisms of these MOEP molecules. Very rarely we found domain boundaries of MOEP on HOPG, whereas there were plentiful on Au(111). This suggests that all of the above mentioned processes may be different on the two substrates. Quantitative evaluation of these parameters is beyond the scope of present study. Instead, we focus on measuring an effective
relative overall rate for monolayer formation. We can state that the relative rates of monolayer formation of CoOEP and NiOEP [on both HOPG and Au(111)] are similar.

We now turn attention to the desorption process. Based on our experience with MOEP on Au(111), we expected that with increasing temperature the rate of desorption from HOPG will become significant and measureable. However, the in situ experiments reported above become less effective at higher temperatures. In cases where steady state will only occur in a time of the order of an hour or longer, a different method is used -- the procedure reported in reference 33. First, a dense monolayer of one of the MOEP (CoOEP) on HOPG was prepared. Then, an excess of the species not present in the monolayer (NiOEP) was added such that the solution in contact with the surface has a mixture of both MOEP species. Because of the excess amount of the second species in the solution, if any desorption of the first species occurs then the second species is more likely to fill the vacant site on the surface and can be easily detected in an STM image due to the difference in molecular contrast. The sample is then heated to higher temperatures (>70 °C), held at that temperature for a certain time period, and then rapidly cooled to room temperature to perform STM imaging. Because of the fast adsorption and slow desorption below 80 °C of either MOEP, this ex-situ technique captures the results of the adsorption-desorption processes that occur at higher temperatures.

To show that this method correctly reflects the very low desorption rates seen near room temperature, a confirming experiment was performed. STM images were obtained at 25 °C of a monolayer of CoOEP prior to and following being covered for 24 hours with a solution having $X_N = 0.80$. These images (Figure 4-6) clearly show that at low temperatures no exchange is occurring even on a time scale of many hours. Obvious exchanges can be observed only above 80 °C after 30 min of heating. In related experiments at 25 °C, the surface was first exposed to a pure solution
of one MOEP and then a mixed solution was added within a few seconds. In both cases, only the first MOEP was ever observed in the monolayer. Thus, monolayer formation on HOPG (as in the case of Au(111)) is very fast and forms within a few seconds.

At temperatures above 70 °C the stability of the initial monolayer is lost. At 90, 100, and 110 °C, significant changes in the monolayer were seen. Thus, these three temperatures were used to determine the rates of desorption and subsequently the activation energy for desorption of CoOEP from HOPG at the phenyloctane-HOPG interface. Here, focus will be placed on CoOEP desorption from HOPG in order to compare it to the known value on Au(111). It is worth noting that NiOEP followed a similar trend to that observed for CoOEP and that its desorption is uniform on the HOPG surface. This surface uniformity of desorption of NiOEP on HOPG is quite different than the case of NiOEP desorption from Au(111). As demonstrated by Bhattarai and coworkers, NiOEP preferentially desorbs from step edges and reconstruction lines. No such position dependent desorption was observed on HOPG.

Monolayer samples of CoOEP were deposited from pure CoOEP in phenyloctane solutions and imaged by STM. Then, a large excess of a solution of NiOEP and CoOEP \((X_N = 0.80)\) was added. This sample was then heated to 90, 100, or 110 °C for time intervals of 30 min each up to 4 h in total. After each time interval, the sample was cooled quickly to room temperature and multiple measurements of 6 to 15 different areas of \(50 \times 50 \text{ nm}^2\) sized areas (one image has roughly 2000 total molecules) were taken to ensure statistical significance. Figure 4-7 shows STM images of a sample (initially covered by a monolayer of CoOEP at the phenyloctane solution-HOPG interface) after 30 min exposure to a solution of \(X_N = 0.80\) at 90, 100, and 110 °C. It is clear that as the temperature is increased, more CoOEP is desorbed and is replaced by NiOEP.
Figure 4-6. STM images obtained at 25 °C. (a) Solution of CoOEP in phenyloctane on HOPG; (b) monolayer from (a) following a 24 hour exposure to a solution having $X_N = 0.80$. Scale bar is 5 nm.

Figure 4-7. 50 x 50 nm$^2$ STM images of a surface initially covered by a monolayer of CoOEP on HOPG following 30 min exposure to a solution of $X_N = 0.80$ at 90 °C (left), 100 °C (middle), and 110 °C (right). Set point conditions were +0.7 V bias and 50 pA tunneling current. Scale bar is 10 nm.
Values of $\Theta_N$ obtained by repeated annealing of samples in 30 min intervals for a total of up to 4 h at 90, 100, and 110 °C are given in Figure 4-8. What is obvious from the raw data is that the rate of desorption is still slow even at 110 °C, with hours of heating time required for the surface composition to reach steady state. It is also a bit surprising at first that at the highest temperature the steady state surface concentration of NiOEP is greater than $X_N$. On reflection, this result is expected if the rate of desorption of CoOEP is greater than for NiOEP at 110 °C. In order to extract quantitative desorption rates and energies, the model used for CoOEP desorption from Au(111) was used. In this model, the rate of appearance of NiOEP on a complete monolayer covered by both NiOEP and CoOEP is equal to: (the rate of disappearance of CoOEP × the probability that this vacant site will be filled by NiOEP) – (the rate of disappearance of NiOEP × the probability that this vacant site will be replace by CoOEP). This takes into account the possibility that a desorbed MOEP might be replaced by a CoOEP rather than a NiOEP. For the case of fast adsorption where we assume $k^a_N = k^a_C$, and slow desorption, $\Theta_N$ after an annealing time, t, is given by,

$$\Theta_N(t) = \left( \frac{1}{b} \right)(1 - e^{-b k^d_N X_N t}) = \frac{k^d_C X_N}{k^d_C X_N + k^d_N (1 - X_N)} \left[ 1 - e^{-b X_N k^d_C t} \right]$$  \hspace{1cm} (eq 4-3)

and,  \hspace{1cm} $b = \left[ 1 + \left( 1 - X_N \left( \frac{k^d_N}{k^d_C X_N} \right) \right) \right]^{-1}$ \hspace{1cm} (eq 4-4)

The most direct approach to determining the parameters in this expression is to fit the complete set of $\Theta_N(t,T)$ data to equation 4-3. However, since the $k^d_i$ are temperature dependent, this gives six parameters that must be determined. Our data set is too small to give reliable values for so many parameters. Thus, some simplification is required in order to provide a useful analysis.
We approached the problem in two different ways. The critical parameters of desorption energy and $k_c^d$ that result are essentially independent of method.

In the first method, use is made of the Arrhenius model for the temperature dependence of the rate constants, $k_i^d = k_i^0 e^{-\Delta E_i/RT}$, where ‘i’ represents either ‘C’ for CoOEP or ‘N’ for NiOEP, and $\Delta E_i$ is the desorption energy of species i. It is also useful to define the ratio $K^d = \frac{k_N^d}{k_C^d} = K^0 e^{(\Delta E_C - \Delta E_N)/RT}$, where $K^0 = \frac{k_N^0}{k_C^0}$. Using these definitions and assumptions, equation 3-3 can be rewritten as follows:

$$\Theta_N(t) = \frac{1}{1 + \left(\frac{1 - X_N}{X_N}\right)K^0 e^{(\Delta E_C - \Delta E_N)/RT}} \left[1 - \exp\left(\left(-X_Nk_C^0 e^{-\Delta E_C/RT}\right)\left(K^0 e^{(\Delta E_C - \Delta E_N)/RT}\left(\frac{1 - X_N}{X_N}\right) + 1\right)t\right)\right] \quad (eq \ 4-5)$$

This reduces the number of parameters from six to four. It is found, however, that least squares fitting yield results where the uncertainties in several of the parameters exceed their values. Thus a further reduction in the number of parameters is required. Given the similar nature in size, weight, and solubility of CoOEP and NiOEP and similar ionic radii of Co$^{+2}$ and Ni$^{+2}$ one would expect the vibrational motion of the entire molecule normal to the HOPG surface would be similar for both species. Interpreting the $k_i^0$ to be an attempt frequencies and relating it to this vibrational frequency leads one to conclude that $k_i^0$ should be very similar for both porphyrins and therefore $K^0 \approx 1$.

Fixing $K^0 = 1$, we used non-linear least squares to optimize equation 4-5 to the $\Theta_N(t,T)$ data taking $\Delta E_C$, $\Delta E_N$, and $k_c^0$ as adjustable parameters. The result of this optimization is given as the smooth curves in Figure 4-8(a). Optimized values of $\Delta E_C$, $\Delta E_N$, and $k_c^0$ were found to be $1.05 \times 10^2 \pm 0.028 \times 10^2$ kJ/mol, $1.05 \times 10^2 \pm 0.027 \times 10^2$ kJ/mol, and $6.2 \times 10^{12} \pm 5.6 \times 10^{12}$ min$^{-1}$
respectively. Using these optimized values, rates of desorption for CoOEP from HOPG are estimated. For CoOEP, average $k_{cd}$'s are found to be 0.0048, 0.012, and 0.030 min$^{-1}$ at 90, 100, and 110 °C respectively. Obtaining $\Theta_{N \rightarrow x}$ values at all temperatures would allow for a more robust determination of the $k_{Nd}$ values, but there are experimental problems that make this difficult to do accurately. With our current experimental design, long annealing times lead to solvent evaporation and eventually to CoOEP and/or NiOEP becoming saturated and precipitating out of solution. In order to avoid this complication, we restricted measurement times to where the solution concentration remained well under the saturation concentration. Clearly, however, the uncertainty in $k_i^0$ (as determined by this method) are still very large and we should refrain from conclusive statements regarding their values.

![Figure 4-8](image)

**Figure 4-8.** Best fit curves for surface coverage of NiOEP, $\Theta_{NiOEP}$ with reaction time and average $k_{cd}$'s at 90 °C (black curve), 100 °C (blue curve), and 110 °C (red curve) for: (a) $K^0 = 1$ and optimized values of $\Delta E_C$, $\Delta E_N$, and $k_{cd}^0$ for the entire time (t/min) and temperature (T/°C) data set; (b) optimized values of $k_{cd}^0$ and $K^d$ at each T.
In order to determine more precise values of $k_{C}^d$ and to support the validity of the desorption energies, a second analysis method was used. In method 2, one fits the curves given in equation 4-3 (and 4-4) for varying $k_{C}^d$ and $K^d$ values independently at each temperature. $k_{C}^d$ and $K^d$ values were optimized using a non-linear least square fit to produce a best fit curve at each temperature. These optimized curves are presented in figure 4-8(b). At 90 °C, $k_{C}^d = 0.0059 \pm 0.0002 \text{ min}^{-1}$ and $K^d = 0.91 \pm 0.3$; at 100 °C, $k_{C}^d = 0.013 \pm 0.0004 \text{ min}^{-1}$ and $K^d = 0.94 \pm 0.1$; at 110 °C, $k_{C}^d = 0.035 \pm 0.0002 \text{ min}^{-1}$ and $K^d = 0.49 \pm 0.01$. These values of the $k_{C}^d$ are in excellent agreement with those determined by method 1. The $K^d$ values at 90, and 100 °C are close to 1 (0.9) and are the same within one standard deviation. The $K^d$ value at 110 °C is roughly 0.5. Due to the likely differences in the temperature dependence of rate constants for CoOEP and NiOEP, it is possible for the $K^d$ value at 110 °C to be smaller than ones obtained at lower temperatures. Furthermore, $K^d = 0.49 \pm 0.010$ at 110 °C indicates that the CoOEP desorbs from HOPG faster than NiOEP which is also in agreement with the experimental data.

Using the rate values obtained by method 2 at 90, 100, and 110 °C, a plot of $\ln(k_{C}^d)$ versus $1/T$ gives a straight line (Figure 4-9). Assuming an Arrhenius type activated process (as we did above) the slope of this plot gives $-\Delta E_d/R$. Thus, the energy for desorption of CoOEP is calculated to be $1.03 \times 10^2 \pm 0.40 \text{ kJ/mol}$ and the attempt frequency is found to be $3.7 \times 10^{12} \pm 3.9 \times 10^{12} \text{ min}^{-1}$. These values are quite similar to those obtained from the first method. In both methods, $k_{C}^d$ values can be described as $0.0055 \pm 0.0007 \text{ min}^{-1}$ at 90 °C, $0.013 \pm 0.001 \text{ min}^{-1}$ at 100 °C, and $0.033 \pm 0.003 \text{ min}^{-1}$ at 110 °C and $\Delta E_C$ is given by $1.05 \times 10^2 \pm 0.028 \times 10^2 \text{ kJ/mol}$. In order to obtain values of $k_{N}^d$ and $\Delta E_N$ with equal precision, similar desorption experiments with NiOEP as a starting monolayer on HOPG would be of great value and these are underway.
It is useful to consider why the individual two-parameter fits recreate the surface coverage versus time plots so much better than the three parameter fit of the entire data set. The simplest explanation is that the three parameter fit (method 1) forces the ratio of the pre-exponentials to be fixed and independent of temperature. Neither may be the case. A different way of interpreting the rate equation is by using the Eyring equation wherein the entropic and enthalpic contributions to formation of the activated state are considered. In this model, $k_{i0}$ is replaced by $\frac{kT}{h} e^{\frac{\Delta S^{*}}{R}}$. Thus there may be both explicit and implicit temperature dependences in the $k_{i0}$.

Using the values for $\Delta E_C$ and $k_{C}^{d}$ consistent with both methods described earlier, one predicts an average desorption rate of 0.22 min$^{-1}$ for CoOEP from HOPG in phenyloctane at 135 °C. This is 55 times greater than the observed desorption rate for CoOEP in the same solvent but desorbing from Au(111) at 135 °C.$^{33}$ This dramatic change in desorption rate with varying
substrate in the absence of covalent interactions demonstrates the critical role the substrate can play in determining the composition and stability of an adlayer at the solution-solid interface. The choice of substrate can easily cause a particular solvent-solute pair to yield an adlayer that is entirely kinetically controlled, thermodynamically controlled, or slowly evolving with time.

