Lateral Mobility of Amphiphiles Adsorbed at the Air/Water Interface

by

Eric David Carlson

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate Division of the University of California, Berkeley

Committee in charge:

Professor Marcin Majda, Chair
Professor Angelica Stacy
Professor John Newman

Fall 2009
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Abstract

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Dynamic properties of the air/water interface were explored using Langmuir monolayer methods, ring and drop shape tensiometry, Brewster angle microscopy, and above all, cyclic voltammetry with 2D line and barrier microelectrodes. The goal is to gain insight into the rate of lateral self-diffusion of water molecules in the air/water interfacial region, defined as the space in which water transitions from 90 to 10 percent of its bulk density.

Because measuring the rate of water self-diffusion directly is experimentally impossible, 2,2,6,6-tetramethylpiperidiny1-1-oxy (TEMPO) was employed as a surfactant probe molecule. The dynamics and kinetics of TEMPO partitioning to the interface were thoroughly investigated under a variety of conditions. TEMPO was found to have a partition constant of $380 \pm 30 \text{ M}^{-1}$ in solutions of 1 mM HClO$_4$ and 2 mM LiClO$_4$. The partition constant of TEMPO can be adjusted by synthesizing derivatives of varying hydrophobicity at the C-4 position in the carbon ring. Placing a hydoxy group results in a compound that does not partition to the air/water interface. Adding an ethyl group results in approximately an order of magnitude increase of the partition constant.

The first attempts to determine the lateral diffusion coefficient of TEMPO ($D_{surf}$) employed 2D line microelectrodes. However, these measurements were found to be insufficient for determining $D_{surf}$ of TEMPO for several reasons. The kinetics of TEMPO partitioning to the interface are fast relative to the experiment. This allows the surface population of TEMPO, as it is oxidized to TEMPO$^+$, to be replenished by the solution population of TEMPO, thereby enhancing the surface current. It is therefore impossible to independently determine $D_{surf}$ without knowing the desorption rate constant, $k_{des}$. Numerical simulation with COMSOL Multiphysics allowed us to obtain a number of $D_{surf}$, $k_{des}$ pairs, and a calibration plot was created showing possible values of $D_{surf}$ as a function of $k_{des}$ for 2D line microelectrodes.

The limitation of 2D line microelectrodes is that they exhibit degradation of the voltammetric signal over the time scale of our experiment (15–45 s), burdening the experiment with a systematic negative error. The characteristics of the signal decay indicate that it stems from a loss of the gold/air/solution triple phase line, thereby preventing electrooxidation of TEMPO from occurring precisely at the microline. A variety of mechanisms were hypothesized and tested to determine the exact cause of signal decay, with the aim of either eliminating it or finding a correction term to account for it. No hypothesis was successfully confirmed as the cause of decay. Because decay was a function of time the line electrode was in contact with solution, faster scan rates were preferred, typically 50 mV/s. The calibration curve obtained
from 2D line microelectrodes was taken as a lower bound value for \( D_{\text{surf}} \). For values of \( k_{\text{des}} > 10^3 \text{s}^{-1} \), the dependence of the value of \( D_{\text{surf}} \) on \( k_{\text{des}} \) becomes small, and the calibration curve obtained for 2D line microelectrodes gave a value of \( 8 \pm 4 \text{ cm}^2/\text{s} \) for \( D_{\text{surf}} \) in this region.

Further experiments were designed to more accurately determine the value of \( D_{\text{surf}} \). This was done by modifying the electrode geometry. Thin barrier films were placed over the gold surface that prevented direct electrooxidation at the microline. Surface adsorbed TEMPO is still able to influence the voltammetric signal by desorbing to replace TEMPO that has been oxidized in the bulk solution. This allowed the creation of a set of independent calibration curves and the identification of a point of intersection, thereby determining both \( D_{\text{surf}} \) and \( k_{\text{des}} \). Two types of barrier films were employed: spin coated SU-8 photoresist and vapor deposited silicon monoxide. The first type of film employed was the SU-8 photoresist. SU-8 barrier films provided high reproducibility, but there was uncertainty as to the rigidity of the polymer film after breaking. Vapor deposited silicon monoxide was chosen as an alternative barrier film due to its ease of fabrication and greater confidence in its rigidity. Silicon monoxide barrier films were thoroughly characterized and found to break unevenly at the point of contact with solution. Due to their unusual breaking characteristics, SiO barrier electrodes had to be calibrated with a non-partitioning electroactive analyte. Both types of films generated calibration plots that intersected to yield \( D_{\text{surf}} \) values of \( 7 \pm 3 \times 10^{-3} \text{ cm}^2/\text{s} \). However, calibration curves obtained from simulating experiments performed with SU-8 barrier electrodes intersected at a \( k_{\text{des}} \) value of \( 10^4 \text{s}^{-1} \), while the curves obtained using results from SiO barrier films intersected at a \( k_{\text{des}} \) value of \( 10^3 \text{s}^{-1} \). Resolving the discrepancy between these two values is a possible direction for a future project. It is encouraging to note the remarkably good agreement between the values of \( D_{\text{surf}} \) obtained from the 2D microline experiments and the barrier electrodes. This value for \( D_{\text{surf}} \) is approximately a factor of 4 greater than the value obtained by Pohorille and Wilson in MD simulations. Applying the 2D diffusive model described by Hughes and coworkers, the viscosity of the air/water interfacial region is estimated to be one third of the viscosity of bulk water.
This dissertation is dedicated to the amazing woman who has supported me through all the ups and downs of graduate school.

I love you, Polly.
Acknowledgements

There is a part of me that is amazed that this day has finally come. I am actually going to graduate from UC Berkeley and depart into the real world. Sort of. Since I’m working to become a high school teacher, I’ll still be working in the world of academia. But I have always enjoyed teaching, and have no doubt that I will enjoy the career I am embarking on.

I have written numerous drafts of my acknowledgements in my head over the years. This is the one space in my dissertation where I am free to express myself using my own tone, with no stylistic expectations or constraints. This is the one part that hasn’t been proofread or commented on by any one on my committee. This is where I get to say what I want, how I want to say it. So, what am I going to say?

Dallin H. Oaks gave a talk on the importance of giving thanks in all things. And so I wish to express my thanks to everyone I have come in touch with in any significant capacity over the years in my time in graduate school, as well as those I have come into contact in any insignificant capacity. I wish to give thanks for what has worked well, as well as for what has not worked well. It is perhaps unfortunate that I am typing this the day before I plan on submitting my dissertation, because like all writings, it would be sure to benefit from a proofreading and comments from another person. But it won’t get them.

I’m not at all sure who to thank first, but I feel myself inclined to start with the academic part of my acknowledgements, starting with those who worked on my project in some capacity. I’ll begin by thanking Marcin for his patience over the years. Marcin, you have always been very understanding when ever family matters disrupted the progress of research, and have always been very patient with my slow rate of progress. And to be completely honest, I find myself inclined to be grateful for your glacial pace of publishing. If all my publishable work had been written up and published in a timely manner, I might have done more research, published more papers, and gone on to a post-doctoral position, despite knowing in my heart that it wasn’t what I wanted to do with my life. Not having any publications to show for my graduate career is something I find myself truly grateful for at this time, because it gave me the strength and courage to walk away from this path I’ve been on, and find something to do that I am truly interested in doing. Marcin, for all your attributes as a graduate student advisor, I find myself truly grateful at this time.

I don’t think it is possible for me to overemphasize at this point the influence that Nicolas Glandut had on me and more especially on this project. When I first began studying the air/water interfacial region, I had no clue what I was doing, and had no clue about how little a clue I had. Nicolas remains to this day the only person who I saw think about the relevant issues and explore a wide variety of conceptual alternatives in order to obtain a theoretical understanding. From Nicolas I also observed how to ignore inconsistencies in your data that might undermine your theory, though it would be years before I learned to imitate his example. His willingness to publish results that were far less than perfect also helped me see that science is about progress, not perfection. Nicolas, I can’t even imagine how limited in progress this project would be if it weren’t for your contributions to it. Even though there is virtually no chance you will read these words, I wish to express my gratitude to you for what you did here.
I think it is time for me to thank Andy now. Andy, your innumerable connections in the department were the oil that kept this machine running. From you I learned to never go read in the literature anything that you could possibly ask a colleague about. You introduced me to the joys and frustrations of Fantasy Football (and as much as I enjoyed it, I think I’m better off without it). Your final push to complete your dissertation has been an inspiration to me as I have worked to complete mine, as much as your dissertation has been an invaluable resource in guiding the construction of my dissertation. Andy, thank you for all you did in the lab and making this place fun to work in.