We also report on the molecular spacing for the pure CoOEP and NiOEP monolayers at the phenyloctane solution-HOPG interface. For CoOEP, \( A = 1.27 \pm 0.02 \) nm, \( B = 1.40 \pm 0.02 \) nm, and \( \alpha = 57^\circ \pm 1^\circ \); for NiOEP, \( A = 1.28 \pm 0.02 \) nm, \( B = 1.39 \pm 0.02 \) nm, and \( \alpha = 57^\circ \pm 1^\circ \). Under UHV conditions, the eight ethyl groups of NiOEP vapor deposited on Au(111) were resolved.\(^{74}\) These data showed that there are 2 molecules per unit cell on Au in UHV, where the unique molecules were slightly rotated with respect to one another. In this work, we were not able to resolve the ethyl groups and hence we chose a unit cell consisting of only one molecule. Given the precision of our measured spacing, both the CoOEP and NiOEP can be described as having a unit cell dimensions of \( A = 1.28 \pm 0.02 \) nm, \( B = 1.40 \pm 0.02 \) nm, and \( \alpha = 57^\circ \pm 1^\circ \) with an area of \( 1.79 \pm 0.04 \) nm\(^2\)/molecule on HOPG. On Au(111), both NiOEP and CoOEP occupy \( 1.87 \pm 0.04 \) nm\(^2\)/molecule. Based on the similarity of the packing on the two substrates, it is likely that MOEP have similar adsorbate-adsorbate interactions on HOPG and on Au(111). Also, with similar solubility (3.9 \( \times 10^{-4} \) and 5.4 \( \times 10^{-4} \) M for CoOEP and NiOEP respectively), they are likely to have similar adsorbate-solvent interactions. Hence, the difference in adsorption strength of CoOEP on HOPG and Au(111) may arise almost entirely from differences in adsorbate-substrate interactions. If one attributes the difference in desorption rates from HOPG and from Au at 135 °C as entirely due to differences in desorption energy, one predicts that the desorption energy from Au(111) into phenyloctane should be roughly \( 1.19 \times 10^2 \) kJ/mole.
4.5 Conclusions

For the first time a complete quantitative analysis of the kinetics of molecular desorption at the solution-solid interface has been performed using scanning tunneling microscopy. The surface dependence of the adsorption/desorption kinetics at the solution solid interface has been analyzed. At temperatures near 20 °C, monolayer coverage of MOEP both at phenyloctane solution-HOPG and phenyloctane solution-Au(111) interfaces is completely controlled by kinetics. In both cases, a dense monolayer of MOEP forms within seconds, whereas desorption is extremely slow even above 70 °C. For a mixture of CoOEP and NiOEP in phenyloctane, the overall rates of adsorption (to form a complete monolayer) on either Au(111) or HOPG are nearly species independent and proportional to the relative concentration of each species in solution. On the other hand, significant MOEP desorption into phenyloctane on a scale of hours occurs only above 80 °C from HOPG and 130 °C from Au(111). The rate of desorption of CoOEP from HOPG is two orders in magnitude larger than from Au(111) at 135 °C. Due to the similar areas occupied by NiOEP and CoOEP on both surfaces, and similar solubility in phenyloctane, the difference in adsorption strength is likely due to the difference in MOEP-HOPG and MOEP-Au(111) interactions. Another distinguishing feature of the substrate dependence of desorption is that it is site specific for NiOEP on Au(111) but uniform desorption is observed from HOPG terraces.

CoOEP desorbs twice as fast as NiOEP at the phenyloctane-HOPG interface at 110 °C. Given the similar nature in size and solubility of CoOEP and NiOEP and similar ionic radii of Co^{+2} and Ni^{+2}, these differences most likely arise from differences in Ni-HOPG and Co-HOPG interactions. The desorption rates reported here are for molecules desorbing from a full monolayer. Desorption rates from grain boundaries and defects, or from small islands of molecules may differ.
4.6 Supplemental Section

**Tip-induced effects and their avoidance:** Tip-induced effects have been used in the reversible isomerization of azobenzene,\(^\text{103}\) polymerization of organic molecules,\(^\text{104,105}\) manipulation of the reconstruction of Au(111),\(^\text{106}\) inducing chemical reaction at the organic-metal interface,\(^\text{107,108}\) and many other applications. Most relevant to our study was the tip-induced surface desorption of porphyrins and porphyrin like materials at the solution-solid interface. In porphyrins, it has been shown that this desorption process can occur via two different mechanisms; (i) either by applying a pulse of high voltage (>|2| V) to the tip,\(^\text{102}\) (ii) or by scanning at a low bias voltage such that the tip-surface separation is very low in which case the adsorbed molecules are scrapped off by the tip. The adverse effects of tip-surface interaction in our experiments can be easily detected in ex-situ experiments. First, deposit a certain mixture or only one species on HOPG. Then, add a solution with an excess of the other species such that any compositional changes in the monolayer due to tip effects can be easily detected by STM imaging. For example, a sample was prepared with \(X_{\text{NiOEP}} \approx \Theta_{\text{NiOEP}} = 0.42\). Excess NiOEP was then added to the solution cell such that \(X_{\text{NiOEP}} = 0.80\). When a pulse of -3 V was applied between the tip and the sample, the resulting surface appears as in Figure 4-S1. We can clearly see the changes in \(\Theta_{\text{NiOEP}} (\approx X_{\text{NiOEP}} = 0.80)\) within the yellow oval clearly demonstrating the surface desorption of MOEP induced by the voltage pulse (followed by rapid adsorption reflecting the concentration of species in the second solution). In general, pulsing affected an area of radius up to 50 nm in size, consistent with similar studies done in the past.\(^\text{102-104}\)

Figure 4-S2 shows the effects of a second mechanism by which tip-induced desorption occurs. In Figure 4-S2(a), there are very few (≈5%) NiOEP on the HOPG surface. Then, an excess of NiOEP is added on top such that the \(X_{\text{NiOEP}} = 0.80\). As described in (ii) above, a series of
sequential STM images are taken of with a low bias of +0.2 V, one of which is seen in Figure 4-S2(b). The fuzzy areas appear due to the fast adsorption/desorption process. Finally, after reversing the set point conditions back as in Figure 4-S1(a), the compositional changes in the monolayer can be easily seen in Figure 4-S1(c), where $\Theta_{\text{NiOEP}}$ changes from roughly 0.05 to 0.80.

In order to verify that these tip-effects do not occur during each scan and have an effect on the composition of the surface monolayer, we continuously recorded sequential STM images of the area where a tip-induced change had occurred. A portion of such a sequence is shown in Figure 4-S3. While there is some small thermal drift, it is none the less clear that each CoOEP molecule (bright molecule) in Figure 4-S3(a) is present in the entire sequence. Moreover, no new bright molecules replace NiOEP molecules. Thus, the monolayer composition is kinetically stable immediately after a tip-induced desorption event (but at a coverage consistent with the current covering solution).
Figure 4-S1. STM image of “tip-induced” desorption by pulsing the tip with -3 V. Prior to the pulse, \( \Theta_{\text{NiOEP}} = 0.42 \) and \( X_{\text{NiOEP}} = 0.80 \). After the pulse, area within the yellow curve is \( \Theta_{\text{NiOEP}} \approx X_{\text{NiOEP}} \).

Figure 4-S2. STM images of “tip-induced” desorption of CoOEP from HOPG by scanning at a low bias; (a) STM image of nearly 100% CoOEP monolayer with excess NiOEP in solution at +0.5 V and 20 pA; (b) STM image after few scans (5 min) of (a) imaged at a lower bias: +0.5 V and 20 pA; (c) STM image showing changes in monolayer composition after few scans (15 min) of ‘a’.
Figure 4-S3. Sequential STM images of MOEP on HOPG of an area after the tip-induced desorption. Each image is separated by 108 sec. Set point conditions were +0.5 V bias voltage and 50 pA tunneling current.

Additional to these deliberate tip-induced desorptions, very rarely a random spike in voltage or current during scanning would induce desorption followed by rapid repopulation of the surface with species in proportion to the existing solution concentration. Because these changes are localized they are fairly easy to spot. Our response was always to move to a new area of the sample to continue measurement.
Chapter 5. Influence of the Central Metal ion in the Desorption Kinetics of Porphyrin from the Solution/Solid Interface

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5.1 Abstract

A scanning tunneling microscopy (STM) study of the kinetics of desorption for cobalt(II) octaethylporphyrin (CoOEP) and free base octaethylporphyrin (H\textsubscript{2}OEP) at the 1-phenyloctane/HOPG interface was investigated to determine the influence of a central metal on the adsorption energy. In-situ temperature dependent studies of mixtures of CoOEP and H\textsubscript{2}OEP show that the resulting monolayer compositions are stable up to 70 °C and are controlled by kinetics. In order to determine the rates of desorption, ex-situ temperature dependent studies were performed on both CoOEP and OEP at 90, 100, and 110 °C. Assuming an Arrhenius process for desorption, the activation energies were found to be (1.25 ± 0.01)×10\textsuperscript{2} kJ/mol. The rates of desorption and the adsorption for both porphyrins were very similar to each other, indicating that the replacing the central protons with a cobalt ion had little influence on adsorption. Thus, the adsorption strength is mostly dominated by the interactions between the porphyrin ring and HOPG.
5.2 Introduction

One of the important components for building modern electronic devices is the use of organic adlayers, and self-assembled structures. These are mainly constructed using “bottom-up” methods, primarily self-Assembly. Self-assembly can be used to manipulate surface structures by using different types of molecules where the intermolecular interactions are controlled, thereby generating diversified building blocks.\textsuperscript{109,110} Self-assembly of porphyrins on a surface is of prominence due to their versatile nature and the fact that they are candidates for use in modern electronics such as solar cells\textsuperscript{111} and sensors.\textsuperscript{112,113} Moreover, porphyrins are present abundantly in nature and are involved in the complex chemistry of electron transfer,\textsuperscript{114,115} photosynthesis in plants,\textsuperscript{116} and oxygen binding in heme.

Porphyrins are highly conjugated systems which can provide electron transport pathways\textsuperscript{114,115} that are significant for their application in electronic materials. Porphyrins are strong absorbers of visible light which makes them candidates for use as sensitzers in solar cells.\textsuperscript{45-47} In a porphyrin, the metal center, eight beta, and four meso positions can be substituted and these modifications can be synthesized in almost any combination desired and/or required. In addition, the porphyrin core is nearly planar in geometry and is more likely to lie flat on surfaces providing a rigid foundation for any potential surface supported three-dimensional network. These versatilities allow one to design self-assembled monolayers on surfaces with a wide range of possibilities. In some cases, porphyrins and phthalocyanines have been stacked on top of each other with a coordinating metal sandwiched between the macrocyclic planes.\textsuperscript{36,37,117,118} It was shown that these double-decker complexes can act as a single-molecule magnet and can be useful in molecular spintronics.\textsuperscript{118,119} At the solution-solid (SS) interface, it is also important to note that, depending on desorption and adsorption kinetics, self-assembled monolayers might replenish
themselves on the surface and could thus form long-range defect free systems. For systems where desorption kinetics are favorable, this allows the nanostructure to “self-heal” and can prolong the life of the system.

While various surface sensitive techniques such as XPS, UPS, and UHV-STM have been used to investigate the surface processes in vacuum, STM is the primary tool for studying the SS interface at the single molecule level. It provides the adlayer molecular structure at the SS interface and can help understand and provide quantitative data on the dynamics occurring at various sites at the interface. STM has the potential to track single molecules on a time scale of milliseconds to hours and allows one to study the dynamics of monolayer formation on surfaces. As advancements in STM continue, new doors open for investigating and understanding various surface phenomenon under previously inaccessible conditions. For example, Jahanbekam et al. showed that by enclosing the whole STM body in a controlled chamber one can perform temperature dependent study on volatile solvents such as toluene (up to 75.4 °C).34

Distinguishing between thermodynamically and/or kinetically formed surface structures lies at the heart of understanding the SS interface. A recent work by Jahanbekam et al.39 has highlighted the importance of distinguishing the formation of surface structures where a kinetic product can easily be misinterpreted and treated as an equilibrium species. Although such misinterpretations have been reported in the past,36 researchers are becoming more cautious in their claims.95 For surface processes that occur in a reasonable time frame (few seconds to minutes), sequential STM imaging of the same area can be useful in determining whether the surface is a thermodynamic or a kinetic product. Using this sequential STM imaging technique, Friesen and co-workers successfully showed that oxygen binding to CoOEP at the 1-phenyloctane/HOPG interface is an equilibrium process.31 On the other hand, sequential STM
imaging studies on porphyrins have shown that the monolayer formation on HOPG and Au(111) are predominantly kinetically controlled.\textsuperscript{32,33,41,42} On a quantitative level, temperature dependent studies can provide a vast wealth of information at the SS interface. It can provide thermodynamic quantities such as $\Delta G$, $\Delta S$, and $\Delta H$\textsuperscript{31} and kinetic parameters such as rate constants and activation energies.\textsuperscript{32,33} For surface structures where more than one phase is present, temperature and/or concentration dependent studies can yield valuable information regarding the nature and stability of the surface structures.\textsuperscript{28} Unless sequential STM imaging and temperature dependent studies are performed, a kinetically trapped system can easily be misinterpreted as a thermodynamically stable system. In some cases, metastable phases have been identified.\textsuperscript{39,95,122,123}

For a single component system, the difficulty in distinguishing between thermodynamic and kinetic control is that a vacant site on the surface created by molecular desorption is replaced by the same species in solution and hence the changes are not recognizable. To address this issue, one can use a two-component system comprised of two chemically very similar molecules that appear different under STM. Many two-component systems have been appearing in literature to address the relative stability of the adlayer at the SS interface.\textsuperscript{32,33,36,37,39,41,42,124} One of the earliest examples of such two-component systems dealt with a mixture of saturated and unsaturated acids and mixture of an alcohol and a thiol.\textsuperscript{89} It was shown that the residence time of these molecules on a HOPG surface was as short as 0.03 to 0.3 s and that the exchange at the interface was rapid. Similarly, alkanes or ethers mixed with thioethers of varying lengths show dynamic changes at the interface with residence times of up to 18 s.\textsuperscript{90,125} Exchange dynamics of two very similar donor-acceptor-donor triads was also studied.\textsuperscript{126} The replacement of one triad with the other at the interface occurred within minutes of addition of the second triad and the exchange halts when an equilibrium is established between the surface and solution. Another similar study in an
an electrochemical environment was performed earlier on a mixture of iron and free base protoporphyrins.\textsuperscript{127} Although it was shown that the surface coverage was the same as the solution mole fraction of the porphyrins, no effort was made to study the exchange dynamics at the interface. And recently, two-component studies on porphyrins have shown that the surface structures of porphyrins are kinetically controlled at the SS interface.\textsuperscript{32,33,41,42}

In this study, STM is used to determine and compare the desorption kinetics of a metallated porphyrin, cobalt(II) octaethylporphyrin (CoOEP) and a metal free porphyrin, octaethylporphyrin (H\textsubscript{2}OEP) from highly ordered pyrolytic graphite (HOPG) into 1-phenyloctane at 90, 100, and 110 °C. It is well known that the cobalt porphyrins and phthalocyanines appear brighter in an STM image compared to a metal free porphyrins and phthalocyanines.\textsuperscript{75,76,101,127,128} Hence, either one of the porphyrins can be used as a tracer for surface desorption of the other at the SS interface. Here, we extend our previous studies on the CoOEP desorption from Au(111)\textsuperscript{33} and HOPG\textsuperscript{32} to include the desorption of H\textsubscript{2}OEP, a metal free octaethylporphyrin. These results will provide direct insights into the effect of the central metal in a porphyrin on the adsorption/desorption process from HOPG.

We will show that the rates of desorption for both porphyrins from HOPG are similar at the temperatures studied. These observation show that the metal centers have little impact on the stability of OEPs on HOPG. Hence, their adsorption strength is most likely dominated by the interaction between the porphyrin core and graphite. Furthermore, we will show that desorption from graphite step edges and grain boundaries occurs faster than from terraces.
5.3 Experimental Section

The experimental methods employed in this study are similar to those previously reported\textsuperscript{32,33} so attention primarily is placed on the unique aspects of the work done here.

2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine cobalt(II) [CoOEP] and 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine [H\textsubscript{2}OEP] were purchased from Aldrich and PorphyChem respectively. Phenyloctane (98\%) was purchased from Aldrich and Alfa Aesar and was subjected to further purification as described elsewhere.\textsuperscript{33} HOPG were purchased from SPI Supplies (grade-I and II) and \(\mu\)masch (spread 0.8\(^\circ\) ± 0.2\(^\circ\)). HOPG was freshly cleaved before a new sample was prepared.