I don’t know that Deng Wu deserves his own paragraph (because our time of overlap was so brief), but I don’t know who to lump him with, so he’ll end up getting one. Deng Wu, you are a shining example of diligent experimentation. I envy your data producing capability, and hope that I can be as competent in my chosen profession as you were in yours.

Anthony Fong, I think you deserve your own paragraph. I’d like to thank you for your patience with me as your mentor. I’m all too aware of the many shortcomings I had, but I hope I was able to provide you with some insights into the project, and I hope even more that I was able to provide you with some insights into life. I fear that it is all too likely that I did not, because I served as a mentor to you at a time when I was profoundly lost myself, whether you or I knew it or not. To life someone up, you must be on higher ground, and I’m not entirely sure that I was on higher ground. At the very least, it was fun discussing baseball with you. Regardless of my shortcomings, I’d like to thank you for your time, efforts, and persistence in the lab.

Jarrod McClean, your time in this group was all too brief. You helped me out in more ways than you can imagine with your calculations. I wish I could have found more for you to do with us, but you are much better served in a theoretical group, where you currently are. You are bright and motivated, and I have no doubt that you will go far. Thanks for your services.

Anita and Robyn, you two have the privilege of being lumped into one paragraph of thanks. From you I learned how much fun it is to teach fundamental principles and I think I am the better for our interactions. Robyn, I commend you in particular for recognizing that a research problem did not interest you, and not wasting any more time on it just because you could.

Jack, I’m not sure what to thank you for. You vanished into thin air! This shows that I need to reflect on our interactions a bit more and search for relevant lessons. So I guess I can thank you for giving me cause to think. Ilsup, I thank you for providing for me an eternal and shining example of why undergraduates who are seeking to pad their résumé have no place in a research lab. I can only hope that I truly learn the lessons you taught me.

Jan, I’d like to thank you for casting doubt on the established value of the partition constant for TEMPO. Without your efforts, I would currently be obtaining calibration curves that indicate a lateral diffusion coefficient at least 25% greater than what I’m currently working with, for better or for worse.
Sean, you are bright, ambitious, and a lot of fun to talk to. Who knows, maybe too much fun. We’ve always had the greatest conversations about the history of science and a number of scientific issues that weren’t always related directly to the project at hand. I thank you for your parting present, and am looking forward to reading the books. I hope I can find a good parting present for you. Perhaps this dissertation will be my return book gift. Sean, thank you for your time and efforts, and I wish you the best of luck in your efforts to further this project.

Franziska, it was great having someone to practice my German with. You helped me refresh it quite a bit. I hope I didn’t retard your progress in English too much by giving you a crutch to fall back on! Maybe some day I’ll be good enough at chess to play you to a draw. Maybe not. I hope our paths can cross again someday.

Ewa, Keita, and Chika, thanks for the instruction in Polish and Japanese, respectively. I don’t think I’ve retained much of my Polish, but I’ve still got some Japanese fundamentals in place. Don’t know that I’ll ever have too much practical application for those languages, but I still love learning them.

To Araina and Eliot, thank you for showing me what I came so close to being at times. I’m not sure exactly what made the difference between me pushing through to Ph. D. instead of flaming out. Although I knew that when it comes to graduate school, you either need to get in and invest yourself, or get out, I was still half-heartedly approaching things. You reminded me that I needed to get in or get out, and helped me reflect on what I was trying to accomplish with my life. I hope both of you find what you love to do in life, and do it.

It seems appropriate to thank Eric Scott at this time, because you are the one who got out of what you didn’t want to do and got into something you knew you wanted to do. I hope to have the courage of my conviction to get out when I know I’m not where I need to be in the future. I also found your assessment of previous lab results quite inspirational in a number of ways.

To Kasha and Heather, thank you for just being there. But I need to give more particular thanks to Heather. Thanks for the electrodes you made, and your willingness to accommodate my preferred working conditions. Thanks for some good Age of Empires games, and thanks for your scientific input in conversations.

I’d like to thank the undergraduate assistants of other researchers. Laura, Shab, and Cyrus, you all made this place a much more fun and interesting place to work. You are very different individuals, and I’m glad I had the chance to work with each of you, or at least in the same laboratory as you.

Jamie, you are the future of this lab. You have unquestionably been the best example of some one who comes to the lab to do research, and not to surf the internet or play computer games. I can say with the utmost honesty that you are the best worker in the lab I’ve seen in my time here. I’ll miss you as a chess opponent, and I’m sorry that you are going to be working under lonely lab conditions. Like Eric Scott, your insights and commentary into your project have provided inspiration for me to complete my dissertation.
And Chris, I’ve been saving you for last—in the fellow researcher section of thanks, at least. It’s unbelievable how many years two random roommates at BYU ended up working together. I know you and your family wish to end up in Utah, and I hope you are able to do so. Thanks for all the study time together at BYU, and for all the research advice and opinions in graduate school. I can say with complete honesty that the work you did to earn your doctorate inspired me to complete the work I did to earn mine, and for that, I owe you no small debt of gratitude.

I do wish to thank Luciano Moretto for letting me lecture Chem15 on the subjects of polarography and chromatography, so that I could get a feel for what I was choosing as a career path.

Of course I owe a debt of gratitude to Angelica Stacy and John Newman for their feedback and signatures on my dissertation. It’s amazing what value a single sheet of paper with the right signatures on it can acquire.

I’d like to thank the hard drive that had all my data on it for not crashing irrevocably until the day after I backed it up. I’d like to thank whoever left the couch in the lab. I’ve lost count of how many nights I have spent on it, but I would guess it is close to two dozen.

I need to thank my Chem1A students in this last semester. Teaching Chem1A took a lot of time, and I might not be facing this deadline crunch if I hadn’t had to do it. But you guys gave me something to look forward to everyday, and gave me the best feel for the profession I am choosing. I have been truly touched by your gifts and the gratitude you have shown to me, and I wish all of you the best in life, and hope that our paths may cross again someday.

I’m grateful to all the members of the Hilltop 2nd ward. I’ve enjoyed serving in your ward. We all knew it was only temporary, but I managed to drag it out about as long as I could, didn’t I? I wish all of you the best of luck and success in your future efforts.

Of course I need to thank my family, both immediate and extended. I owe my parents a debt of gratitude that I can never hope to repay to them, so it falls to me to pay it forward to my children. I certainly hope to do so. Thanks for all you have done for me over the years. I’m looking forward to living in the same state as you once more.

I am also grateful to the parents of my children, and the sacrifices that you have made so that Polly and I could have them. There can be no question that your decision had a huge impact on my research ☺, but an even bigger one on my life. I don’t know that any of you will read or make sense of what is in here, but I want to thank you all the same.

Of course I need to thank my wife for her love and patience with me. I know I don’t show anywhere near enough appreciation for all that you have done for me, and I hope to repent and do so in the future. Thank you for sticking with me in all these times when I didn’t know where I was going or what I wanted to do. Thanks for supporting me through getting done what needed to get done, and I hope we never have to do anything like that again. I love you!

1. Conference Report, April 2003
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Chapter 1: The Introduction and Historical Background

1.1 The Air/Water Interface

“God Made Solids, but surfaces were the work of the devil” --Wolfgang Pauli

The air/water interface is perhaps the most abundant interface on the planet. Oceans, lakes, rivers, bays, gulfs, seas, streams, creeks, and gullies cover over 75% of the earth’s surface, to say nothing of the water droplets that exist in clouds, rain drops, fog, dew, and any other form of water condensation. Unsurprisingly, this ubiquitous interface has attracted a great degree of attention from researchers. There may be no interface as well studied as the air/water interface\textsuperscript{1–8}. Though it is difficult to overemphasize the importance of this interface, throughout the length of this dissertation, I will do my best to do so.

In order to help focus the reading, I’ll begin with an outline of the dissertation. The introduction begins with a justification for the study of amphiphiles adsorbed at the air/water interface, including a summary of a number of important results obtained so far. The remainder of the introduction covers the histories of the studies of diffusion and of monolayers at the air/water interface, touching on the techniques used to study the air/water interface. It also includes some theory behind the analytical methods. Chapter two treats the experimental methods and procedures. Chapter three discusses optimization of the electrochemical system used to study the air/water interface, and then treats in detail the results obtained from 2D microline electrodes and the limitations of the experiment. Chapter four, presents the results obtained from barrier electrodes, a modified geometry of the microline that allows us to accurately determine the rate of lateral diffusion, as well as desorption rate constant, for our amphiphilic probe. A model to relate lateral diffusion to viscosity in a 2D system will be presented, and the results will be interpreted in light of the model, followed by some concluding remarks.