UV-Visible spectroscopy on saturated and filtered solutions of porphyrins in phenyloctane was used to determine their solubility at room temperature. The measured solubility of CoOEP in phenyloctane was 3.9\times10^{-4} M or 0.23 g/L and that of H\textsubscript{2}OEP was 1.1\times10^{-4} M or 0.06 g/L. The concentration range for solutions used in these experiments for CoOEP was 6.4\times10^{-5} M to 1.1\times10^{-4} M and for H\textsubscript{2}OEP was 5.0\times10^{-5} M to 7.3\times10^{-5} M. Thus, all solutions were well below the solubility limit.

STM images were recorded using a Molecular Imaging (now Agilent) Pico 5 STM equipped with a scanner capable of imaging a maximum area of 1 \(\mu\)m\(^2\) and having an overall current sensitivity of 1 nA/V. The Agilent environmental chamber was used for all experiments and argon atmosphere was maintained. STM tips were primarily prepared by cutting and sometimes electrochemically etching. Pt\textsubscript{0.8}Ir\textsubscript{0.2} wire was purchased from California Fine Wire Company. Images were typically obtained in constant current mode at a sample potential of +0.5 to +0.7 V and a tunneling current of 20 pA. Images of sizes ranging from 35×35 nm\(^2\) to 50×50
nm² were collected at a scan rate of 4.7 lines/sec, giving a total image time of just under 2 min. Images larger than 50×50 nm² were scanned at a slower scan rate of 3.3 to 3.9 lines/sec, giving a total image time of roughly 2.5 min. The temperature of the sample was controlled by a variable-temperature hot stage using a Lakeshore 330 auto-tuning temperature controller. The environmental chamber was purged with 99.996% Ar (A-L Compressed Gases, Inc., Spokane, WA) at all times. It is important to maintain an inert atmosphere due to CoOEP’s capability of binding O₂ from atmosphere at room temperatures. The O₂-CoOEP adduct appears dim in an STM and can be misinterpreted as a H₂OEP molecule. Before imaging, samples were allowed to sit for 30 minutes to one hour inside the environmental chamber purged with Ar at 2.5 standard cubic feet per hour (scfh). During imaging, Ar was continuously purged at 0.5 scfh into the environmental chamber.

Solutions of CoOEP and H₂OEP were prepared by dissolving solid porphyrin compounds in purified 1-phenyloctane. Concentrations were measured using a UV-visible spectrophotometer where the extinction coefficient of each species had been previously measured by applying Beer’s law to a series of dilutions of known concentration solutions. A custom-made STM solution cell was used to accommodate large volumes (up to 100 µL) of solution in contact with the HOPG surface.

During the sample heating, the temperature of the sample was ramped at a rate of 5 °C per minute, allowing the sample to reach the desired temperature (within the 90 - 110 °C range) in 20 min. The sample then was held at the desired final temperature for the desired time period. After this fixed time heating, samples were rapidly cooled to room temperature by turning the heater off. Samples were then allowed to equilibrate for at least 60 minutes prior to recording any images. All STM images were background subtracted using SPIP image processing software.
Tip induced desorption was seen for both porphyrins as was previously reported for CoOEP. Further information on these induced desorption events is presented in the supplemental section. Whenever a tip induced desorption was observed, the scanner was moved to a new area and data collection was restarted.

5.4 Results and Discussions:

![Figure 5-1](image)

**Figure 5-1.** 20×20 nm² STM images at the 1-phenyloctane/HOPG interface of (a). CoOEP (only) and (b). H₂OEP (only) at a sample bias of +0.7 V and current of 20 pA. The scale bars shown are 5 nm.

Pure monolayers of CoOEP and H₂OEP on HOPG are formed by drop casting individual solutions prepared in 1-phenyloctane. STM images shown in Figure 5-1 of both porphyrins were
taken under Ar at room temperature. Line profiles clearly indicate that the CoOEP centers appear bright whereas a depression is seen at the center of H$_2$OEP. A half-filled d$_z^2$-orbital of the cobalt ion gives rise to the brightness of the molecule, whereas the lack of states in H$_2$OEP near the Fermi level is responsible for the depression.\textsuperscript{76,101,127,128} The intensities given by line profiles of an STM image can only be compared between molecules within the same image (or when same tip is used) and hence should not be confused with the absolute height of the molecule. In any case, a solution mixture of CoOEP and H$_2$OEP deposited on HOPG surface gives a mixture of clearly identifiable bright and dark sites indicative of CoOEP and H$_2$OEP respectively. As the solution ratio of CoOEP is increased relative to H$_2$OEP, the number of bright sites also increases on the HOPG surface as is shown in Figure 5-2. This is consistent with our expectation that CoOEP is bright and H$_2$OEP is dark.

\textbf{Figure 5-2.} Room Temperature STM images of mixtures of CoOEP and H$_2$OEP in phenyloctane at the HOPG-solution interface at (a) $X_C = 0.34 \pm 0.03$ and $\Theta_C = 0.32 \pm 0.02$, (b) $X_C = 0.46 \pm 0.03$ and $\Theta_C = 0.46 \pm 0.02$, and (c) $X_C = 0.66 \pm 0.03$ and $\Theta_C = 0.65 \pm 0.01$. Set point conditions: sample bias of +0.7 V and current of 20 pA. The scale bars shown are 10 nm.
Here, we define \( X \) as the ratio of no. of XOEP to the total no. of porphyrins in solution. Similarly, \( \Theta \) as the ratio of XOEP to the total number of porphyrins on the surface (\( X \) is \( C \) for CoOEP and \( H \) for H\(_2\)OEP). In both definitions, solvent molecules are excluded. Figure 5-2(a) represents \( X_C = 0.34 \pm 0.03 \) and \( \Theta_C = 0.32 \pm 0.02 \); 5-2(b) represents \( X_C = 0.46 \pm 0.03 \) and \( \Theta_C = 0.46 \pm 0.02 \); 5-2(c) represents \( X_C = 0.66 \pm 0.03 \) and \( \Theta_C = 0.65 \pm 0.01 \). It is not surprising considering previous works on porphyrins that the relative surface coverage is effectively the same as the mole fraction in solution. To determine the stability of the adlayer, in-situ temperature dependent studies and sequential STM imaging of mixed monolayers were performed. Figure 5-3 shows in-situ temperature dependent STM images of \( X_C = 0.34 \pm 0.03 \) at 25, 50, and 70 °C. In all three cases \( \Theta_C \) was found to be \( 0.32 \pm 0.04 \). Furthermore, sequential images of the same mixture at 50 °C (as depicted in Figure 4) show that the detailed molecular distribution of the monolayer does not change in a time scale of minutes. Out of many sequential images analyzed, our only indication of molecular exchange was seen at 70 °C. To be more specific, only three molecules were found to exchange between the surface and solution (Figure 5-S1). This number is extremely small compared to the total number of molecules observed over many sequential images analyzed at 70 °C (> 7000 molecules!) and suggest that the monolayer is stable up to 70 °C. Thus, the molecules do not exchange between the surface and solution on a time scale of days and the monolayer formation observed is completely controlled by kinetics below 70 °C.
Figure 5-3. In-situ temperature dependent STM images of $X_C = 0.34 \pm 0.03$ and $\Theta_C = 0.32 \pm 0.04$ at 25, 50, and 70 °C. Set point conditions: sample bias of +0.7 V and current of 20 pA. The scale bars shown are 10 nm.

Figure 5-4. In-situ sequential STM images of $X_C = 0.34 \pm 0.03$ at 50 °C show no changes in the monolayer with respect to the marker indicated with a red circle. Each image is separated in time by 2 minutes. Set point conditions: sample bias of +0.7 V and current of 20 pA. The scale bars shown are 10 nm.
The fact that the surface coverage of a species is essentially the same as its solution mole ratio tells us that both the porphyrins have similar rates of adsorption. More precisely, they have very similar diffusion rates and sticking probability on the HOPG surface. However, how fast is the rate of adsorption and how long does it take for a complete monolayer to form? To answer this, an experiment was performed where; first, only one species of OEP was deposited. Then, it was exposed to an excess solution of the other OEP within 10 s. Imaging this perturbed system only showed the original OEP i.e. when H₂OEP was deposited first followed by an addition of excess CoOEP, only H₂OEP was seen in the STM image and is illustrated in Figure 5-5. Similarly, a CoOEP monolayer at room temperature was unaffected when exposed to the free base within a few seconds of initial CoOEP solution exposure. Hence, the monolayer formation is extremely fast and forms within seconds. This very fast and stable monolayer formation was also seen in the CoOEP/NiOEP system. Monolayers of both OEP’s at room temperature had domain sizes in the range of hundreds of nanometers. Thus, only a handful of grain boundaries were observed. This shows that the process of monolayer formation for both porphurins is very similar and that the cobalt ion does not have a large influence on the adsorption process on HOPG.

For adsorption of mixtures of OEP, a kinetic analysis (provided in references 32 and 33) can be performed and results in the expression for relative coverage given below, where we have assumed that the rate of adsorption is many orders faster than the rate of desorption.

\[
\theta_C = (1 - e^{-\bar{k}MT_c}) \left( \frac{k_C^a X_c}{\bar{k}} \right) \quad \text{… (eq 5-1)}
\]

and, \[
\bar{k} = \left( k_C^a X_C + k_H^a X_H \right) = k_C^a X_C + k_H^a (1 - X_C) \quad \text{… (eq 5-2)}
\]
where, $k^a_C$ and $k^a_H$ are the adsorption rate constants for CoOEP and H2OEP respectively. $X_C$ and $X_H$ are the mole fractions of CoOEP and H2OEP in solution respectively and $M$ is the total molarity of porphyrins in solution. As explained above, at lower temperatures the rate of desorption is extremely slow so ($t \to \infty$) and

$$\theta_C = \left( \frac{k^a_C X_C}{k} \right).$$

Thus, $\theta_C$ depends only on the mole fraction and relative rates of adsorption of the OEP.$^{32,33}$

**Figure 5-5.** STM images at 25 °C of H2OEP (a) before and (b) 24 h after the addition of CoOEP within 10 s. In both cases only H2OEP is seen on the surface. Final $X_C = 0.80$. Set point conditions: sample bias of +0.7 V and current of 20 pA. The scale bars shown are 10 nm.

For desorption, it is clear from in-situ temperature dependent images described earlier that the rates are extremely slow even at 70 °C. Hence, in order to obtain quantitative information we will either need to gather images at 70 °C for at least ~16 hours (for only 15% desorption) and for at least 350 hours to achieve equilibrium;$^{129}$ or, ex-situ desorption (explained in detail below) can
be performed at higher temperatures where substantial desorption of OEP from HOPG occurs within a few hours. Hence, in order to account for complete desorption within a reasonable time frame we opted to follow the ex-situ desorption scheme.

In the ex-situ desorption scheme, initially a monolayer of either OEP is prepared. Then, an excess of the other OEP (tracer) is added to the solution such that the final mole fraction of tracer OEP in solution, \( X(\text{tracer}) \) is 0.80. As shown in Figure 5-5 and in-situ temperature dependent studies (Figure 4), the initial OEP is unlikely to desorb below 70 °C. The mixture is annealed at 90, 100, and 110 °C for time intervals of 30 or 60 min and immediately cooled back down to room temperature and imaged. *Due to the fast adsorption and slow desorption rates the images obtained after cooling the sample mimics the surface at the annealed temperature and time.* The choice of annealing temperature, heating rate, and cooling rate are extremely important. Choosing too high of a temperature and/or too slow a heating and cooling rate results in significant desorption during the the ramping up and cooling down of temperature; thus, the observed surface coverage value, \( \Theta \) will be more than the amount desorbed at the higher temperature. This subsequently leads to over estimating the rates. An indicator of the error caused by this procedure is the difference in coverage observed for a series of short heating times compared to the coverage seen after one long time equal to the sum of the individual times.

After a particular heating-hold-cool cycle, sufficient STM images were captured (up to 15,000 molecules per data point analyzed). Then the sample was annealed at the same temperature for another cycle and the process is continued for up to 4 h of total annealing time. To minimize the errors in \( \Theta(t) \) values determined from a series of short annealing cycles were checked against STM data obtained from images resulting from a single annealing performed for a total time t.
Hence, the $\Theta(t)$ values in figure 5-7 are a collection of both the above mentioned ex-situ annealing schemes.

**Figure 5-6.** Ex-situ STM images of OEP desorption taken at RT. Comparison between CoOEP and H$_2$OEP desorption at similar time and temperature is given. Set point conditions: sample bias of +0.7 V and current of 20 pA. The scale bars shown are 5 nm.
After each annealing cycle, surface coverage, $\Theta(t)$ values were collected and plotted with respect to time for each temperature as given in Figure 5-9. In order to extract rate parameters, we used a model developed in references 32 and 33. In this model, the rate of appearance of (x)OEP 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\} – \{the rate of disappearance of YOEP $\times$ the probability that this vacant site will be replace by XOEP\}. Here, if ‘X’ is CoOEP then ‘Y’ is H$_2$OEP and vice-versa. This model is based on the assumption where the rates of adsorption are many orders in magnitude faster than the rates of desorption. Also, from our earlier assessment of the adsorption process, it is correct to assume that the rates of adsorption for both the OEP are the same, $k^a_{H} = k^a_{C}$ and that the probability of replenishing the vacant site after desorption for either OEP is the same as its mole fraction in solution, $P_i = X_i$. The following equations result from the above model:

$$
\Theta_y(t) = \frac{X_x}{X_x + K^d_y(1 - X_x)} \left[1 - e^{-bX_x k^d_x t}\right] \ldots (eq \ 5-3)
$$

Where, $K^d_y = \frac{k^d_x}{k^d_y}$ and $b = \left[1 + \left(1 - X_x \left(\frac{K^d_y}{X_x}\right)\right)\right]$

And again, the subscripts here denotes which porphyrin. If ‘x’ is CoOEP then ‘y’ is H$_2$OEP and vice-versa, $\Theta_x(t)$ represents the surface coverage of the XOEP (tracer) for YOEP desorption, $k^d_y$ denotes the desorption rate constant for YOEP, $K^d_y$ is the relative rate of desorption of XOEP to YOEP, and $X_x$ is the mole fraction of XOEP in solution.
Assuming an Arrhenius type desorption, equation 3 can be expanded using:

\[ k_x^d = k_x^0 e^{-\Delta E_x/RT} \]

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

\[
\Theta_y(T,t) = \left[ \frac{1}{1 + \left( \frac{1 - X_x}{X_y} \right) k_x^0 \left( \frac{k_y^0}{k_y^0} \right) e^{\frac{(\Delta E_x - \Delta E_y)}{RT}}} \right]^{-1} \exp \left[ -X_y k_x^0 e^{-\frac{\Delta E_x}{RT}} \left( \left( \frac{k_y^0}{k_y^0} \right) e^{\frac{(\Delta E_x - \Delta E_y)}{RT}} \left( \frac{1 - X_x}{X_y} \right) + t \right) \right]
\]

(4)

Here, \( X_y \) and \( X_x \) is the mole fraction of YOEP and XOEP in Solution. In equation 4, \( \Theta_y(T,t) \) has four unknowns with \( k_x^0, k_y^0, \Delta E_x \), and \( \Delta E_y \). Multiple curve fitting methods can be performed using equations 3, and 4. Equation 4 can be used to fit all four parameters (\( k_C^0, k_H^0, \Delta E_C \), and \( \Delta E_H \)) to obtain an estimated activation energies and the rate constants for desorption.