Among the techniques that have been employed to study the air/water interface are x-ray reflectivity and vibrational sum frequency. These spectroscopic approaches have yielded a wealth of information about the structural properties of the air/water interface, such as the degree of hydrogen bonding and the average orientation of the water dipole\textsuperscript{9–11}. It has been found that surface water molecules form an average of 2.1 hydrogen bonds per molecule (compared to 3.8 in the bulk) and that about 20% of the water molecules are oriented with one O-H bond out of the surface by about 38 degrees to the plane of the interface\textsuperscript{11, 12}. In addition, x-ray reflectivity measurements indicate that the 10:90 region, where the liquid phase transitions from 10 to 90 percent of its bulk density, is 3.2 Å thick\textsuperscript{10, 11}. This high degree of structuring at the air/water interface has caused it to be described as “ice-like.” Because these techniques are fundamentally incapable of providing insights as to the dynamic properties of the air/water interface, there has been much speculation as to the nature of the dynamic properties. It may be that the high degree of structuring hinders movement, and that processes such as the reordering of hydrogen bonds and lateral diffusion are slower than in the bulk. On the other hand, it is possible that the reduced density of the interfacial region lowers the energy needed to rotate, and reduces the number of intermolecular collisions that slow down diffusion in the bulk. It is the purpose of this work to help bridge that gap in understanding of the air/water interface.

Although the dynamic properties of the air/water interface have been experimentally inaccessible, it has been the subject of a variety of simulation studies, including the approaches of Monte Carlo and molecular dynamics simulations. These simulations have generally
predicted the same structural properties that have been experimentally determined. Specifically, these simulations have given a 10:90 region about 4 Angstroms thick, show a high degree of orientational ordering, and reduced degree of hydrogen bonding for water molecules in the interfacial region\textsuperscript{13–16}. Results from molecular dynamics simulations suggest that the rate of lateral self-diffusion for interfacial water indicate that it is 50 to 100\% higher than in the bulk phase\textsuperscript{8, 15, 17, 18}. It is generally assumed that agreement between theory and experimental results gives sufficient reason to trust theoretical predictions regarding experimentally inaccessible parameters.

In this work, we seek to experimentally measure some aspects of the dynamic properties of the air/water interface. Though determining the lateral self-diffusion coefficient for pure water remains experimentally unavailable, it is possible to measure the rate of lateral diffusion of a surfactant probe molecule. Once this value has been obtained, models relating 2D diffusion to viscosity (described in chapter 4) will be employed to estimate the value of water’s lateral self-diffusion constant. Stringent criteria must be met for the surfactant probe to provide the insights sought. It must be electrochemically active (because we will probe the system using electrochemical methods), and it must immerse no deeper than the 10:90 region. The advantages and viability of this approach are discussed below.

This approach carries the disadvantage of not yielding insights into the behavior of pure water, but this is perhaps more than compensated for by the insights that will be gained into the behavior of monolayers at the air/water interface. Indeed, systems of amphiphiles at air/water interfaces are of as much, if not more, interest than pure air/water interfaces. Amphiphiles, which may be broadly categorized as molecules containing a polar and a nonpolar region, are ubiquitous and broadly employed in both biological and industrial processes. They form the basis of soaps, foams, dispersions, colloids, and emulsions. Adsorption and desorption of amphiphiles at liquid/liquid interfaces is known to retard drop motion\textsuperscript{1}. Amphiphiles are used to enhance underground oil recovery, treat wastewater, improve wettability, and stabilize various systems. Insoluble monolayers in Langmuir-Blodgett films are applied directly in industrial processes to fabricate various optical and electronic devices, protective coatings, thin-film insulators, thin-film conductors, lubricants, and liquid crystal display devices\textsuperscript{1–4}. Understanding the intermolecular interactions of these films at the air/water interface greatly enhances the ability to control the films to create optimally functioning devices.

Perhaps even more significantly, a study of monolayers at an air/water interface has profound biological significance. Phospholipids, which are amphiphilic compounds, constitute the main structural component of cell membranes. In skin cells, the membranes are interposed between air and aqueous cell contents\textsuperscript{19}. The lungs of all mammals present an air/water interface with a lipid/protein membrane. It follows that understanding this membrane is critical in the study of biochemistry.

Molecular dynamics has also been applied to study amphiphiles adsorbed at the air/water interface. The predictions made by these simulations are highly relevant to the work presented in this dissertation. In particular, studies of systems containing phenol, p-pentylphenol, methanol, and ethanol adsorbed at the air/water interface have been published by Pohorille and coworkers\textsuperscript{20–22}. They report that the hydrophobic structure of an amphiphile can be used to predict immersion depth for interfacial species. The most probable location of pentylphenol, whose center of mass coincides roughly with the C4 carbon, is 2 Angstroms above the Gibbs dividing surface. The Gibbs dividing surface is a plane dividing the interfacial region located at the point where water the density of water is 50\% of its bulk density. The most probable
location of phenol is only 1 Å above the Gibbs dividing surface\(^{20-22}\). The general conclusion is that polar groups are immersed in the water, while the non-polar groups are not. In addition, the relative polarity of the hydrophilic portion influences the immersion depth. These two conclusions support the assumptions made in our model for diffusion.

In light of the previous background, our proposal to use an amphiphilic probe to measure the dynamic properties of the air/water interface appears justified. Measurements made on a shallowly immersed probe, with an immersion depth no greater than the interfacial region, will yield information about the dynamic properties of this region. As discussed below, the viscous drag on the unimmersed portion of the probe can be assumed to be negligible.

It is important at this point to distinguish between two kinds of monolayers, those made of insoluble molecules (Langmuir monolayers) and those made of soluble molecules (Gibbs monolayers). Langmuir monolayers are commonly formed by spreading a solution of amphiphilic compounds dissolved in a highly volatile solvent, such as stearic acid dissolved in chloroform. These monolayers derive their name from Irving Langmuir, who made the first systematic study of two dimensional systems at the air/water interface\(^{23-27}\). Phospholipids, noted above as the main structural component of cell membranes, form Langmuir monolayers at the air/water interface.

Gibbs monolayers are formed at liquid/vapor interfaces by the spontaneous partitioning of soluble amphiphiles. In Gibbs monolayers, the balance between the hydrophilic and lipophilic sections of the molecule is shifted towards the hydrophilic portion relative to the molecules that form Langmuir monolayers. The surface excess reduces the surface tension of the liquid by an amount called the surface pressure. In other words, the surface pressure is the difference in surface tension of the pure liquid phase and the surface tension in the presence of a surfactant. Because the molecules obey the Gibbs equation at equilibrium, the partition constant for a solute can be determined by measuring the surface pressure as a function of concentration. This will be treated more fully below. Some examples of molecules that form Gibbs monolayers at the air/water interface are soaps and emulsifiers\(^ {1-4} \).

### 1.2 An Historical Overview of Diffusion

Diffusion may be defined as the process by which matter translates in the absence of any external directional force. Although it would still be millennia vocabulary was developed to describe it, the basic concepts of diffusion would have been impressed upon cavemen who observed smoke from fire spread out and fill up their cave. Within the formal tradition of western science, effects due to this phenomenon have been observed and reported since the 18\(^{th}\) century, when Abeel Nollet filled a pig’s bladder with ethanol and placed it in a water bath. He observed with great interest that the bladder swelled greatly beyond its original size\(^ {28}\). What the pig thought of this experiment was not reported.

The process of diffusion across a semi-permeable membrane received its first systematic treatment 75 years after Nollet’s publication. Joachim Dutrochet, both a physician and a chemist, found that when two liquids of varying composition are separated by a semi permeable membrane, two opposing currents of unequal strength exist. Dutrochet termed these currents endosmosis and exosmosis, which has come to be described as binary diffusion in modern terms\(^ {29}\).

The next major influential figure in diffusion research was the Scotsman Thomas Graham. While Graham enjoyed a fair amount of success in his studies on the diffusion of
gasses, his 1850 report on the diffusion of various solutes in a wide variety of solvents did not result in any laws or models governing diffusion.

This brings us to the story of Adolf Fick. Born and raised in Germany, Fick had planned on becoming a mathematician, but was persuaded to become a doctor instead. As a doctor, he sought as much opportunity as possible to engage in scientific research, and especially enjoyed opportunities to apply mathematical treatments to experimental data.

Fick reasoned that Fourier’s model for heat diffusion should serve as a model for molecular diffusion as well. The concentration of solvent molecules is analogous to the temperature, the quantity of solute molecules is analogous to heat, and the diffusion coefficient is analogous to the thermal conductivity. Fick’s confidence in this analogy grew when he observed that the model made predictions consistent with Graham’s work. Fick ultimately summarized his theoretical results in two equations, commonly called Fick’s Laws of Diffusion.