Here, we analyzed the CoOEP and H₂OEP desorption using five different curve fitting parameters. (1) All four parameters \( k_C^0, k_H^0, \Delta E_C \), and \( \Delta E_H \) are used to optimize equation 4. (2) Three parameters where \( k_C^0 = k_H^0 = k^0 \), \( \Delta E_C \), and \( \Delta E_H \) are used. (3) Three parameters where \( k_C^0, k_H^0, \Delta E_C = \Delta E_H \) are used. (4) Two parameters where \( k_C^0 = k_H^0 = k^0 \) and \( \Delta E_C = \Delta E_H = \Delta E \) are used. (5) Two parameters where \( k_C^0 \) and \( k_H^0 \) are used with an average value of \( \Delta E_C \) and \( \Delta E_H \) of 1.25×10² kJ/mol are used. Table 1 provides all the four parameters and calculated rate constants at each temperatures for all the five curve-fitting models described above.
Table 5-1. Rate parameters for both CoOEP and H₂OEP using five different curve-fitting models.

<table>
<thead>
<tr>
<th>Fitting Methods</th>
<th>CoOEP</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>H₂OEP</th>
<th></th>
<th></th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_d$</td>
<td>$k_d$</td>
<td>$k_d$</td>
<td>$k_d$</td>
<td>$\Delta E_C$</td>
<td>$\Delta E_H$</td>
<td>$%$ error</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$90^\circ C$</td>
<td>$100^\circ C$</td>
<td>$110^\circ C$</td>
<td>$(10^{13} \text{ sec}^{-1})$</td>
<td>$(10^5 \text{ J/mol})$</td>
<td>$(10^5 \text{ J/mol})$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-para fit</td>
<td>0.096</td>
<td>0.29</td>
<td>0.84</td>
<td>2.7</td>
<td>1.25±0.04</td>
<td>0.14</td>
<td>0.46</td>
<td>0.84</td>
<td>4.2</td>
</tr>
<tr>
<td>3-para.</td>
<td>0.096</td>
<td>0.28</td>
<td>0.84</td>
<td>3.5</td>
<td>1.26±0.04</td>
<td>0.13</td>
<td>0.40</td>
<td>1.14</td>
<td>3.5</td>
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<tr>
<td>$(k_C=k_H)$</td>
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<tr>
<td>3-para.</td>
<td>0.12</td>
<td>0.37</td>
<td>1.08</td>
<td>3.3</td>
<td>1.25±0.01</td>
<td>0.15</td>
<td>0.46</td>
<td>1.32</td>
<td>4.1</td>
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<tr>
<td>$(\Delta E_C=\Delta E_H)$</td>
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<tr>
<td>2-para.</td>
<td>0.12</td>
<td>0.37</td>
<td>1.08</td>
<td>2.1</td>
<td>1.24±0.004</td>
<td>0.12</td>
<td>0.37</td>
<td>1.08</td>
<td>2.1</td>
</tr>
<tr>
<td>$(k,C,\Delta E)$</td>
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<tr>
<td>2-para.</td>
<td>0.11</td>
<td>0.34</td>
<td>0.96</td>
<td>3.1</td>
<td>1.25</td>
<td>0.14</td>
<td>0.43</td>
<td>1.26</td>
<td>3.8</td>
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<td>$(k_C,k_H)$</td>
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<td></td>
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<tr>
<td>$\Delta E_C=\Delta E_H$</td>
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<tr>
<td>$=1.25x10^5$</td>
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<tr>
<td>Avg.</td>
<td>0.106</td>
<td>0.320</td>
<td>0.93</td>
<td>3.1</td>
<td>1.25</td>
<td>0.14</td>
<td>0.44</td>
<td>1.14</td>
<td>3.9</td>
</tr>
</tbody>
</table>

From Table 1, it is clear that the desorption energy remains relatively constant and same for both CoOEP and H₂OEP with $(1.25 \pm 0.05)\times 10^2 \text{ kJ/mol}$. Given the exponential dependence of rate constant with the desorption energy, the margin for changes in rate constant with changes in activation energy are extremely large which limits large changes in the activation energy.
Hence, in all analysis, $\Delta E$ for both OEPs turns out to be the same within the error range. Figure 7 shows the best fit curves for a 3 parameter ($k_C^0=k_H^0=k^0$, $\Delta E_C$, and $\Delta E_H$) model that has the lowest % error as shown in Table 1.

Given the differences in desorption kinetics (individual rates), we tend to believe that the CoOEP desorption energy is slightly greater than for the free base. However, the uncertainties in the calculated activation energies are such that one cannot with confidence attribute the rate differences solely to a difference in activation energy. These activation energies for both OEP are the same and indicate that they adsorb to the HOPG surface with near equal strength. In a computational study, Chilukuri and coworkers\textsuperscript{130} show that the CoOEP on Au(111) induces additional density of states which was attributed to the cobalt ion interaction with the Au(111) surface. Whereas, no such states were seen when HOPG was used indicative of minimal or no interaction between the central metal and the HOPG surface. This supports our experimental observations that when cobalt ion replaces the protons in the center of the porphyrin, the adsorption strength on HOPG does not change significantly.
Figure 5-7. Three parameter best fit curves for desorption rates using equation 4 with $k_C^0 = k_H^0 = 3.5 \times 10^{13}$ sec$^{-1}$, $\Delta E_C = (1.26 \pm 0.04) \times 10^2$ kJ/mol, and $\Delta E_H = (1.25 \pm 0.04) \times 10^2$ kJ/mol for (a) H$_2$OEP at 90 (black), 100 (blue), and 110 °C (red), and (b) CoOEP at 90 (black), 100 (blue), and 110 °C (red).

This analysis leads us to compare the rates of desorption of CoOEP in this study versus a previous work given in reference 32. In the previous work, NiOEP was used as a tracer for the CoOEP desorption whereas, H$_2$OEP is used in this work with similar experimental parameters. In both cases CoOEP appears brighter than NiOEP and H$_2$OEP under similar STM conditions. Table 5-2 provides the rate constants for CoOEP desorption when NiOEP and H$_2$OEP were used as tracers. Based on the data in Table 5-2, CoOEP desorbs faster in presence of NiOEP than in presence of H$_2$OEP from HOPG. While this discrepancy could potentially arise from the differences in solubility of NiOEP and H$_2$OEP in 1-phenyloctane, the solutions used in both studies were well below their solubility limits. Hence, solubility should not account for this difference.
On careful analysis of the initial desorption process, it appears that the surface coverage of tracers (NiOEP and H$_2$OEP) are very similar to each other. After 30 min of annealing time at 90 °C, with NiOEP, $\Theta_N (30) = 0.11 \pm 0.04$, and with H$_2$OEP, $\Theta_{H_2} (30) = 0.11 \pm 0.04$. These values are very close to each other. However, as desorption of CoOEP progresses, surface coverage of NiOEP increases more rapidly than H$_2$OEP. This can be explained as a cooperativity effect. In the CoOEP replaced by NiOEP case, as the surface coverage of NiOEP increases it is more likely to be surrounded by similar NiOEP molecules on the surface. In other words, it is more likely to destabilize the CoOEP monolayer and hence the rates of desorption of CoOEP will appear faster. Desorption experiments with both NiOEP and H$_2$OEP in the presence of each other would be interesting.

Table 5-2. Comparison between rate constants for CoOEP desorption when H$_2$OEP is used as a tracer (this work) and when NiOEP is used as a tracer (reference 32).

<table>
<thead>
<tr>
<th>Rate constants for CoOEP desorption, $k_{dC}^d$ (min$^{-1}$)</th>
<th>When H$_2$OEP is used as a tracer</th>
<th>When NiOEP is used as a tracer$^{32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 °C</td>
<td>0.0022 ± 0.0008</td>
<td>0.0055 ± 0.0007</td>
</tr>
<tr>
<td>100 °C</td>
<td>0.0047 ± 0.001</td>
<td>0.013 ± 0.001</td>
</tr>
<tr>
<td>110 °C</td>
<td>0.017 ± 0.008</td>
<td>0.033 ± 0.003</td>
</tr>
</tbody>
</table>
5.5 Desorption from step edges and grain boundaries

All of the above analysis for kinetics of desorption for OEP are related to desorption from terraces of HOPG. It has been well documented in the past that the kinetics of adsorption and desorption can be different along step edges and grain boundaries.\textsuperscript{131,132} High catalytic activity along step edges\textsuperscript{133} and molecular exchange mechanisms through grain boundaries have also been reported.\textsuperscript{134} In a similar experiment of NiOEP desorption from Au(111) at the phenylloxate/Au(111) interface, it was shown that NiOEP preferentially desorbs from the step edges and reconstruction lines. In this work we also report preferential desorption of H\textsubscript{2}OEP from step edges and grain boundaries, whereas CoOEP does not show preferential desorption from step edges. Since single domains of OEP on HOPG extend to hundreds of nanometers in size, we did not encounter any grain boundaries during CoOEP desorption and hence we will leave this analysis for our future work where we will explore this possibility and calculate the rates of desorption from these surface sites.
Figure 5-9. STM images of site specific desorption. (a) Desorption from a grain boundary: H$_2$OEP desorption after 30 min at 110 °C shows higher surface coverage of CoOEP (bright sites) along the grain boundary shown by the white curve. Red and blue lines show two different lattice directions separated by the grain boundary. The scale bar shown is 20 nm. (b) Desorption from a step edge: H$_2$OEP desorption after 90 min at 90 °C shows higher surface coverage of CoOEP (bright sites) close to the step edge. The scale shown is 10 nm. In both images, set point conditions used are 0.7 V and 20 pA tunneling current.

5.6 Conclusions

Desorption kinetics of CoOEP and H$_2$OEP at the solution/solid interface has been performed using STM. At temperatures below 70 °C, monolayers of OEP on HOPG are controlled by kinetics and the rates of desorption are extremely slow. Significant desorption in a time scale of few hours occurs at 90, 100, and 110 °C. Thus, an ex-situ desorption scheme is used to
determine kinetic parameters at these temperatures. The rates of desorption and activation energies of both OEP are very similar and show only weak effects due to the presence of cobalt ion. This shows that the adsorption strength most likely arises from the interactions between the porphyrin core and the HOPG surface. The activation energy is in the range of ~125 kJ/mol. When compared to an earlier study of CoOEP desorption from HOPG and Au(111) (with NiOEP as a tracer), this value is comparable and the overall activation energy for OEP can be given as 100 – 130 kJ/mol.

Both OEP occupy similar area on HOPG with $A = 1.3 \pm 0.02$ nm, $B = 1.4 \pm 0.02$ nm, and $\alpha = 57.5^\circ \pm 2^\circ$ (assuming one molecule per unit cell). For NiOEP on Au(111) under UHV conditions, the ethyl groups were resolved and the unit cell was found to consist of two molecules.\textsuperscript{74} Since we were not able to resolve the ethyl groups, we only used one molecule per unit cell. Although solubility values for both OEP are different, the concentrations used to perform all the experiments are significantly lower than their solubility limits and we can assume that the solvent-OEP interactions are similar. Finally, due to the similar rates of desorption and activation energies for both OEP measured in this work, the adsorption strength must primarily arise from the interaction between the porphyrin core and the HOPG surface neglecting any contributions from the Co – HOPG interaction. Although it is possible and likely that the cobalt ion can have significant impact when different substrates are used.
5.7 Supplemental Section

In-situ temperature dependence study of mixture of CoOEP and H₂OEP at 70 °C: Figure 5-S1 shows a sequential STM images for a mixture of $X_C = 0.34 \pm 0.03$ at 70 °C and $\Theta_C = 0.32 \pm 0.04$. Out of many images analyzed (>7000 molecules!) at 70 °C, our only indication of molecular exchanges were seen in these images, where only three molecules encircled with yellow and blue have exchanged between the surface and solution.

![Figure 5-S1](image)

**Figure 5-S1.** In-situ sequential STM images of $X_C = 0.34 \pm 0.03$ at 70 °C show three molecules exchange between the surface and solution encircled by yellow and blue. The red circle is used as a marker present in all three images. Each image is separated by 2 min apart. Set point conditions: sample bias of +0.7 V and current of 20 pA. The scale bars shown are 10 nm.

**Tip induced desorption:** Tip induced desorption of CoOEP has been previously reported in an earlier study. Here, we will only focus on desorption for H₂OEP. To study tip induced desorption, first a monolayer of H₂OEP is created, then an excess of CoOEP is added to the solution. Imaging this surface only shows H₂OEP (figure 5-S1 (a)). When a pulse of -4 V is
applied between the tip and the sample, H₂OEP molecules desorb from the surface and is immediately replaced by the OEP molecules in solution (figure S2 (b), (c), and (d)). Due to the excess CoOEP in solution, the tip induced desorbed section is replenished mostly by CoOEP and can be clearly seen in sequential images in figure 5-S2 with bright patches of molecules.

**Figure 5-S2:** Sequential STM images shows tip induced H₂OEP desorption from HOPG (a) represents pure H₂OEP monolayer with excess CoOEP added after monolayer formation (b), (c), and (d) pulse of –4 V is applied during scanning in each of the sequential images, and (e) is the final image taken after all three pulses are applied. White arrows show the scanning directions.
Chapter 6. Single Molecule Imaging of Oxygenation of Cobalt Octaethylporphyrin at the Solution/Solid Interface: Thermodynamics from Microscopy

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6.1 Abstract

For the first time, the pressure and temperature dependence of a chemical reaction at the solid/solution interface is studied by scanning tunneling microscopy (STM), and thermodynamic data are derived. In particular, the STM is used to study the reversible binding of O\(_2\) with cobalt(II) octaethylporphyrin (CoOEP) supported on highly oriented pyrolytic graphite (HOPG) at the phenyloctane/CoOEP/ HOPG interface. The adsorption is shown to follow the Langmuir isotherm with \(P_{1/2}^{298K} = 3200\) Torr. Over the temperature range of 10−40 °C, it was found that \(\Delta H_P = -68\pm 10\) kJ/mol and \(\Delta S_P = -297 \pm 30\) J/(mol K). The enthalpy and entropy changes are slightly larger than expected based on solution-phase reactions, and possible origins of these differences are discussed. The big surprise here is the presence of any O\(_2\) binding at room temperature, since CoOEP is not expected to bind O\(_2\) in fluid solution. The stability of the bound oxygen is attributed to charge donation from the graphite substrate to the cobalt, thereby stabilizing the polarized Co–O\(_2\) bonding. We report the surface unit cell for CoOEP on HOPG in phenyloctane at 25 °C to be \(A = (1.46 \pm 0.1)n\) nm, \(B = (1.36 \pm 0.1)m\) nm, and \(\alpha = 54 \pm 3°\), where \(n\) and \(m\) are unknown nonzero non-negative integers.
6.2 Introduction

Temperature-dependent studies of surface structures can provide a great wealth of information. They can yield diffusion and reaction rates, activation energies, and thermodynamic quantities, such as entropy and enthalpy of adsorption and/or surface reaction. Because different surface species reach equilibrium at different temperatures and because some surface reactions are kinetically controlled, a study of a given solution–surface pair as a function of temperature can lead to the discovery of new materials and phases. In some cases, the ability to even observe the surface structure is confined to a relatively narrow temperature window, while in others, different structures are observed over a wide temperature range. The ability to observe surface structures as a function of temperature at the solution/solid interface has particular relevance to modern technology, self-assembly, catalysis, friction, film growth, organic electronics, and many other areas.