Fick’s first law states:

$$J_x = -D \frac{\partial C}{\partial x}$$

where $J_x$ is the flux per unit area, $D$ is the diffusion coefficient, $C$ is the concentration, and $x$ is the distance. The negative sign arises from the fact that particle flux goes against the concentration gradient. Fick’s second law declares for linear diffusion:

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{C}{A} \frac{\partial A}{\partial x} \right)$$

Typically, $D$ is not a function of $x$, and the cross sectional area, $A$, does not change with respect to distance. In this case, Fick’s second law reduces to the form

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

A more general formulation that includes any geometry is

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

where $\nabla^2$ is the Laplacian operator corresponding to the relevant geometry. In this dissertation, hemi cylindrical and hemispherical diffusion will be considered in addition to linear diffusion.

Fick was able to verify these equations experimentally by using a glass cylinder with a small cylindrical well. In the bottom of the well he placed a large amount of sodium chloride. By periodically changing the water in the cylinder while leaving the well undisturbed, he was able to establish a steady-state concentration gradient, in which he could measure the concentration of sodium chloride as a function of height in the well. The experiments were also carried out using a conical well, which requires the $\partial A / \partial x$ term shown in equation 1.2.

Fick also contributed to the understanding of diffusion through semipermeable membranes, though his contributions to this area were purely qualitative. Treating the membrane as an array of capillaries with hydrophilic walls, he hypothesized that water would travel along the walls of the capillary, with the solute passing along the central axis of the capillary, thereby creating a bidirectional flow of material, consistent with the results of Dutrochet. If the capillaries were too small to permit water and solute to flow through, flow in only one direction would be observed, consistent with the result of Nollet.

Twenty years later, Wilhelm Pfeffer made significant quantitative contributions to the understanding of diffusion in osmosis. A botanist by trade, Pfeffer used the semipermeable
membranes of plant walls and measured the osmotic pressure inside the cells. Doing so, he was able to demonstrate that, in addition to composition, temperature and pressure are controlling variables in determining the osmotic pressure.

In order to obtain more control over the semipermeable membranes, Pfeffer initiated research on the ability of inorganic materials to serve as semipermeable membranes. He was able to create suitable membranes by precipitation thin films of copper ferrocyanide in porous ceramic cups. With these artificial membranes, Pfeffer was also able to establish the effect of concentration on osmotic pressure. The study of osmotic pressure by Dutrochet, Fick, and Pfeffer showed the power of a biophysical approach to understanding physiological processes, and indicated that organic and inorganic processes are governed by the same physical laws.

The pace of understanding began to quicken substantially at this point. Ten years after Pfeffer’s work, Jacobus van’t Hoff made his contributions to the understanding of osmosis. Building on the work of his predecessors, van’t Hoff applied analogies from the gas laws to the systems of osmotic pressure. Van’t Hoff formally defined osmotic pressure as the excess pressure that develops in a solution contained in a vessel that is in contact with a reservoir of pure solvent across a semipermeable membrane. With this definition, van’t Hoff used the gas laws to make predictions about the magnitude of the osmotic pressure versus the nature of the solute, the pressure, and the temperature of the system. The major shortcoming of his treatment was neglecting to take into account the ionic character of many solutes.

This flaw was soon addressed by Walter Nernst in the following year. Aware of van’t Hoff’s work, Nernst also noted that Fick had observed the diffusion of solutes in the direction of decreasing concentration thirty years earlier. However, as Fick derived his laws by analogy from the work of Fourier, he did not create them with a full understanding of the governing forces. Using the terms “impelling forces” and “resistive forces” stemming from osmotic pressure and molecular collisions, respectively, Nernst expressed the flux of the solute in terms of the gradient of the osmotic pressure. He noted that for dilute solutions, the osmotic pressure is linear with respect to concentration and obtained identical results to those reported by Fick. For electrolyte solutions, ions migrate independently. Nernst hypothesized that differences in ion velocities created by osmotic pressure would soon be compensated by electrostatic forces, resulting in uniform diffusion rates and a junction potential.

This remained the standard model for osmotic pressure for nearly twenty years until Berkeley’s own Gilbert N. Lewis brought his talents to bear on the matter. There have been no substantial changes to the understanding of osmotic pressure since Lewis’s treatment of the subject. Lewis described osmosis as the attraction of water by the solutes. Lewis’s thermodynamic explanation was to interpret osmosis in terms of this chemical attraction. This broader treatment enabled Lewis to develop a theory of solutions that also included a description of three other colligative properties of solutions: vapor pressure depression, freezing point depression, and boiling point elevation. He also applied chemical potentials in his treatment, which he described as the force which drove the movement of solvent molecules across a semipermeable membrane. His view was that water with a solute in it has a lower vapor pressure because of the lower “escaping tendency” of the solvent. Quantitatively, this means that the chemical potential of water is lower in solution than in pure water, resulting in a flow of water from the solvent side to the solution side of a semipermeable membrane until chemical potentials become equal. The increase of chemical potential on the solution side results from the increase
in osmotic pressure, and the flow of water can be reversed (or extended) by the appropriate application of an external pressure\textsuperscript{38}.
Figure 1.1 The one-dimensional walk of a drunkard down a sidewalk. Each step covers a distance $L$. If forward and backward steps are equally probable, the mean displacement after $N$ steps is zero, and the mean square displacement is $NL^2$.
At this same time, theory was developing to describe the stochastic processes governing self-diffusion. In 1905, Karl Pearson wrote a short letter describing the process that has come to be known as the random walk\textsuperscript{39}. Pearson described a drunkard walking down a sidewalk. Due to his advanced state of inebriation, not every step carries the drunkard in the direction of his destination. Every step contains a certain probability that the drunkard will move backwards instead of forward. In the limit of maximum inebriation without losing the ability to locomote, a step backwards has the same probability as a step forward. Remarkably, the drunkard is assumed to maintain a uniform stride. Figure 1.1 illustrates the problem for one dimension. It may be asked where is the expected location of the drunkard after a given number of steps. The purpose of Pearson’s communication was to see if anyone had a solution to this problem.

Fortunately for him, and for the rest of the scientific community, Lord Rayleigh had solved the problem 25 years earlier, and replied to Pearson citing his statistical analysis of the situation\textsuperscript{40–42}. This exchange of letters forever enshrined the term “random walk” in the theoretical studies of diffusion. In the same year that Pearson and Rayleigh made this exchange, Einstein published his landmark work on Brownian motion, the term used to describe the movement of small particles suspended in a stationary liquid. Drawing on the work of van’t Hoff, Einstein established the molecular kinetic basis of heat, still a matter of debate in the early 20\textsuperscript{th} century (it was in 1906 that Boltzmann committed suicide, attributed in part to his depression due to a lack of general acceptance of his atomistic viewpoint). Even so, there was a general consensus that Brownian motion was caused by the random collision of highly energetic molecules with the much larger colloidal particles, thereby causing the suspended particles to take random walks\textsuperscript{43}.

Einstein started his work by extending the concept of osmotic pressure to suspended colloidal particles, stating that at low concentrations (minimizing cross interactions of colloidal particles) colloidal particles should exhibit the same behavior as solute molecules. If solute molecules create osmotic pressure, then so should colloidal particles, because in both cases their motion is governed by collisions with solvent molecules. The implication is that the osmotic pressure created by a certain number of colloidal particles is the same as that created by the same number of solute molecules, and colloidal particles will be driven in the direction of decreasing osmotic pressure. By assuming the force due to the osmotic pressure to be equal to the force related to the viscous drag, Einstein obtained the relation:

\[
D = \frac{RT}{N_A 6\pi \eta r} \tag{1.5}
\]

where \(D\) is the diffusion constant, \(R\) is the ideal gas constant, \(T\) is the temperature, \(N_A\) is Avogadro’s number, \(6, \eta\) is the coefficient of viscosity, and \(r\) is the radius of the colloidal particle, which is treated as spherical. Stokes’ law for viscous forces is also assumed to apply.

Completing the statistical analysis of the equation, Einstein noted that it predicted a root-mean-square displacement proportional to the square root of the time step contained in a random walk process, a well known relation\textsuperscript{43}. Einstein’s paper on Brownian motion unified osmotic pressure, the kinetic energy associated with heat, the recursive relation of a random process, and the notion of mean intensity of a statistically determined value.

Random walk principles have nearly universal application. In addition to molecular diffusion, applications are also found in heat transfer, current flow in conductors, and flow in porous media. Even the pricing of modern derivatives and securities assumes a random walk of the price of a security\textsuperscript{32, 37, 39–42, 44}. 
1.3 An History of Monolayer Films

It has long been known that water and oil do not mix. The earliest known literature sources attest to this fact. Four thousand year old clay tablets from Babylon report spreading thin films of oil on the surface of water. The Babylonians’ purpose was to make a spiritual inquiry rather than scientific one, as the spreading was done to perform divination. This practice is known as lecanomancy, or “bowl divination”\(^{45}\). Some Romans and Greeks had a more scientific approach, and Pliny and Plutarch note that thin oil films produce a calming effect on water. Plutarch cites Aristotle for a source, but unfortunately, Aristotle’s work on this subject has been lost. Pliny remarks that, “Everything is soothed by oil, and this is the reason why divers send out small quantities of it from their mouths, because it smooths every part which is rough.” He hypothesized that the calming effect might be due to oil’s slipperiness, causing the wind to slide over it with minimal interaction\(^{46, 47}\). Molecular mechanics were not well enough established at his point in time for him to formulate a better hypothesis.

Not too long after Pliny and Plutarch’s work, barbarian tribes invaded southern Europe, and science was put on hold for several centuries. The first reporting of monolayer phenomena in modern literature is Benjamin Franklin’s famous Clapham Pond experiment. Although his experiment would probably result in fines and penalties for violation of environmental protection laws today, Franklin operated under no such constraints. His paper before the Royal Society of London merits citing at length. Franklin states:

In 1757, being at sea in a fleet of 96 sail bound against Louisbourg, I observed the waves of the two ships to be remarkably smooth, while all the others were ruffled by the wind. which blew fresh. Being puzzled with the differing appearance, I at last pointed it out to our captain and asked him the meaning of it. “The cooks,” says he, “have, I suppose, been just emptying their greasy water through the scuppers, which has greased the sides of those ships a little,” and this answer he gave me with an air of some little contempt, as to a person ignorant of what everybody else knew. In my own mind I at first slighted his solution, though I was not able to think of another…

At length being at Clapham, where there is, on the common, a pond, which I observed one day to be very rough with the wind, I fetched out a cruet of oil, and dropt a little of it on the water. I saw it spread itself with surprising swiftness upon the surface, but the effect of smoothing the waves was not produced, for I had applied it first on the leeward side of the pond, where the waves were the largest, and the wind drove my oil back upon the shore.

I then went to the windward side where they began to form, and there the oil, though no more than a teaspoonful, produced a calm over the space of several hundred yards square, which spread amazingly, and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass.\(^{48}\)

Though entirely qualitative in nature, this is often cited as the first study of monolayer films at the air/water interface. Over one hundred years later, Lord Rayleigh would make the first quantitative contributions to the field. He measured the change in surface tension due to the contamination of the water surface\(^{42}\). Rayleigh extended work done earlier by Agnes Pockels. Working in a homemade tin trough in her kitchen, Pockels discovered that surface films could be
manipulated by pushing them with barriers that extended the width of the trough \cite{49, 50}. Rayleigh used this technique to confirm that there was a dramatic change in surface tension when the oil is confined to below a critical concentration. From this, Rayleigh hypothesized that there was no more than a single monolayer of oil, and estimated the size of an olive oil molecule to be about one nanometer. Rayleigh’s atomistic views, though controversial at this time, ultimately formed the foundation of all subsequent monolayer studies \cite{42, 49, 50}.

The next significant advances were made by Irving Langmuir. Langmuir developed many of the experimental tools (including the Langmuir balance, a moveable float that can directly measure the force of a spreading film) and techniques for the study of monolayers as well as a systematic approach to the understanding of the relationship between molecular constitution and monolayer properties. Critical to Langmuir’s advances was his use of purified organic compounds instead of vegetable oils. He also pioneered the use of solid surfactants, which he introduced to the water surface by spreading them in solutions of a volatile organic solvent \cite{23–27}. Langmuir was the first to study the relationship between chemical functional groups and film properties. It is in honor of his work that monolayers of insoluble compounds are referred to as Langmuir monolayers.

Langmuir also developed a quantitative theory of adsorption. By employing general terms, his theory was able to serve as a model for adsorption at solid/liquid, solid/vapor, and liquid/vapor interfaces. Perhaps ironically, Langmuir’s model for adsorption is often used in the treatment of Gibbs monolayers. This will be elaborated below.

Another important contribution made by Langmuir is his study of molecular orientation in monolayer films. In a study of homologous surfactants ranging from 14 to 34 carbons in the alkyl chain, he discovered that the surface pressure versus mean molecular area curves all had the same qualitative shape, rising almost negligibly as concentration increased, until reaching a mean molecular area around 20 Å²/molecule. At this point, the surface pressure increased dramatically, reached a maximum value, and then plateaued. The surface pressure is defined as the difference in surface tension in the absence and presence of the surfactant, and is expressed with the letter $\pi$ (presumably for pressure)

$$\pi = \gamma_0 - \gamma$$

From this Langmuir concluded that at low mean molecular area the molecules were oriented vertically at the interface with the polar group immersed in water and the carbon chain pointing into the air. The plateau region was due to the collapse of the monolayer \cite{23–27}. After Langmuir, the field grew like mushrooms after rain, with further advances being made by Rideal \cite{51}, Adam \cite{1}, Harkin \cite{4}, and Gaines \cite{52}.

### 1.4 Techniques for Studying Monolayer Films at the Air/Water Interface

No dissertation involving a study of monolayer films would be complete without a treatment of the $\pi$-$A$ isotherm. One of the oldest methods for studying monolayer films, it is also widely used. The experiment is performed as follows: A hydrophilic plate, known as a Wilhelmy plate hangs from a sensitive balance and is partially immersed into the aqueous phase of a system containing a monolayer film. The plate must be hydrophilic in order to maintain a low contact angle (ideally 0°). Typically, roughened platinum or filter paper are employed. The vertical orientation of the plate causes the surface tension to pull down on the plate, increasing the apparent mass. The equation quantifying the increase is:

$$m = P \gamma \cos \theta$$

where $P$ is the perimeter of the plate, $\gamma$ is the surface tension, and $\theta$ is the contact angle between the plate and the aqueous phase. For a contact angle equal to zero and a plate of negligible
thickness, equation 1.7 reduces to \( m = 2w\gamma \) with \( w \) being the width of the plate. Buoyant forces must be accounted for by taring the balance after inserting the plate into solution. Impurities are then removed from the surface by aspiration. Once the balance shows no change in mass reading upon compression of the motor driven barriers, the monolayer film of interest is spread from a solution of volatile organic solvent. After a short period of time, the solvent evaporates from the surface, leaving behind the monolayer of interest. A schematic of the experimental set up can be seen in Figure 1.2

Gaines has detailed the properties of an ideal spreading solvent\(^{47,52}\). The solvent must be chemically inert, highly pure, volatile, insoluble in water (or whatever the subphase is), and able to completely dissolve the compound of interest. HPLC grade chloroform often serves as a suitable solvent. Once the solvent has evaporated, the surface concentration can be controlled by adjusting the position of the barriers. The surface pressure can then be recorded as a function of mean molecular area (A) at a constant temperature. The mean molecular area is the simply the surface area of the trough divided by the number of molecules. This means that \( \pi - A \) isotherms are the 2D analogue of PV isotherms for three dimensions. Figure 1.3 shows an idealized \( \pi - A \) isotherm.

At low densities, the monolayer exists either in a fully gaseous (G) state, or in a liquid expanded (LE) and gaseous coexistence state. The low density insert is a theoretical approximation and is not experimentally well known. In either case, the surface pressure measurements show an essentially zero reading. The first appreciable rise seen in the \( \pi - A \) isotherm upon compression occurs at point A, where the monolayer is converted from a LE/G coexistence state to a fully LE state. The pressure begins to rise as the liquid monolayer is compressed. It is noteworthy the 2D liquid films exhibit about an order of magnitude greater degree of compressibility than 3D liquids. The compressibility is expressed by a 2D analogue to 3D compressibility:

\[
\kappa = \frac{1}{A} \left( \frac{dA}{d\pi} \right)_T
\]

(1.8)

The lower viscosity of the liquid state of monolayer films is an important consideration in the study of monolayer films, and will be discussed later. At point B, another phase transition occurs as the monolayer converts to the LC (liquid condensed phase). The leveling of surface pressure during this compression phase is a manifestation of the Gibbs phase rule

\[
F = C - P + 2
\]

(1.9)

where \( F \) is the number of degrees of freedom, \( C \) is the number of components in the system, and \( P \) is the number of phases present. Increasing the number of phases reduces the number of degrees of freedom. When only one phase is present, both the MMA and \( \pi \) can be varied, but with two phases present, as the MMA is varied, \( \pi \) must remain constant. Once the phase transition is complete, seen at point C, the pressure begins to rise upon continued compression. Frequently, a small kink is seen as MMA continues to decrease, indicating the transition from LC to solid (S) monolayer film. Monolayer systems at the air/water interface often have a variety of condensed phases that can form\(^2\).