The study of molecular and even atomic processes at surfaces has been dramatically advanced by the application of the scanning tunneling microscope (STM). There are now about 27 000 papers having “scanning tunneling microscopy” in the title or abstract. If one narrows a SciFinder search to include the “solution interface”, the number of citations drops to about 500, still a massive body of literature. There are many tens of papers where samples are separately heated, returned to ambient, and then measured. If one then searches for those papers where molecular level studies are actually performed at the solid/solution interface at a temperature significantly different from room temperature, the total publications drop to a very few, with many of these at a single fixed temperature and at least one of the very recent papers inspired by our recent work. A few more papers relate to hot stage designs
appropriate for this application (but often focused on atomic force microscopy (AFM) applications).\textsuperscript{137-140}

In this work we will use variable temperature STM imaging at the solution/solid interface to determine the thermodynamics of the reversible binding of dioxygen to CoOEP adsorbed on highly oriented pyrolytic graphite (HOPG). Both the variable temperature and single molecule resolution capabilities of the STM are critical for this study. To our knowledge this the first single molecule level study of the temperature dependence of a chemical reaction at the solution/solid interface of any system, not just the dioxygen–CoOEP system. The STM offers unique features including submolecular resolution, sensitivity to electronic structure, ability to function at the solution/solid interface, and variable temperature capability that make it an ideal tool for the study of temperature-dependent surface reactions.

Metalloporphyrins and metallophthalocyanines are a highly versatile family of molecules with widely varying properties and potential applications. Porphyrins and phthalocyanines may serve as components in solar cells,\textsuperscript{5} fuel cells,\textsuperscript{141} nonlinear optical devices,\textsuperscript{142} sensors,\textsuperscript{143} and catalysts,\textsuperscript{144} serve as sensitizers in photodynamic tumor therapy,\textsuperscript{145} and as components in nanostructured materials.\textsuperscript{146,147} The binding of small molecules to metalloporphyrins and metallophthalocyanines is a topic of great interest for a number of reasons. Metalloporphyrins are analogs of hemes, and consequently knowledge of the binding of dioxygen to metalloporphyrins is critical for our understanding of life.\textsuperscript{148} Several gas-sensing systems employing metalated porphyrins and phthalocyanines have been reported in the literature. Cobalt phthalocyanine molecules deposited on gold electrodes via organic molecular beam epitaxy show promise as sensors for a variety of species including the Sarin analog dimethyl methylphosphonate.\textsuperscript{149,150} The cobalt “picket fence” porphyrin, meso-\(\alpha,\alpha,\alpha,\alpha\)-tetrakis(o-pivalamidophenyl)}
porphyrinatocobalt(II) imbedded in a polymer matrix functions as an oxygen sensor.\textsuperscript{151} Cobalt porphyrins also show promise as electrocatalysts for oxygen reduction.\textsuperscript{152-155}

While the binding of dioxygen to cobalt porphyrins is wellknown, much of the data reported was gathered at low temperatures (below −20 °C) either in solution\textsuperscript{156-163} or in frozen solutions.\textsuperscript{164,165} There are relatively few cobalt porphyrins capable of reversibly binding dioxygen at ambient temperatures,\textsuperscript{166} most notably cobalt substituted myoglobins\textsuperscript{167,168} and the aforementioned cobalt “picket fence” porphyrin meso-\textsuperscript{166} α,α,α,α-tetrakis(o-pivalamidophenyl) porphyrinatocobalt(II). This porphyrin binds dioxygen at room temperature in solution\textsuperscript{166-173} and in the solid state,\textsuperscript{171} but only when a basic axial ligand is present. Kinetic data on the adsorption/desorption of dioxygen to this molecule have been reported at 40 °C, wherein a two-stage adsorption model was proposed.\textsuperscript{170}

The enthalpy and entropy changes associated with dioxygen binding to cobalt substituted porphyrins are of interest because cobalt porphyrins serve as model systems for the study of oxygen binding to hemes. Much of the compiled thermodynamic data on cobalt substituted naturally occurring and model porphyrins has been gathered in solution with enthalpy and entropy values ranging from −33 to −56 kJ/mol and −170 to −245 J/(mol K), respectively, when referenced to a 1 Torr standard state for O\textsubscript{2}.\textsuperscript{156-171} The entropy change associated with dioxygen binding is largely due to the loss of translational and rotational entropy by the bound oxygen as predicted by statistical mechanical calculations.\textsuperscript{174}

While it is expected that the affinity for dioxygen binding is strongly dependent on porphyrin species, coordination of the cobalt ion by a fifth ligand can strongly influence equilibrium. Stynes et al. reported on the effects of coordination of basic ligands to the fifth position on dioxygen binding to cobalt(II) protoporphyrin IX dimethyl ester below −30 °C.\textsuperscript{156,157}
Variation in enthalpy and entropy of oxygenation up to 24% and 15%, respectively, was achieved by changing the fifth ligand. The same study also investigated Hammet relationships among a series of para-substituted pyridines and concluded that oxygen binding is favored by ligands capable of donating electron density to the metal ion to help offset the loss of electron density associated with binding oxygen. Collman et al. have also investigated the effect of coordination of a fifth ligand on oxygenation of cobalt “picket fence” porphyrin at room temperature. They showed that cobalt “picket fence” porphyrin binds oxygen to a degree comparable to cobalt substituted myoglobins so long as an imidazole was also bound to the cobalt (in the fifth coordination site). In the absence of a bound imidazole the porphyrin did not bind oxygen at room temperature, thereby underscoring the importance of the fifth coordination site. We also note that Summers and Stolzenberg indicated that ligand binding to the fifth coordination site on cobalt(II) porphyrins relieved strain within the ring system.

Reversible dioxygen binding to cobalt porphyrins and phthalocyanines on surfaces has been reported by groups researching gas sensors and gas selective membranes. Cobalt(II) “picket fence” porphyrin affixed to imidazole and pyridine bases imbedded in membranes is capable of reversibly binding dioxygen with half oxygen saturation pressures ($P_{1/2}$) lower than in solution or as a crystal. The $P_{1/2}$ of Co “picket fence” porphyrin in toluene with 1-methylimidazol coordinated at the fifth site is 140 Torr at 25 °C, while the same porphyrin bound to an imidazol-terminated polymer reaches half saturation at 74 Torr at 25 °C; close to the $P_{1/2}$ of crystalline porphin/1-methylimidazol (61 Torr) at 25 °C. The enthalpy of oxygenation for the porphyrin/imidazol pair increases in the order of solution (~51.0 kJ/mol) to solid state (~55.6 kJ/mol) to the membrane-bound porphyrin (~58.6 kJ/mol). The entropy change, referenced to a 1 Torr standard state, upon oxygen binding is less dramatic in this case.
The values increase from $-214 \text{ J/(mol K)}$ in toluene solution\textsuperscript{43} to $-223 \text{ J/(mol K)}$ in the solid state.\textsuperscript{171} Summers et al. state that the entropy change for the membrane is similar to that in solution.\textsuperscript{177}

The subject of this study, CoOEP, is a known electrocatalyst for the reduction of oxygen\textsuperscript{153,178} and shows promise as a gas sensor due to its capability to bind volatile organic molecules.\textsuperscript{179,180} Interestingly, Yamazaki et al. have demonstrated that substrate choice can impact the onset potential of oxygen reduction by cobalt porphyrins by almost 200 mV.\textsuperscript{153} CoOEP reversibly binds carbon monoxide at ambient temperature\textsuperscript{181} but will bind dioxygen only at low temperatures ($<-90 \text{ °C}$).\textsuperscript{182-185} The dioxygen complex was investigated by Raman, infrared, Mössbauer, and electron spin resonance spectroscopies. In all but one of the studies an axial base was used. In that latter study, the dioxygen adduct was reported to form in argon matrices at 15 K without the addition of a fifth ligand.\textsuperscript{182} No thermodynamic data for adduct formation were reported.

6.3 Experimental Section

2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine cobalt(II) [CoOEP] was purchased from Aldrich. Reagent grade chloroform was purchased from J.T. Baker. Phenyloctane (99%) was purchased from Alfa Aesar. All reagents were used without further purification. The 1 cm$^2$ highly ordered pyrolytic graphite (HOPG) substrates (grade 2) were purchased from SPI supplies (West Chester, Pa., no. 436HP-AB, lot no. 1160321). STM images were recorded using a Molecular Imaging (now Agilent) Pico 5 STM equipped with a 1 μm$^2$ head and an environmental chamber. STM tips were made by cutting or electrochemically etching Pt$_{0.8}$Ir$_{0.2}$ wire (California Fine Wire Company Grover Beach, Ca.). Images were typically obtained at a sample potential of $-0.5 \text{ V}$ and a tunneling current of 20 pA. Scan rates typically were 4.7 lines/sec, giving a total image time of
2.0 min. The temperature of the sample was controlled by either a variable temperature hot stage or a 1X Peltier stage using a Lakeshore 330 autotuning temperature controller. Temperature was monitored with a calibrated Pt resistance thermometer. Stock solutions of CoOEP were prepared by dissolving sufficient solid CoOEP in chloroform to make a solution of concentration 200 μM. This solution was subsequently diluted to about 9 μM in chloroform. STM samples were prepared by dropping a 25 μL aliquot of the 9 μM CoOEP solution on a freshly peeled 1 cm² HOPG substrate and allowing the solvent to evaporate. The dried surface was then covered with phenyloctane, and the resulting sample was then placed on the heating stage and transferred into the controlled atmosphere chamber of the STM. It should be noted that samples prepared from pure chloroform in this way showed no structured adsorbates and appeared to be clean graphite. This is worth noting since the weight/weight ppm of CoOEP in chloroform is 3.6 ppm, and the solid residue specification for the reagent used is <1 ppm.

The partial pressure of oxygen over the sample was controlled by flowing mixtures of argon and oxygen gas into the STM chamber. Oxygen and argon flows were controlled by individual flow meters (model 7200 King Instrument Company, Garden Grove, CA). Partial pressures were determined as the ratio of O2/(O2 + Ar) times the measured barometric pressure. The gases used had the following purity: 99.995% Ar with water < 5 ppm, and THC < 2 ppm; 99.995% O2 with water < 5 ppm, and THC < 2 ppm; and N₂ with water < 5 ppm, and THC < 2 ppm.

The sample (in the STM chamber) was first annealed at 100 °C for 10 min under pure argon flowing at 2.5 standard cubic feet per hour (scfh). Prior to recording images the samples were allowed to equilibrate for at least three hours at the oxygen partial pressure and temperature of interest. All images were recorded while scanning in a drop of phenyloctane. All STM images
were background subtracted using SPIP\textsuperscript{186} image processing software and drift corrected using a linear drift correction algorithm.\textsuperscript{187,188}

Solution-phase oxygen binding studies were carried out using a Perkin-Elmer model 330 spectrophotometer with 1 cm path length cuvettes. All samples for solution-phase oxygen-binding experiments were prepared in reagent grade toluene degassed by boiling for 45 min followed by cooling to room temperature. The toluene was continuously purged with nitrogen during the degassing process. A 1 μM solution of CoOEP prepared using the degassed toluene was split into two equal samples. Oxygen gas was bubbled through one of the samples for 24 h. After oxygen exposure, the CoOEP solution was analyzed by UV−vis spectroscopy. A duplicate control sample was exposed to nitrogen for 24 h and subsequently analyzed by UV−vis spectroscopy. Appropriate blanks were prepared by exposing toluene to either oxygen or nitrogen gas.

6.4 Results and Discussion

Figure 6-1 is the structure of CoOEP in the all-up or crown configuration of the ethyl groups. This is the known orientation of the ethyl groups for NiOEP adsorbed on Au(111)\textsuperscript{74} and is the presumed configuration for CoOEP on HOPG. The space filling models used later are based on optimization of this configuration by DFT calculations using the B3LYP functional and the 6-311++G(d,p) basis. The actual optimized structure is provided as a Gaussian03 com file in the Supporting Information. We also used the B3LYP functional and a much larger basis 6-311++G(d,p) on C, N, and H and 6-311+G(3df) on O and Co to estimate the structure of the O\textsubscript{2}−CoOEP adduct.
Figure 6-1: Model of “crown” configuration of CoOEP derived from DFT calculation. Black atoms are carbon, white are hydrogen, blue are nitrogen, and red are cobalt. The Gaussian03 com file for this structure is available as supplemental material.

To confirm previous results that pure CoOEP will not bind $O_2$ in solution at room temperature, we measured UV–vis spectra of $O_2$ and $N_2$ saturated solutions in toluene after 24 h of exposure. Figure 5-2 demonstrates that there is no change in either the Soret or Q bands, indicating that no adduct forms under these conditions.
Figure 6-2: UV-Vis spectrum of CoOEP in toluene solution after 24 hours exposure to O$_2$ and to N$_2$, respectively. The oxygenated solution data is manually offset upward to aid comparison.

Figure 6-3 presents a representative image obtained from the HOPG supported CoOEP surface covered in phenyloctane and at equilibrium with a pure O$_2$ atmosphere at 25 °C. There are clearly three types of sites in the image. Those enclosed by squares are very deep and are vacancies in the monolayer. Those enclosed by circles have apparent heights about half that of the other molecular features. By performing the same measurements on monolayers annealed at 100 °C in pure argon, it is clear that the bright (high) features are simply CoOEP. This is consistent with a number of previous studies wherein it was demonstrated that tunneling through the half- filled dz$^2$ orbital produces the bright molecular center.$^{73,100,101}$
Figure 6-3: Drift corrected constant current STM image of the phenyloctane - CoOEP/HOPG interface under conditions of O₂ saturation at 25 °C. STM data was acquired at -0.5 V and 20 pA setpoint. Note that the molecules enclosed in circles are considerably dimmer than others, and the squares identify vacancies in the monolayer. The inset is a cross section emphasizing the differences between the bright and dim molecules.

The components of a mixed monolayer of cobalt(II) hexadecafluoro-29H,23H-phthalocyanine and nickel(II) tetraphenyl 21H,23H-porphine can easily be differentiated in STM images by the bright half-filled dz² orbital in the cobalt species as opposed to the darker Ni atoms. The STM is also capable of detecting axial groups attached to porphyrins and
phthalocyanines. Vanadyl phthalocyanine centers appear dark in STM images due to oxygen’s lack of states near the Fermi level. The striking difference in the STM contrast of bright cobalt with dark vanadyl octaethyl porphyrins adsorbed on graphite was also well demonstrated by Miyake et al. It is the STM’s ability to differentiate the bright half-filled dz\(^2\) orbital in cobalt coupled with the expected attenuated signal in the oxygenated species which allow oxygenated and deoxygenated cobalt porphyrins to be distinguished and consequently thermodynamic data to be gathered on a molecule by molecule basis.