There are a variety of theoretical approaches to interpreting \( \pi - A \) isotherms. With highly sensitive surface balances, some studies have been performed on gaseous monolayers. There has been some success in treating gaseous monolayer films using the 2D Volmer equation of state\(^2,52\).

\[
\pi A = kT
\]

(1.10)
Figure 1.2 An illustration of the Wilhelmy plate method for measuring surface tension. On the left is a front view, showing the plate width. On the right is a side view, showing the contact angle of the meniscus, which ideally is 0°. The surface tension of the solution exerts a downward force on the plate, determined by the perimeter of the plate and the contact angle between the solution and the plate.
Figure 1.3 An idealized $\pi$-A isotherm obtained from the compression of a Langmuir trough. The flat regions correspond to phase transitions in the monolayer, with the letters $A$–$D$ representing the points at which phase transitions begin. Specifically, $A$ marks the end of the liquid expanded (LE) and gas (G) coexistence region; $B$ marks the beginning of the combined liquid compressed (LC) and LE region; $C$ marks the end of the LC and LE coexistence region; $D$ marks the phase transition from LC to solid (S). This latter phase transition happens very rapidly and appears as a kink in the graph rather than a full flat region. The region of gas (G) and liquid expanded (LE) coexistence is very large.
It is easily seen that this is a 2D analogue of the ideal gas law. At higher densities, corrections for deviation from ideal behavior must be taken into account. Again, the methods of treatment are commonly 2D analogues of 3D systems, and include adjustments to account for the volume occupied by the molecules and the intermolecular attractions, such as in the van der Waals equation. Additional terms are sometimes needed to account for ionic attractions and repulsions, something generally not seen in 3D gases. Other analyses of $\pi$-A isotherms treat the system with an osmotic model, with the monolayer treated as a 2D assembly of amphiphiles and water molecules. The competing models have various degrees of success, depending on the nature of the amphiphile. A generalized model that is successful in treating a large variety of amphiphilic monolayers remains to be developed. This makes molecular information about microscopic properties of monolayers difficult to assess from a $\pi$-A isotherm. Nonetheless, the simplicity of the experiments and the macroscopic knowledge gained from performing $\pi$-A isotherms make them a valuable and widely performed technique.

Brewster angle microscopy (BAM) is a powerful optical tool for imaging monolayers at the air/water interface. It can be used to directly image the texture of a monolayer film. Its main applications are qualitative in nature, although advanced setups are capable of providing quantitative information. The theoretical basis for BAM comes from the nature of the plane polarized light as a function of angle of incidence. The Brewster angle is the angle at which incident p polarized light shined on a medium is reflected in the same plane as the surface of the medium. This angle depends on the refractive indices of the optical media. For the air/water interface, the Brewster angle is calculated from the following relation:

$$\tan \theta = \frac{n_{\text{water}}}{n_{\text{air}}}$$

where $\theta$ is the incident angle of the beam and $n$ represents the refractive index. If the incident light is completely p polarized, there will be no reflection at this angle. For water, this angle was determined to be 53.15° by David Brewster. When a monolayer exists at the air/water interface, the refractive index is altered, and p polarized light is reflected. The intensity of the reflected light depends on the thickness, density, and optical properties of the film. Lateral resolution is typically 1–2 µm. BAM is a very useful technique for studying mixed monolayers because of its sensitivity in detecting domains with different dielectric properties and isotropy. Its ability to detect the latter property makes BAM widely employed in investigations of phase transitions, particularly the LE/G to LE phase transition. During the period of phase transition, the film is typically heterogeneous, resulting in regions of varying intensity of reflected light. In the image, the gas phase may be identified as regions of low intensity of reflected light, with the LE phase visible as bright regions.

Higher order transitions that are difficult to detect with $\pi$-A isotherms can also be detected with BAM, such as the LC/S transition, characterized by a tilting of the aliphatic chains in the hydrophobic section. The azimuthal tilt angle strongly affects the surface reflectivity of the p polarized light. This property also allows BAM to be a useful technique for studying chiral domains at the air/water interface.

Monolayer morphology may also be studied with epifluorescence microscopy. In this method, some of the molecules residing within the film are tagged with a fluorescent moiety. Differences in density can then be measured as a function of fluorescence intensity. The obvious disadvantage of this approach is that the addition of the probe molecules may cause the monolayer to exist in a perturbed state, especially at high density. It has been reported that the commonly used fluorescent probe dipalmitoylnitrobenzoxadiazol-phosphitidylethanolamine (say that ten time fast!) separates from condensed lipid phases even in concentrations as low as 1
mole percent, while still remaining soluble in the liquid phase\(^2\). In BAM, these perturbations are no longer present, as probe molecules are not needed. The native monolayer is directly imaged, rendering BAM superior to competing methods for determining monolayer morphology.

The disadvantages of BAM include a lower resolution and the inability to image some monolayers due to small signal to noise ratios created by mechanical vibrations. The disadvantages are less significant with improved optics of detection and when active vibration isolation is employed.

### 1.5 Methods for Studying Gibbs Monolayers

I will now shift my attention to Gibbs monolayers. In fact, in light of the experimental work that will be presented in later chapters of this dissertation, there probably wasn’t any need for me to talk about Langmuir monolayers at all, as I did a minimal amount of experimental work on Langmuir monolayers. Gibbs monolayers, as noted above, are formed by the partitioning of soluble surfactants. Monolayers formed in this manner share a number of characteristics with Langmuir monolayers, particularly the increase in surface pressure with respect to increasing surface concentration. In the case of Gibbs monolayers, the surface concentration is obtained as a function of bulk concentration.

The change in surface tension due to the adsorption of aqueous species with respect to pure solvent is related to the surface excess by the Gibbs equation, a macroscopic thermodynamic relation shown in equation 1.12.

\[
- d\gamma = \sum \Gamma_i d\mu_i \quad (1.12)
\]

where \(\gamma\) is the surface tension, \(\Gamma_i\) is the surface excess relative to the Gibbs dividing surface of the solvent, \(\mu_i\) is the chemical potential, with the sum being taken over all solute species. The surface excess with respect to a particular position at the interface is the difference between the actual concentration integrated over the whole interfacial region and the integration of the bulk concentrations extended to and truncated at that particular position. Surface excesses may be positive or negative quantities. For the air/water interface, the Gibbs dividing surface is typically defined as the point where the water surface excess is zero, where water is approximately 50% of its bulk density\(^2, 47\).

In a simplified model, the aqueous phase and the air phase are separated by a geometrically flat surface. It follows that the only species in excess at the surface is the surfactant. In dilute solutions, the change in chemical potential may be expressed as:

\[
d\mu = RTd\ln C \quad (1.13)
\]

where \(C\) is the bulk concentration of the solute. Substituting this value into the Gibbs equation and solving for the surface excess concentration yields:

\[
\Gamma_s = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln C} \right) \quad (1.14)
\]

From equation 1.14 it can easily be seen that, for a constant temperature, a positive surface excess is associated with a decrease in surface tension (and conversely, a negative surface excess results in an increase in surface tension). If the concentration dependence of \(\gamma\) is known, the surface excess may be predicted, as well as the area occupied by each surfactant molecule.

It is now of interest to discuss models that explain the surface excess in terms of bulk concentration. I personally find it highly amusing that this dissertation will use the Langmuir model to describe Gibbs monolayers. The Langmuir model is a simple but powerful model that successfully describes a wide array of adsorption phenomena. Its simplicity rests on four
fundamental assumptions. First, there are a fixed number of interfacial sites for adsorption, which includes limiting the system to the formation of no more than one monolayer. Second, all sites are assumed to be equivalent and uniform, implying homogeneity on the microscopic level. Third, it is assumed that the energy associated with adsorption is independent of the surface concentration of the adsorbing species. This implies that solute-solute and solute-solvent interactions are identical or that solute-solute interactions are negligible. Fourth, it is assumed that there is no depletion of the bulk. More advanced models account for multiple adsorption layers, interaction between adsorbed species, surface irregularities, and bulk depletion. However, for dilute aqueous systems with a large volume to surface area ratio, such as those described in this dissertation, these assumptions hold. In addition, the Langmuir adsorption model has been experimentally validated for our system, as will be discussed in a later chapter.

After making the aforementioned assumptions, the system is divided into a bulk and a surface region with an equilibrium of exchange between of solvent (V) and solute (U) species between the two regions. Under these conditions, the equilibrium of exchange is described as

\[
V_s + U_B \rightleftharpoons V_B + U_S
\]

with the S and B subscripts denoting surface and bulk species, respectively. The Langmuir model derives from rewriting the equilibrium constant by changing to mole fractions in the surface region, with the maximum surface concentration described as \( \Gamma_s^{\text{max}} = [V_s] + [U_s] \) and solving for the surface concentration of the solute

\[
K = \frac{[V_B][U_S]}{[V_S][U_B]}
\]

(1.16)

\[
K[V_s][U_B] = [V_B][U_S]
\]

\[
K([\Gamma_s^{\text{max}} - [U_S]]/[U_B] = [V_B][U_S]
\]

\[
K \Gamma_s^{\text{max}} [U_B] = [U_S]([V_B] + K[U_B])
\]

It is conventional to express the surface concentration in terms of fractional mole coverage, expressed with \( \theta \):

\[
\theta = \frac{[U_S]}{\Gamma_s^{\text{max}}} = \frac{K[U_B]}{([V_B] + K[U_B])}
\]

(1.17)

From here, the right side of the equation can be divided by the total bulk concentration to obtain bulk mole fraction. Denoting bulk mole fractions as \( x_i \) and surface mole fractions as \( y_i \), the Langmuir equation can then be written:

\[
y_U = \frac{K x_U}{x_V + K x_B}
\]

(1.18)

The Langmuir model describes the relation between bulk and surface mole fractions. If \( K \) is equal to one, then there is no energetic difference between the surface and bulk species, and the mole fraction will be equal in both phases.

For dilute solutions, the bulk solvent concentration is assumed to be constant and omitted from the equation. This requires expressing the system with a new equilibrium constant \( K' = K/[V_B] \). Dividing the right side of equation 1.17 by \([V_B]\) and denoting the bulk concentration of the surfactant as \( C \) yields the most familiar form of the Langmuir isotherm:

\[
\theta = \frac{\Gamma_s}{\Gamma_s^{\text{max}}} = \frac{K'[C]}{(1 + K'[C])}
\]

(1.19)
It is worth noting at this point that the Langmuir isotherm can also be obtained by a statistical mechanical argument. It was originally designed to describe gas adsorption onto solid surfaces. That it can be used to model solutes adsorbing at the air/water interface is a testament to generality of the system and the validity of its underlying assumptions. It can be applied to any system that can be divided into two regions connected by a chemical equilibrium. In the case of a liquid surface, a surface site is an empty volume that can be occupied either by a solute or a solvent molecule. The maximum surface concentration then becomes the maximum number density of solute molecules that can be accommodated at the surface.

Combining the Langmuir isotherm with the Gibbs equation and equation 1.6 and integrating yields the Langmuir-Szyszkowski equation, which relates the surface pressure directly to surfactant concentration without the need to measure the derivative of the curve. This is especially advantageous because experimental error is magnified when taking derivatives.

\[
-\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln C} \right) = \frac{\Gamma_{\text{max}} K[C]}{(1 + K[C])}
\]

\[
-\partial \gamma = R T \Gamma_{\text{max}} \left( \frac{K[C]}{(1 + K[C])} \right) \partial \ln C
\]

\[
-\int_{C=0}^{C=C} \partial \gamma = R T \Gamma_{\text{max}} \int_{C=0}^{C=\infty} \left( \frac{K[C]}{(1 + K[C])} \right) \partial \ln C
\]

\[
-(\gamma - \gamma_{0\circ}) = R T \Gamma_{\text{max}} \left( \ln(1 + KC) - \ln(1 + K \times 0) \right)
\]

\[
\pi = R T \Gamma_{\text{max}} \left( \ln(1 + KC) \right)
\]

Several methods exist for determining the dependence on the surface pressure on bulk concentration, including BAM\textsuperscript{2}. Due to its cheap cost and simplicity of design, one of the most widely used methods is the du Nouy ring tensiometer. This method measures the force required to detach a ring of wire from the surface of a liquid. The wire ring is connected to a beam carried on a horizontal tension wire whose constants are known. The ring is commonly a Pt-Ir alloy. The simplest theoretical interpretation of the experiment assumes that the force to detach the ring is simply the perimeter multiplied by the surface tension. The resulting relation of the force to the surface tension of the liquid is

\[
f = 4\pi r \gamma
\]

This only holds if the contact angle is 0° and if the inner and outer radii of the ring are identical. Generally, neither assumption is valid, and a correction factor must be applied, giving equation 1.23 when solving for the surface tension.

\[
\gamma = \frac{\beta f}{4\pi r}
\]

where \(\beta\) is a correction factor that is a function of the thickness of the Pt-Ir ring and the density of the liquid\textsuperscript{66}. Figure 1.4 illustrates the sources of error inherent in this experiment. The ring method can also be used to measure liquid-liquid interfacial tensions, provided both phases wet the ring. It is essential that the surface and the ring be as clean as possible before taking any measurements. This is ensured by aspirating the surface prior to taking any measurements and flaming the ring in between measurements.

Another commonly used method is the bubble shape analysis. A capillary is inserted into solution, and a small bubble of air is passed through the capillary, such that it remains suspended
at the tip. There is a pressure gradient between the bubble and the solution with the difference in pressure being expressed by the Young-Laplace equation:

\[ P_{in} = P_{ex} + \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  

(1.24)

where \( P_{in} \) and \( P_{ex} \) represent the internal and external pressure of the bubble, respectively, and \( R_1 \) and \( R_2 \) are the principle radii of curvature of the bubble. For spherical bubbles, \( R_1 = R_2 \), and the equation reduces to \( \Delta P = 2\gamma/R \). In the case of a suspended bubble the upward buoyant force distorts the bubble from being spherical. The bubble shape analysis method allows for a study of the evolution of surface pressure over time. From a knowledge of the difference in density between the drop and the ambient phase, as well as the principal radii of curvature for the drop (and the local value of \( g \), the gravitational acceleration constant), it is possible to calculate the surface tension of the drop. Figure 1.5 has a lovely illustration of a drop and the relevant shape parameters. Typically, the image of the drop is captured by a camera and analyzed by software designed for this very purpose\(^{67}\).

Other methods of measuring surface tension include the drop-weight method, the capillary rise method, the pendant drop method, the ripple method, the sessile drop method, and the maximum bubble pressure method. As all surface tension data in this dissertation were obtained using either the ring or the bubble shape method, a discussion of the other techniques is beyond the scope of this work.
Figure 1.4 A cartoon showing the cross section of a Pt-Ir ring. In the case of solution breaking directly off the ring, and in the limit of a negligible radius, the force exerted at the point of breaking would be $4\pi r\gamma$, as shown on the left. In practice, the solution is distorted as it is stretched, and the breaking occurs along the dotted line shown in the image on the right. By applying complicated mathematical procedures, a correction factor can be determined to account for the true point of breaking.
Figure 1.5 Cartoon schematic showing the important parameters used in the drop shape analysis technique. $R_0$, $R'$, and $R''$ are the radii of curvature. It is vital that the drop be axis symmetric. Under these conditions, $R' = R''$. $D_S$ is the diameter of the drop at a height of $R' + R''$ from the apex. The arc length from the apex of the drop to a given point is $s$, which can be expressed as a function of the angle, $\theta$, made between the point and the radius from the drop’s apex. The surface tension can be calculated from the value $R_0$ and the difference in density between the drop and the ambient phase. A computer captures the image and does all the math for you.
1.6 Methods of Studying 2D Diffusion

While BAM is the most powerful technique for studying surface film morphology, it provides no insights into the dynamic properties of interfacial films. One technique that provides insight into the dynamic properties is fluorescence recovery after photobleaching (FRAP). Currently, this is the most commonly used technique\(^\text{64, 68–73}\). A fluorescent probe is incorporated into the system of interest, typically in a concentration of about 1–4 mol %. The rate of lateral diffusion is independent of probe concentration in this range, indicating that the system has not been significantly perturbed. A circular area of the film of interest is photobleached with a high intensity laser pulse, with the recovery of the fluorescence signal being measured by the same laser at a lower intensity. For the simplest case of a circular bleached area, the lateral diffusion coefficient (D) of the molecules in the monolayer is:

\[
D = \frac{0.22r^2}{t_{1/2}}
\]

where \(r\) is the radius of the bleached spot and \(t_{1/2}\) is the half time of fluorescence recovery.

While simple, the experiment has a number of significant disadvantages. Convection caused by the heat of the bleaching laser introduces error in the determination of D both by affecting the local diffusion and by blurring the boundary of the bleached spot. This error, coupled with the blurring caused by diffraction, is probably the source of the disagreements of up to 30% for D from different sources\(^\text{74}\).

In the late 1970s, nuclear magnetic resonance (NMR) began to be used to study diffusion in artificial membranes\(^\text{75–77}\). In spite of substantial improvements in pulse sequences\(^\text{78}\) and the selection of sensitive nuclei\(^\text{79}\) such as \(^{31}\)P, the low sensitivity of NMR has severely limited its general utility in determining the rates of lateral diffusion in 2D systems.