In order to verify our interpretation of the bright and dark features, STM images at varying equilibrium partial pressures of O\(_2\) were measured and analyzed. Defining the surface coverage of dark molecules, \(\Theta\), as the number of dark molecules divided by the total number of surface molecules, one would expect the quantity \(\Theta/(1 - \Theta)\) to be proportional to the partial pressure of O\(_2\) provided that the dark molecules were sites of O\(_2\) adsorption, and the Langmuir isotherm is followed. Figure 5-4 clearly shows that this is the case. Thus, the equilibrium constant for the O\(_2\) adsorption process, \(K_P\), is given by

\[
K_P = \frac{\Theta}{(1 - \Theta) \left( \frac{P}{P^0} \right)}
\]

where following the convention in solution-phase studies we have taken the standard state to be \(P^0 = 1\) Torr. Alternatively, one might relate the equilibrium constant to the molal concentration of O\(_2\) in solution, \(K_c\),

\[
K_c = \frac{\Theta}{(1 - \Theta) \left( \frac{c}{c^0} \right)}
\]

where \(c^0\) is the hypothetical ideal state of 1 m of O\(_2\) in solution. Using \(\Delta G_{P,c} = -RT \ln(K_{P,c})\), one can determine the free energy change for the

\[
O_2 + \text{CoOEP/HOPG} = O_2\text{-CoOEP/HOPG}
\]
system in the appropriate standard state. \[ \Delta S_{P,c} = -(\partial G/\partial T)_{P,c} \] for the appropriate standard state, and \[ \Delta H_{P,c} = \Delta G_{P,c} + T \Delta S_{P,c} \], thereby allowing all the thermodynamic functions to be obtained from a series of STM measurements at various temperatures. The two sets of thermodynamic quantities (at fixed c or fixed P) are connected by the temperature-dependent Henry’s law constant. The thermodynamics that are derived from their temperature dependences differ by the heat and entropy of solution of O\(_2\) in phenyloctane.

**Figure 6-4:** Langmuir plot of relative surface coverage of dark molecules as a function of O\(_2\) partial pressure at 25 °C.

Before proceeding with the thermodynamic analysis, it is important to ascertain the reliability in the values of \(\Theta\) obtained. Thus, the \(\Theta\) value used for each temperature was the average of a large number of separate measurements of STM images. The standard deviations in these measurements were used to determine the vertical error bars (±1 SD) in each figure. To ensure that the system had come to equilibrium, these were measured after a considerable wait and over
a long period of time. A representative set of such measurements is displayed in Figure 6-5. The data in Figure 5-5 were collected after the system had been allowed to come to equilibrium for 4 h. We note that each image analyzed contained about \( N = 250 \) molecules. However, at 25 °C and 176 Torr, the average coverage of oxygenated species is only about 7% of the 250 molecules or 18 oxygenated molecules, resulting in an expected statistical fluctuation of \( \frac{1}{\sqrt{N}} \), or ±23%, which is of the order observed in Figure 5-5.

![Graph showing variation in measurements of \( \Theta \) with time for \( P(O_2) = 176 \) Torr and 25°C.]

**Figure 6-5:** Variation in measurements of \( \Theta \) with time for \( P(O_2) = 176 \) Torr and 25°C.

In order to determine \( K(T) \), values of \( \Theta \) were extracted from STM images acquired at various temperatures and 100% \( O_2 \) saturation and 704 Torr. Figure 6-6 shows three of the many images analyzed as a function of temperature between 10 and 40 °C. Data were not acquired above 40 °C because the number of oxygenated sites had become too few to have statistical significance. It should be noted that the appearance of the bright center varied with tip quality. For a very sharp tip the bright region was small and intense. For a dull tip, most of the molecule appeared bright.
In all cases it was easy to distinguish the dim and bright molecules within a given image. It should be further noted that the “dim” molecules can also be distinguished from vacancies in the monolayer. The central image in Figure 6-6 shows a cross section through three bright molecules, one dim one and a true vacancy (surrounded by a square).

![Image](image-url)

**Figure 6-6**: Representative constant current STM data acquired at 10ºC (left), 25ºC (middle), and 40ºC (right).

Using average values and standard deviations for Θ determined in the manner above for 100% O₂ atmosphere (P = 704 Torr) at various temperatures, one can determine values of ΔG_P as a function of temperature, as shown in Figure 6-7. From the slope of these data with temperature,
$\Delta S$ may be determined. With these, one may calculate $\Delta H$. Thus, one arrives at $\Delta H_P = -68 \pm 10$ kJ/mol and $\Delta S_P = -297 \pm 30$ J/(mol K).

**Figure 6-7:** $\Delta G_P$ as a function of temperature. The slope of the solid blue line is the measured $\Delta S_P$, the entropy change relative to the 1 Torr standard state. For reference, a line with slope equal to the $\Delta S_P$ based solely upon the entropy of $O_2$ at 298 K.

One may also report thermodynamic values referenced to the hypothetical ideal 1 m (of $O_2$) state. These are denoted by subscript c. Thus, $\Delta G_P = \Delta G_c + \Delta G_{H}$, $\Delta H_P = \Delta H_c + \Delta H_{H}$, and $\Delta S_P = \Delta S_c + \Delta S_{H}$, where the H subscript refers to the change in thermodynamic quantity with respect to formation of the solution from the ideal gas phase (Henry’s law). While the Henry’s law constant for phenyloctane is not available as a function of temperature, values for two closely
related compounds, toluene and octane, are available.\textsuperscript{190,191} Thus, one can estimate $\Delta H_c$ and $\Delta S_c$ based on the range seen for these solvents. $\Delta H_c$(toluene) = $-72 \pm 10$ kJ/mol, and $\Delta S_c$(toluene) = $-211 \pm 30$ J/(mole K), while $\Delta H_c$(octane) = $-68 \pm 10$ kJ/mol, and $\Delta S_c$(octane)= $-204 \pm 30$ J/(mole K). Because $\Delta H$ for solvation of $O_2$ is small in these solvents, there is no significant effect on $\Delta H_c$, and we can reasonably say that $\Delta H_c$ (phenyloctane) = $-70 \pm 15$ kJ/mol. While $\Delta S$ for solvation of $O_2$ is large, it is essentially the same for both these solvents. Thus, it is reasonable to estimate $\Delta S_c$ (phenyloctane) = $-208 \pm 24$ J/(mole K). Because it is common to do so in the solution-phase oxygen-binding literature, we used our data to determine the $P_{1/2}(298 \text{ K})$, the $O_2$ partial pressure at which half the sites on the CoOEP/HOPG surface would be occupied by $O_2$. We found that $P_{1/2}(298 \text{ K}) = 3200$ Torr, or about four atmospheres of oxygen.

These results are extremely surprising. Qualitatively, the reversible binding of $O_2$ by CoOEP/HOPG is a surprise. Based on solution-phase studies, one does not expect to see reversible binding of $O_2$ by CoOEP at room temperature. Even the addition of pyridine bases to the fifth coordination site is not sufficient to produce $O_2$ binding at 298 K. Nevertheless, the HOPG-bound CoOEP is binding oxygen and doing so with sufficient residence time to allow observation by STM imaging. Extending arguments derived from solution-phase studies, such as those of Collman\textsuperscript{171,174} and Stynes,\textsuperscript{156,157} it appears that the HOPG surface is strongly donating electrons to the cobalt center, thereby stabilizing the polarized Co−$O_2$ complex. Quantitatively, the results provide a mixed message. The value of $\Delta H_P$ ($\sim 68$ kJ/mol) is more negative than the larger values reported for cobalt complexes in solution (about $\sim 60$ kJ/mol) but is consistent with the unusually large binding and long residence time observed for $O_2$ on CoOEP/HOPG. The value of $\Delta S_P$ [$\sim 297$ J/(mol K)] is more negative than previous reports for solution and solid-state binding by cobalt.

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complexes [about \(-230 \text{ J/(mol K)}\)] and also slightly larger than the negative of the absolute entropy for the \(O_2\) molecule at 1 Torr and 298 K calculated from statistical mechanics (\(-268 \text{ J/mol K}\)).

Since \(\Delta S_P\) is based on the slope, it is less accurate than the change in free energy, and the possibility of numerical error must be addressed. To that end, a line of slope \(-268 \text{ J/(mol K)}\) and \(\Delta H_P = -60 \text{ kJ/mol}\) is drawn over the actual free energy data in Figure 6-7. In order for the correct value of the slope to be \(-268 \text{ J/(mol K)}\), it would require only a slight deviation from the least-squares best fit line and would fall within 1 SD of all but one of the measured values. We consider this very good agreement with the expectations derived from statistical mechanics. We also note that the associated \(\Delta H_P\) is close to values determined for other room temperature oxygen binders. One might argue that not all the rotational entropy of \(O_2\) is lost because there is probably some hindered rotational motion over the four-fold porphyrin pocket. Where then might this additional entropy be lost? A possibility is that the \(O_2\) binding is inducing some additional order in the solvent, the porphyrin ring, or both.

A possibility worth considering is that there is more than one type of adsorption/desorption process and that the second (or more) process is occurring too fast to be followed by STM. While we cannot eliminate this from consideration, the implication is that there is significantly more bound \(O_2\) than we have observed. Since the amount seen with the STM is already higher than expected, the existence of an unrelated fast mechanism appears less likely.

The large binding of \(O_2\) on CoOEP adsorbed on HOPG is not so surprising when viewed in the context of recent ultrahigh vacuum (UHV) studies of metal porphyrins on surfaces. It was shown in the 1980s that cobalt(II) tetraphenylporphyrin (CoTPP) supported on TiO\(_2\) powder catalyzes the reduction of NO and NO\(_2\) in the presence of CO and H\(_2\) with high efficiency despite the fact that neither the free-standing CoTPP nor the TiO\(_2\) powder is reactive on its own.\(^{192}\) This
was explained by saying that electronic structure of the Co ion was modified by partial electron transfer from the TiO$_2$ support. Recently there have been a number of UPS, XPS, and STS studies suggesting that metalloporphyrins couple electronically to metal surfaces.\textsuperscript{128,193,194} A very recent systematic study of metal tetraphenylporphyrins on silver clearly shows the surface behaving as a fifth coordination site in a “surface trans effect”.\textsuperscript{195} Thus, there is precedent in the literature for a substrate to act as an electron-donating fifth ligand on the metal ion of an adsorbed metal porphyrin.

A different facet of this study of interest to surface science is the structure of the monolayer of CoOEP. Figure 6-8 shows a portion of a drift corrected STM image and one possible set of molecular orientations that generate the observed surface pattern. Unlike the UHV study of NiOEP, we could not resolve the ethyl groups.\textsuperscript{74} Thus, we were forced to rely on simple model building to arrive at a possible structure. Correctly scaled models (based on the DFT calculated geometry) were placed over the image in a manner that appeared to minimize overlap of ethyl groups. As shown in Figure 6-8, this resulted in a body centered unit cell at 25 °C having $A = 2.92 \pm 0.15$ nm, $B = 2.73 \pm 0.15$ nm, and $\theta = 54 \pm 3^\circ$. This cell results from a relative rotation of $18^\circ$ between molecules along the A direction. If one ignores the attempt to optimize packing and simply uses the molecular pattern, a smaller lattice having only one molecule per unit cell results with $A' = 1.41 \pm 0.1$ nm, $B' = 1.36 \pm 0.1$ nm, and $\alpha = 54 \pm 4^\circ$. These values can be compared to those reported for CoOEP/HOPG deposited from 1-tetradecene by Miyake et al.\textsuperscript{81} They gave $A' = 1.48 \pm 0.1$ and $B' = 1.42 \pm 0.1$, in reasonable agreement with the low-resolution pattern. In the absence of high-resolution images, any integer multiple ($nA', mB'$) of $A'$ and $B'$ might be the actual surface structure.
Figure 6-8: Possible unit cell parameters for CoOEP/HOPG in phenyloctane. \( A = (1.46 \pm 0.1 \text{ nm})n, B = (1.36 \pm 0.1 \text{ nm})m, \text{ and } \alpha = 54.3 \pm 4^\circ. \)

6.5 Conclusions

It has been demonstrated that variable-temperature STM can be used to determine adsorption isotherms and thermodynamic data for processes occurring at the solid/solution interface. We have shown that the solid support (in this case HOPG) can act in a manner similar to an electron-donating ligand bound to the fifth coordination site on the cobalt ion of CoOEP, thereby greatly increasing the compound’s affinity for oxygen. The free energy, enthalpy, and entropy changes associated with the \( \text{O}_2 \) binding process are determined for the first time and found
to be qualitatively correct but larger than previously observed for purely solution-phase reactions. While this difference may be due to surface and solvent reorganization, certain determination will require extending the temperature range of these measurements to lower temperatures, which we plan to do. Another obvious extension of this work is the measurement of the binding process on substrates having different chemical properties and work functions. This is also underway.

This work presents a novel approach for obtaining thermodynamic quantities and a better understanding of the fundamental chemistry of reactions of dioxygen with metal–organic complexes at the single-molecule level in solution environments. The experimental conditions used here allow one to mimic the chemical events of biological oxidation and in situ heterogeneous catalysis. Using a metal substrate as the fifth ligand allows for the formation of transition metal–dioxygen binding complexes, where the bound dioxygen is held in a sterically protected site, which in principle precludes dimerization and other unwanted reactions that may occur in a solution phase.
Chapter 7. Oxygen Binding to CoOEP at the 1-phenyloctane/Au(111) Interface

One obvious extension of the work discussed in chapter 5 is to study the oxygenation of CoOEP adsorbed on a substrate with different chemical properties and work functions than HOPG. Hence, for this work we used Au(111) to replace HOPG and studied the oxygenation of CoOEP/Au(111) system. From our STM observations in Figure 7-1, it was clear that even at −25 °C, CoOEP does not bind any O₂ molecules. The difference in O₂ binding capacity for CoOEP/HOPG and CoOEP/Au(111) surface might be attributed to their differences in work function (Φ). \( \Phi_{\text{HOPG}} \approx 4.5 - 4.8 \text{ eV}\) \(^{196-198} \) and \( \Phi_{\text{Au}} = 5.3 \text{ eV} \) i.e. HOPG acts as more electron donating than Au. This is in excellent agreement with previous works where the less electron donating ligands reduces the O₂ binding capacity of the cobalt porphyrins. \(^{156,161-164,166,169} \) Hence, in this work we have shown that the O₂ binding capacity of the CoOEP is significantly reduced, to the point that even at lower temperatures of −25 °C oxygenation doesn’t occur when supported on Au(111).

![Figure 7-1: STM images of 100% O₂ saturation CoOEP on 1-phenyloctane/Au(111) interface at −25 °C (left), 0 °C (middle) and 25 °C (right) with set point conditions of −0.7 V and 20 pA.](image-url)
Chapter 8. Partial Monolayer Adsorption of CoOEP at 1-phenyloctane/Au(111) Interface

While all the adsorption/desorption works performed in this thesis are based on a fully covered monolayer on HOPG and Au(111), studies on partial monolayer coverage can provide insights into the mechanisms of initial monolayer formation. During the early stages of a complete monolayer formation, islands of molecules form from various nucleation sites and grow. It is shown that the fully covered monolayer is kinetically controlled, forms within few seconds, and the adlayer is stable up to 70 °C. But there still could be a possibility that some form of both kinetics and thermodynamics come into play during the initial phase.

To study this, we first take a very dilute concentration of CoOEP (3.1 × 10^{-7} M) and add 10 μL on to the Au(111) surface of an area of 1.1 × 10^{-5} m². If we take CoOEP as a circular disk, then the radius of the disk is approximately 6 × 10^{-10} m with an area of 1.1×10^{-18} m². Total number of CoOEP molecules in 10 μL volume and 3.1 × 10^{-7} M concentration can be calculated from simply by multiplying the volume by concentration and Avogadro’s number (10 μL × 3.1 × 10^{-7} M × 6.023 × 10^{23} = 1.9 × 10^{12} CoOEP molecules). This total can be multiplied by the area of individual porphyrin to give the total area covered by all the porphyrins in a 10 μL volume and 3.1 × 10^{-7} M concentration [(1.9 × 10^{12} CoOEP molecules) × (1.1×10^{-18} m²) = 2.1 × 10^{-6} m²]. If we consider all the CoOEP molecules adsorb on to the Au(111) then the fraction of the above calculated area of all the porphyrins to the total area of Au(111) is 0.19 and this should be equal to the fraction of molecules obtained using STM images as shown in figure 8-1.
Figure 8-1: 200×200 nm² sized STM images of CoOEP on Au(111) showing partial monolayer coverage. Areas under blue are molecular CoOEP islands on Au(111). The calculated area of each islands are given next to the highlighted area.

Numerous STM images of 200 × 200 nm² sizes as shown in figure 8-1 were analyzed to calculate the fraction of CoOEP islands on Au(111). The fraction of adsorbed CoOEP were calculated by adding the total areas of CoOEP islands on one STM image divided by 200 × 200 nm² area. This fraction is equals to 0.18 ± 0.10. This value obtained using STM to the calculated CoOEP fraction using the area of CoOEP and Au(111) is very close to each other and are probably the same. In other words, all the CoOEP molecules from solution gets adsorbed on Au(111) surface and this shows that there aren’t any possibilities for the CoOEP to be in partially equilibrium between the surface and solution.
Chapter 9. Conclusions and Future Works

Until recently, researchers have struggled to find what controls the surface structures, either thermodynamic, kinetic or even both. This dissertation that is based on the adsorption and desorption kinetics of octaethylporphyrins (OEPs) at the 1-phenyloctane/HOPG and 1-phenyloctane/Au(111) interfaces will provide an unambiguous method in deciphering the surface controlled phenomena. It was shown that the monolayer of OEPs form within few seconds and is kinetically controlled up to 70 °C. Whereas, the rates of desorption of these OEPs from a complete monolayer are extremely slow and occur in a time scale of hours at temperatures above 70 °C (studied temperatures are 90, 100, 110, and 135 °C).

Quantitative comparisons were made on the rate of desorption and activation energy of CoOEP from HOPG and Au(111) surfaces into 1-phenyloctane. On Au(111), significant desorption of CoOEP occurs at temperatures above 120 °C and the rate of desorption was found to be 0.004 min⁻¹ at 135 °C. Whereas on HOPG, significant desorption of CoOEP occurs at temperatures above 70 °C and the calculated rate is 0.22 min⁻¹ at 135 °C, making the rate of desorption of CoOEP from HOPG 2 orders of magnitude greater than from Au(111) (comparisons of rates of desorption and activation energies are given in Table 9-1).

Similarly, effects of metal centers of OEPs on the desorption kinetics were also studied. Rates of desorption of metallated OEP, CoOEP and non-metallated OEP, H₂OEP from HOPG were studied. It turns out that the Co-ion does not have significant contribution on the adsorption strength of OEPs on HOPG. This suggests that the adsorption is controlled by the interaction between the porphyrin core and the HOPG surface. While this might be true on HOPG and for
Co-ion in OEPs, substituting the central metal and/or the substrate (e.g. Au(111)) can have a significant impact on the adsorption strength. The adsorption energies for OEPs are in the range of ~106–140 kJ/mol and are probably the same within the error of our measurements.

Table 9-1. Comparisons of rate constants for OEP from HOPG and Au(111).

<table>
<thead>
<tr>
<th>Rate constants for OEP desorption, (hr⁻¹)</th>
<th>From HOPG</th>
<th>From Au(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>90 °C</td>
<td>100 °C</td>
</tr>
<tr>
<td>CoOEP (NiOEP as tracer)</td>
<td>0.33 ± 0.042</td>
<td>0.78 ± 0.06</td>
</tr>
<tr>
<td>CoOEP (H₂OEP as tracer)</td>
<td>0.13 ± 0.048</td>
<td>0.28 ± 0.06</td>
</tr>
<tr>
<td>H₂OEP (CoOEP as tracer)</td>
<td>0.17 ± 0.012</td>
<td>0.36 ± 0.042</td>
</tr>
</tbody>
</table>

While all the above arguments regarding the adsorption and desorption are true for a completely formed monolayer, it is highly likely that the rates of desorption can be different and probably fast for a partially formed monolayer. In a partially formed monolayer, surface diffusion can play a big role in defining the stability of the molecular islands. In this case, molecules along the edges of the islands have more translational freedom which can lower the intermolecular interactions resulting in a different packing density and eventually different activation energies. Hence, future studies have to focus on the adsorption/desorption processes for partially formed monolayers on surfaces.
In addition to the partial monolayer coverage studies, quantitative studies on site specific adsorption and desorption has to be performed. So far in this dissertation we have qualitatively studied and showed that the rates of desorption of OEPs are faster along step edges, grain boundaries, and reconstruction lines. It was shown that the NiOEP desorbs faster from the step edges and reconstruction lines of Au(111) than from terraces, whereas CoOEP desorbs uniformly. Similarly H$_2$OEP desorbs faster from step edges and grain boundaries of HOPG compared to that from terraces. Measuring the rates of desorption from these specific surface sites will give direct insights into the effects of importance of surface sites where the chemistry could be completely altered.

For processes where the rates of adsorption are extremely fast and kinetically controlled, desorption studies can provide more information than just the rate parameters. Because the adlayer forms within seconds, forming thermodynamically stable surface structure can be elusive. For a surface structure formed from a mixture of more than one type of molecular species, potential cooperativity effects are screened. Desorption studies can allow cooperativity effects to come into play and can be observed in the desorption of CoOEP (Chapter 5). Description of rate parameters in this dissertation is limited and describe ideal rates of desorption. Thus, in future, cooperativity effects need to be integrated in the rate parameters. In addition, intermolecular interactions between different species of molecules needs to be addressed. Similarly, solvent effects needs to be studied. This can be achieved either by performing similar desorption experiments with different solvents with varying solubility or by performing temperature program desorption experiments in vacuum. These will provide valuable insights into the effects of solvent.

Future works on the desorption kinetics can be further expanded in many directions. One obvious extension is to use a different substrate such as MoS$_2$ and compare the rate parameters.
Another is to study the effects on adsorption/desorption of functionalized porphyrins. For e.g. tetraphenyl porphyrins when adsorbed on surfaces have the porphyrin ring lifted above the surface due to the free rotation of phenyl rings that make an angle with the surface, eventually lowering the interaction between the porphyrin and the surface. This can have a significant impact on the adsorption/desorption process and it is possible to achieve equilibrium at lower temperatures. Similarly, long alkyl chain substituted porphyrins can be studied. Phthalocyanines, which are extensively used in modern electronic devices, have extended pi-conjugated system with four nitrogen atoms replacing four carbons on porphyrins. Studying the adsorption/desorption process of these molecules can have an immediate impact on molecular electronics. This dissertation has opened a new door and the extension of this work is only limited to one’s imagination.

The binding of small molecules such as O$_2$, CO, NO, etc. to porphyrins and phthalocyanines highlight an important field of science. Its importance to biology and sensor device fabrication makes it an ever growing subject of research. This dissertation also shows that thermodynamics plays an important role in oxygen binding to CoOEP on HOPG. It was shown that when CoOEP is mounted on top of an electron donating substrate, oxygen binds readily at temperatures close to room temperature. It is surprising for the fact that even highly substituted cobalt porphyrins in solution bind oxygen only at a very low temperature of \(< -20 \, ^\circ C\). Thermodynamic parameters such as $\Delta G$, $\Delta H$, and $\Delta S$ were evaluated for the first time by performing temperature and pressure dependent studies solely based on STM. It was further shown that when HOPG was substituted by a less electron donating substrate such as Au(111) oxygen does not bind to CoOEP even at \(-25 \, ^\circ C\) underscoring the importance of the surface.

This work has opened a new door and understanding towards the visualization of how a chemical reaction occurs in-situ. Expansion of this work towards understanding the chemistry
of small gases such as CO and NO on porphyrins will enhance and better equip scientists in rationally designing modern electronic devices such as sensors and even in biological applications.

All of the studies performed in this dissertation gave a fundamental understanding of how surface processes occur in a molecule–to–molecule basis. It has given a new dimensionality to STM’s capability of acquiring information on a quantitative level. It also provides a proper direction towards detecting whether a surface system is kinetically or thermodynamically controlled. Thus, this research provides a platform to enhance the modern technological aspect of science such as sensors, catalysis, battery developments, and solar cells.


14 Lyubinetsky, I.; Dougherty, D. B.; Richards, H. L.; Einstein, T. L.; Williams, E. D. Step wandering on Al/Si(1 1 1)-(√ 3x√ 3) surface at high temperatures Surf. Sci. 2001 492(1-2) L671-L676.


Allen, C. M.; Drauglis, E. Boundary Layer Lubrication: Monolayer or Multilayer Wear 1969, 14, 363−384.


64 MacLeod, J. M.; Rosei, F. Expanding the Scope of Molecular Self-Organization Studies through Temperature Control at the Solution/Solid Interface Aust. J. Chem. 2011, 64, 1297−1298.


MacLeod, J. M.; Chaouch, Z. B.; Perepichka, D. F.; Rosei, F. Two-Dimensional Self-Assembly of a Symmetry-Reduced Tricarboxylic Acid Langmuir 2013, 29, 7318-7324.


102 Li, Min; den Boer, Duncan; Iavicoli, Patrizia; Adisoejoso, Jinne; Uji-I, Hiroshi; Van der Auweraer, Mark; Amabilino, David B.; Elemans, Johannes A.A.W.; De Feyter, Steven. Tip-Induced Chemical Manipulation of Metal Porphyrins at a Liquid-Solid Interface *J. Am. Chem. Soc.* **2014**, *136*, 17418-17421.


104 Miura, Atsushi; De Feyter, Steven; Abdel-Mottaleb, Mohamed M. S.; Gesquiére, André; Grim, Petrus C. M.; Moessner, Georg; Sieffert, Michel; Klapper, Markus; Müllen, Klaus; De Schryver, Frans C. Light- and STM-Tip-Induced Formation of One-Dimensional and Two-Dimensional Organic Nanostructures *Langmuir* **2003**, *19*, 6474-6482.


129 Using the attempt frequency and activation energy derived in this work and equation 5.3, one can calculate the time dependent change in surface concentration at 70 C.


158 Beugelsdijk, T.J.; Drago, R.S. Thermodynamic data for the binding of molecular oxygen to cobalt(II) protoporphyrin IX dimethyl ester J. Am. Chem. Soc. 1975, 97, 6466-6470.


SPIP is a product of Image Metrology, Lyngsø Alle 3A, DK-2970 Hørsholm, Denmark.


Appendix
A. STM Experimental Section: Procedures and things to consider during In-situ and Ex-situ Temperature Dependent Studies at the Solution/Solid Interface

In this work, three similar porphyrins in CoOEP, NiOEP, and H₂OEP are used. 1-phenyloctane is used as a solvent and is subjected to further purification as described in Appendix B. STM images are recorded using a Molecular Imaging (now Agilent) Pico 5 STM equipped with a scanner capable of imaging a maximum area of 1 µm² and having an overall current sensitivity of 1 nA/V. The Agilent environmental chamber was used for all experiments where either argon, oxygen or a mixture of both gaseous atmosphere was maintained. Pt₀.₈Ir₀.₂ wire were used as STM tips and were primarily prepared by cutting and sometimes electrochemically etching.

**Solubility of porphyrins:** Crystals of these porphyrins are dissolved in 1-phenyloctane. The choice of solvent is critical in performing any high temperature dependent studies. Thus, in order to limit solvent evaporation, 1-phenyloctane which has a boiling point of 261-263 °C (Sigma-Aldrich) is used as a solvent. Solubility measurements in 1-phenyloctane were made by preparing a saturated solution of each compounds and filtering the solid out using filter paper of 100 nm pore size. The filtrate is then diluted such that the absorbance in a UV-vis spectrophotometer is close to 1 in order to get accurate measurements. Using Beers’ law \( A = \varepsilon bc \) the concentration of the diluted mixture is calculated. Then, using the dilution formula \( C_1V_1 = C_2V_2 \) the concentration of the stock solution is calculated. This concentration value is the solubility of the compound in 1-phenyloctane. Measured solubility values for CoOEP, NiOEP, and H₂OEP are 3.9×10⁻⁴ M (0.23 g/L), 5.4×10⁻⁴ M (0.319 g/L), and 1.1×10⁻⁴ M (0.06 g/L) respectively. While the solubility values
differ slightly for all three porphyrins, the concentrations used for performing all the STM measurements were well below their solubility limits which is critical for performing temperature dependent studies.

Solubility measurements can also be calculated slightly differently. A saturated solution is prepared and the undissolved crystals are given ample time to settle down and a specific volume of the saturated solution is transferred to a UV-vis cuvette and diluted by known volume of the solvent.\(^1\) Using this method, CoOEP’s solubility in 1-phenyloctane was found to be $2.6 \times 10^{-4}$ M.\(^2\) While this value is slightly lower than the previously described method, the concentrations used in all the experiments are well below the lowest calculated solubility value of CoOEP. Hence, this difference in solubility does not have any considerable effect in our experiments.

**Solution Cell:** The fundamental experimental basis to study the desorption kinetics of OEPs at temperatures well above room temperature requires the solution/solid interface to be intact for hours. Conventionally, at room temperatures samples are prepared by drop-casting the solution of porphyrin on to the substrate and imaged with STM. At lower temperatures, thin film of solution is visible to the naked eye for 2-3 days (when 1-phenyloctane is used), thus providing a SS interface for days. But, at higher temperatures (>50 °C), the solvent either starts to slowly evaporate or the solution starts to dry on the surface due to acquiring enough energy to break any surface tension consequently disrupting the SS interface and thus limiting any high temperature studies at the SS interface. This issue can be overcome by using a solution cell that acts as a reservoir for the solution and SS interface is maintained at all times. This not only allows but also prolongs the time period of measurements at higher temperatures. Figures 10-1, and 10-2 show the typical STM experimental setup and the solution cell used in this work.
Figure 10-1: Experimental Setup of Solution/Solid STM.

Figure 10-2: Schematic of solution cell, picture of solution cell with and without silicon gascade.

Unit of measurement in the schematic of solution cell is “inch”.
The middle section of the solution cell that comes in contact with the substrate is made of Teflon and has to be smooth in order to prevent solution from leaking out. One of the preventive measures is to use a sandpaper of 2000 grid to smoothen the surface. When Au is used, this should be enough to prevent any leakage. But, when HOPG is used, due to its relatively rough surface compared to Au, a silicon rubber is used as a gascade to prevent the solution leakage. This is shown in the figure below. Before the gascade is made, a small piece of silicon rubber is cleaned with ethanol and placed in the heating chamber of 70 – 100 °C for few hours to few days. This stretches the silicon rubber before the gascade is made and minimizes further stretch after the gascade is made. Then, the gascade is made by punching holes of appropriate sizes to fit the bottom of the Teflon that comes in contact with the HOPG substrate. The gascade is cleaned by rinsing it thoroughly with ethanol and drying it with argon gas and by placing inside a heating chamber for few minutes.

One of the difficulties in using a solution cell for STM is the loss in one’s ability to manually coarse approach the STM tip. Because the STM tip penetrates into the solution to scan the surface, the tip can no longer be manually set. The sample holder where the solution cell is attached, is held by a magnetic tripod. For STM instruments used in this study, only one stand of the tripod is computer controlled. Thus for fine approach (movements of <200 μm) that is controlled by the computer, only one stand of the tripod moves in order for the tip to approach the surface and engage in scanning process. Hence, if the distance between the top of the tip and the surface is greater than 200 μm it is likely for the sample to tilt and never approach the surface. With the solution cell, the position of the tip is completely removed from one’s view, making this extremely difficult to maneuver the STM tip. This problem can be easily solved. First, measure the distance between the tip and the clean substrate that is going to be used for the experiment...
without using a solution cell (similar to a conventional STM experiment). After manual adjustments to the coarse approach where one is comfortable with the tip’s position, disassemble the substrate from the sample holder and put the solution cell on the sample holder. If one is not certain of the coarse approach, go ahead and fine approach the tip using computer. Once the set point is reached, withdraw 100 – 200 μm and use the solution cell. Then, insert the sample holder into the STM chamber and plug in any necessary wires (bias line and temperature controller). Then, add the solution to the sample inside the solution cell. If one has to change the tip, withdraw the existing tip from the sample and measure its length from the base of the STM head using a light microscope and replace it with a new tip with the same distance.

**Temperature Controller:** The temperature of the sample was controlled by a Lakeshore 330 autotuning temperature controller. There are three controller settings, low, medium, and high. The heater current output range for all three settings are given as: high (0-0.1 A), medium (0-0.3 A), and low (0-0.1 A). The temperature steps increases with from low to high settings. Hence, for in-situ STM experiments only low and medium settings are used in order to minimize temperature fluctuations during the scanning process. A small temperature fluctuation can significantly distort the STM image. Thus, for temperature up to 50 °C low, 50 - 70°C medium setting is used. High setting is only used while performing any ex-situ experiments above 90 °C. It is worth noting that a medium setting can be used to heat the sample up to 100 °C but when the temperature is ramped to 110 °C, it take longer time to reach the set point temperature. Due to the nature of our experiments where 90, 100, and 110 °C data were compared with each other using only high setting was used for all three temperatures in order to minimize any errors in effective heating time. It is important to ramp the temperature by 5 °C/min in order for the controller to function properly.
Ramping and stability of the temperature is controlled using three different variables: gain (proportional, P), reset (integral, I), and rate (differential, D). A detail description can be found in the manual. For our purpose, only the values used for the experiments performed in this work will be discussed here. For all experiments, I = 9, and D = 100 were used. Only the P value was altered slightly. For low and medium temperature settings, the range of P used was 25 – 35. One can also use the autotuning setting which automatically uses the best possible P, I, and D values. Although, I personally found this setting affect my imaging process and thus less reliable. Lower the temperature, lesser the P value. For high setting, P was always set between 7-10. Rule of thumb for determining the correct value of P is that, higher the value of P, faster is the rate of increase in temperature and this could constantly fluctuate the temperature (<0.5 °C) which in turn affects imaging process. One also has to consider the heater setting. Higher the heater setting, the ramping of temperature is higher as well, and thus one has to find a balance between the P value and the heater setting. Nevertheless, the values for P, I, and D provided above for various temperature ranges should suffice to smoothly control the temperature for Lakeshore 330 Autotuning.

**In-situ and Ex-situ STM imaging:** For in-situ STM imaging, after the set point temperature is reached, let the sample stabilize for at least 20 min. Longer the wait, lesser the thermal drift. But, one can save time by approaching the surface after 20 to 30 min of heating/cooling and scanning the surface. At first, one can expect to encounter significant amount of thermal drift (higher temperature means higher chances of thermal drift) which seems to get reduced significantly faster if one scans the surface rather than waiting for the sample without scanning.

For ex-situ imaging, at higher temperatures the solution travels through the tip (since the tip is in contact with the solution) through capillary action. This can reduce the amount of usable
solution inside the solution cell. In order to get rid of this problem one can either manually move the STM-head up such that the tip is not in contact with solution anymore and hold the scanner by tightening the screws on the side of the STM or use a different STM-head without a tip.

Details on ex-situ imaging is provided in Chapters 3, 4, and 5. As an example, ex-situ imaging scheme for H$_2$OEP desorption in presence of CoOEP is shown in Figure 10-3. Before depositing any OEP on the surface, solution cell should be attached to the sample holder. Place the sample inside the STM and begin flowing argon gas at 2.5 scfh for at least 15 min prior to depositing any sample. After all the appropriate wires connected (bias and temperature controller lines) one should deposit the sample. This minimizes movements of the sample which eventually minimizes any potential contamination. In this ex-situ example scheme, first, H$_2$OEP is deposited and imaged. One should only find H$_2$OEP monolayer on the surface. Then, an excess of CoOEP is deposited and imaged. Again only H$_2$OEP monolayer is seen under STM. Then, anneal the sample at 135 °C for desired time intervals and cool the sample down to room temperature by simply turning the heater off. Once the temperature is stabilized at around room temperature (roughly 45 min), start imaging the surface. Repeat the process as required.
Preparing Au(111): Au substrates are prepared by epitaxially depositing gold on mica substrates. A detailed description can be found in Reference 1. Making Au(111) substrate requires hydrogen flame annealing of the epitaxially grown Au on mica. First, hydrogen flame is adjusted to roughly half an inch in length. Go around the gold substrate (without touching the Au) until the water vapor on the substrate disappears. One should be able to distinctly see the shrinking of thin water vapor layer on the substrate. Once the substrate is dry decrease the flame length to 1/8th of an inch. This can sometimes be difficult to observe so, turn off all the lights in order to see the flame clearly. Then, start annealing the substrate with the flame by barely touching the substrate in a raster mode. Here, one has to be cautious to not overheat the substrate. To avoid this, the tip
of the flame (blue color) has to touch the surface. Once done, a slight red glow will appear on the Au substrate. It should roughly take 60 – 80 scans in total. Then, place the Au on the sample holder of STM and scan the bare Au(111) surface. If reconstruction lines are seen (separated by roughly 7 – 9 nm apart) then proceed with the experiments to be performed. If not, then repeat the annealing process until clean reconstruction lines are seen.

It is important to observe large areas of annealed Au using STM in order to confirm the existence of surface reconstruction of Au(111) in all areas of the substrate. Sometimes, one may encounter partially reconstructed Au(111) surface as shown in Figure 10-4(a). In that case, one can reanneal the Au such that a complete reconstructed Au(111) is formed which is shown in Figure 10-4(b).

**Figure 10-4:** STM images of (a) partially reconstructed Au(111), where below the red curve reconstruction lines cannot be seen, (b) reannealed Au(111) that was used in (a) showing full reconstruction lines of Au(111).
B. Purification of 1-phenyloctane

1-phenyloctane is a commonly used solvent to dissolve metalloporphyrins for STM studies. It has a boiling point of 261-263 °C (Sigma-Aldrich) and is non-conductive which makes it suitable for solution phase STM studies. In this thesis, 1-phenyloctane was primarily used as a solvent to dissolve porphyrins which is the subject of this study and thus its purity is of utmost concern. Hence, it is essential to have a pure 1-phenyloctane in order for us to be able to do any sort of STM studies which deals with imaging at a nanometer level.

As described in the experimental sections of chapters 2, 3, and 4, 1-phenyloctane purchased from Sigma-Aldrich, Alfa Aesar, and Fisher Scientific were all subjected to further purification. UV–vis spectra of solutions of CoOEP in an undistilled phenyloctane had two Soret bands at 392 and 420 nm instead of a single expected 392 nm band. To get rid of the impurity complexing with CoOEP, phenyloctane was distilled over Al₂O₃ (90% Al₂O₃, 9% H₂O; Alfa products). After several distillations, the UV–vis spectra of CoOEP in this solvent indicated that the impurity had been reduced to less than 10 ppm.

Purification was important due to CoOEP’s affinity towards binding the impurity. This subsequently gave rise to CoOEP appearing as a dark molecule in an STM image that was easily misinterpreted as either a NiOEP or a H₂OEP molecule. Hence, this would completely affect the outcome of the experiments performed by STM, which is the basis for all the work presented in this thesis.

UV-Vis study of CoOEP dissolved in CHCl₃ has a Soret band at 392 nm and Q bands at 520 nm and 550 nm. Similar trends follow when toluene is used. Hence, it is reasonable to expect similar bands for CoOEP in Phenyloctane. Instead, there were two Soret bands at 392 nm and at
420 nm whereas the Q band remained unchanged. It is well known that Cobalt porphyrins (CoP) bind various gases and nitrogen containing compounds. It is also known when CoP bind O₂, there is a shift in the Soret band. Given the shift in Soret band when 1-phenyloctane was used, the probability of an impurity binding to CoOEP was high and thus we opted to perform distillation in presence of Al₂O₃ to remove any impurity from 1-phenyloctane.

Following are the procedures for distilling 1-phenyloctane in presence of Al₂O₃:

1. Take 1 teaspoon Al₂O₃ per 10-15 mL of 1-phenyloctane to be distilled and put it in the three-mec round bottom flask. The flasks are chosen depending on how much Phenyloctane is to be distilled.

2. Add the desired amount of Phenyloctane to the three-neck round bottom flask on top of Al₂O₃.

3. Make sure to stir the mixture well before putting the glassware together.

4. Use Teflon joints where the glassware are connected and clamp it together.

5. Connections to the three heads on the round bottom flasks are as follows: 1) First one is connected for the gas flow; in our case N₂ gas was used, 2) the middle one is connected to the adapter that opens up for connecting thermometer and for the water jacket condenser, and 3) the last one opens to the drying tube.
**Figure 10-5:** Pictures of (a) set up for connections to the round bottom flask, (b) drying tube, and (c) thermometer.

I. The drying tube has anhydrous CaCl$_2$ sandwiched by glass wool on both sides.

II. The thermometer and the gas tube are inserted to a rubber stopper that is joined to the glass adapter which connects to each opening on the round bottom flask.

6. Connect all the glassware as shown in the figure below.

**Figure 10-6:** Complete set up of the distillation apparatus.
7. Since the boiling point of Phenylloctane is fairly high, use a sand bath to heat the flask.

8. A thermocouple is connected at the bottom of the three-neck round bottom flask to monitor the temperature outside the flask.

9. A thermometer is connected inside the flask to monitor the temperature of the vapor of the solvent.

10. When the apparatus is ready to distill, start purging the flask with light flow of N₂ and keep it flowing throughout the whole distillation process. Turn the Variac to the desired power level and monitor the temperature of the thermocouple. As the temperature of the thermocouple gets to 200 °C reflux (hold) the temperature for about 15 min by varying the Variac.

11. Now turn the Variac up and keep monitoring the temperature. The solvent starts to distill when the vapor temperature reaches about 100 °C. This may fluctuate depending on how deep the thermometer is in the apparatus. At this point the thermocouple should read about 330-350 °C. This also is susceptible to change depending on where the thermocouple is. Ideally it should be right underneath the bottom of the flask and touching it.

12. Once distillation starts, throw away the first 1 mL of distilled solvent by thoroughly cleaning the inside of the collection flask.

13. When 9/10th part of distillation is accomplished detach the apparatus from the heated sand bath and let it sit in room temperature and wait until the flask is at room temperature. This will leave a little bit of solvent in the flask so that any possible impurities are left out and we can get the pure solvent.

14. Now, detach the clamps on the distilled Phenylloctane and put a cap on the flask and place it somewhere safe with a label on it.
The following UV-Vis data of CoOEP solution were taken before and after the distillation of 1-phenyloctane. It is clear that after the distillation the initial Soret peak at 420 nm disappears and a clean CoOEP peak is observed.

**Figure 10-7:** UV-vis spectra of CoOEP in before and after distilled 1-phenyloctane. Red curve represents undistilled and blue represents distilled solvent.
C. Calibrating the STM Scanner

STM scanner consist of piezo electric material that controls the fine movements of the STM tip. This is in turn controlled by the applied voltage to the scanner. In order to obtain accurate lattice constants for surface structures using STM, one has to calibrate the scanner. One of the most common way of calibrating the STM scanner is to image the HOPG surface whose lattice constants are well known. The scanner file that is used by the computer program to control the scanner consist of several parameters includes the calibration for X and Y- directions. This value is given in Volts/Angstroms i.e. the amount of voltage required to move the tip by an angstrom length.

In order to calibrate the scanner, both the vertical (Y) and horizontal (X) directions of HOPG is measured. One can rotate the scanner in such a way that one of the lattice directions of the HOPG falls either vertically or horizontally. STM images of vertically oriented HOPG are used to calibrate the Y-piezo, and horizontal for X-piezo.

Figure 10-8 shows each STM image of a vertically and horizontally oriented HOPG surface. Left image shows one of the horizontally aligned and right shows the vertically aligned lattice directions of HOPG. The line shows 10 lattice spacings of HOPG and the angle between the two lattice directions. The known value of one lattice spacing of HOPG is 2.44 °A and the angle between lattice lines is 60°. As can be clearly seen from the Figure 10-8 that the lattice spacing and angles are both wrong. Thus we need to correct this error.
Figure 10-8: STM images of HOPG before the calibration of the scanner. Left image corresponds to the horizontally and right shows the vertically aligned HOPG lattice.

For both X- and Y- corrections, the following formula is used:

For X-correction,

\[
\left( \frac{2.44 \, ^\circ A}{\text{Observed lattice spacing in the } X - \text{ direction}} \right) \times \left( X - \text{ direction piezo parameter } \frac{\text{Volts}}{^\circ A} \right)
\]

And for Y-correction,

\[
\left( \frac{2.44 \, ^\circ A}{\text{Observed lattice spacing in the } Y - \text{ direction}} \right) \times \left( Y - \text{ direction piezo parameter } \frac{\text{Volts}}{^\circ A} \right)
\]

In both cases, X- and Y- direction piezo parameter is given in the software. Now, this new calculated value is used to replace the previous values in the software. Using this new value, STM images are taken as shown in Figure 10-9 below. These newly obtained lattice constants of 2.44, 2.43, and 2.40 °A, and an angle of 61° are close to the known values for HOPG.
Figure 10-9: STM image of HOPG after the new calibration parameters are used.

While this is an example of correcting only the linear parameters, for non-linear corrections one can get the full correction methods from reference 1.
References for Appendix