More promising is the application of electron spin resonance (ESR) in studying diffusion in 2D systems. ESR is much more sensitive than NMR, but has the rather severe restriction of being able to study only systems containing unpaired electrons. Despite this restriction, studies of spin labeled phospholipid vesicles have been performed since the late 1960s\(^\text{80}\). The seminal work of Hubbell and McConnell involved studying membrane fluidity using 2,2,6,6-tetramethylpiperidyn-1-oxy (TEMPO) as a probe molecule. They examined the interaction of extraneous molecules with neural and erythrocyte membranes. A number of anesthetics were found to increase the fluidity of the membrane, whereas other molecules, such as cholesterol and calcium, had the opposite effect. The changes in the packing or ordering of the membrane lipids were interpreted from changes in the partition constant of TEMPO in the neural or erythrocyte membrane which were induced by the cholesterol, calcium, or anesthetics. Also, steroid molecules labeled with TEMPO were added to membranes to probe their fluidity. The fluidity was probed by noting line shape changes in the ESR spectrum\(^\text{80, 81}\). However, their papers admit they cannot associate a certain shape with a given measurement of fluidity or concentration of spins specifically bound in any part of the membrane. That is, the work is primarily qualitative in nature.

Developing their work further, Hubbell and McConnell later measured the diffusion coefficient of phospholipid molecules within bilayers. By spin labeling some phospholipid molecules, depositing them on quartz plates, and surrounding them with other phospholipid molecules, they were able to measure the change of the line shape of the labeled molecules from a highly concentrated state initially to that of a dilute labeled phospholipid in a membrane, as in their previous work. From this work, they were able to show the biological significance of the lateral mobility and more generally the fluidity of the phospholipid bilayers\(^\text{80–82}\).
Similar work was done by Marsh and coworkers in the mid 1980s. In their work they added the capabilities of measuring the lateral diffusion constants of phospholipids in membranes using very low mole fractions of a spin label and the capability to measure the concentration of spin label quantitatively. They also measured the temperature dependence of the lateral diffusion constants of phospholipids. In the 1990s, Shin and Freed measured the later diffusion constants of molecules in membranes via spectral-spatial ESR imaging. Spectral-spatial ESR imaging allows for the use of more concentrated spin labels in membranes. It provides a way to resolve the concentration or position dependent spectral variation in a two-dimensional fashion, revealing not only the macroscopic diffusion, which was measured as in the works above, but also the microscopic diffusion constant measured by Heisenberg spin exchange. The power of spectral-spatial imaging ESR is that from one set of measurements, the macroscopic and microscopic diffusion constants can be determined simultaneously.

Malec sought to extend this technique to the study of TEMPO and various derivatives adsorbed at an air water interface. This experiment presents a number of significant challenges, including the elimination of oxygen from the cell, the design of a horizontal cavity for ESR measurement, and the need for a surfactant with a very high partition constant. The constraints exist because of oxygen quenching of the ESR Heisenberg exchange signal, the horizontal nature of the air/water interface, and the competing signal from interactions between TEMPO derivatives in bulk solution. The latter concern becomes more significant at low surface concentrations of surfactant. Working with C_{18}TEMPO Amide, a TEMPO derivative containing an 18 carbon chain attached via an amide group at the fourth carbon on the TEMPO ring, Malec reports lateral diffusion coefficients of $2 \times 10^{-7}$ cm$^2$/s for 100% monolayer coverage, and $2 \times 10^{-6}$ for 50% monolayer coverage. The latter concentration corresponds to 100 Å$^2$/molecule, a concentration well above the range at which the impact of probe collisions could be considered negligible. Unfortunately, at surface concentrations below this value, the background signal from the bulk begins to overwhelm the surface contribution. The challenges required to measure lateral diffusion coefficients for probes at low monolayer coverage using ESR remain to be overcome.

Finally, and most significantly for this dissertation, is the development of electrochemical methods to measure lateral diffusion coefficients. As far as I can tell, such techniques were pioneered by, and remain largely restricted to, this research group. While there have been many electrochemical studies of monolayers, including self-assembled, Langmuir-Blodgett, and horizontally touched monolayers, there have been few studies of lateral charge transport in monolayers using electrochemical methods. A particularly intriguing challenge (and coincidentally, the one addressed in this dissertation) is the study of lateral diffusion in Gibbs monolayers.

As an addition to the previously mentioned Langmuir and Gibbs monolayer techniques, our group has developed ways to probe both static and dynamic properties in Langmuir and Gibbs monolayers using electrochemical techniques. These techniques have been used to study dynamic properties of both supported lipid bilayers, as well as free floating monolayers at the air/water interface. In the case of Gibbs monolayers, the techniques developed also yield insight to the desorption rate constant of surface species. For the study of monolayers at the air/water interface, the main challenge is to design a suitable working electrode. The electrode design employed in this work is the so-called 2D line electrode, frequently modified with a barrier film. The details of fabrication are discussed in chapter two. Briefly, line electrodes are
placed directly in the monolayer plane (or so we assert), and are then used to measure current as a function of applied potential.

One of the most powerful electroanalytical techniques is cyclic voltammetry\textsuperscript{86}. It can be used to measure the number of electrons involved in a redox process, the redox potential of an unknown species, the mechanism and kinetics of electrode reactions, rates of reactions that occur after a redox reaction, and most importantly for the purposes of this study, mass transport rates. In this dissertation, 2D cyclic voltammetry is applied to determine lateral diffusion coefficients TEMPO adsorbed at the air/water interface.

Cyclic voltammetry is a technique in which a potential linearly varying with time is applied to an electrode called the working electrode. The working electrode is one of three electrodes in potentiostatic systems. The other two are a counter electrode, which completes the electrical circuit, and the reference electrode, whose potential is constant. The potential of the working electrode is controlled relative to the reference electrode. By measuring the current that flows through the circuit, we obtain information about electrochemical reactions that deliver that current. The main experimental parameters that must be selected are the potential range and the rate at which the potential is applied, called the scan rate. The potential range is chosen to encompass the $E^0$ of the redox probe with a large enough potential range both negative and positive of $E^0$ to give both a capacitive background and a well-developed peak current. $E^0$ is the standard potential. For example, in oxidation processes, CVs are typically initiated about 300 mV negative of $E^0$. The potential scan direction is reversed when the potential is about 200 mV positive of $E^0$. Since we are interested in the rate of diffusion of a redox probe to the electrode surface, we need to first make sure that electron transfer kinetics are fast compared to mass transport rates. These are the two phenomena that limit the measured current.

The easiest way to fulfill this requirement is to choose the correct redox group. Equations 1.27 and 1.28 show how both the forward and reverse rate constants for a general redox process depend on both the standard rate constant $k_0$ and the potential. Equation 1.26 shows the reaction that occurs.

\begin{equation}
O + ne^- \rightleftharpoons R \quad (1.26)
\end{equation}

\begin{equation}
k_f = k_0 \exp[-\alpha nf (E - E^0)] \quad (1.27)
\end{equation}

\begin{equation}
k_b = k_0 \exp[(1 - \alpha)nf (E - E^0)] \quad (1.28)
\end{equation}

Here, $k_f$ and $k_b$ are the rates of the forward and backward reactions respectively, $\alpha$ is the transfer coefficient and is typically 0.5, $n$ is the number of electrons, $E$ is the potential applied to the electrode, and $f = F/RT$ where $F$ is the Faraday constant, $R$ is the gas constant, and $T$ is the temperature in Kelvin. When $E = E^0$, the electrode is at equilibrium and $k_f = k_b = k_0$. At equilibrium, while there is no net conversion from the reduced form of the molecule to the oxidized form (or vice versa), molecules are still being oxidized and reduced at a rate depending on the standard rate constant. Redox systems with large $k_0$ values will show large changes in electron transfer rates as the system is shifted away from equilibrium by the application of a potential different from $E^0$. This means that attainment of equilibrium after changing the potential occurs quickly for systems with large $k_0$ values. These types of redox systems are also referred to as reversible. The peak potentials in reversible systems are independent of the scan rate since nernstian, or equilibrium, boundary conditions apply. If the kinetics of electron transfer is fast, the current is limited by mass transport.

In order to interpret the electrochemical signal as arising from diffusion, the two other types of mass transport, convection and migration, must be eliminated or rendered negligible.
Convection in Langmuir and Gibbs monolayer film studies arises primarily from air flow above the monolayer and subphase flow beneath. In addition, molecules become more soluble following oxidation. Desorption of the molecules from the interface can lead to lateral convection, referred to as Marongoni flows. This is the motion of molecules along a surface pressure gradient. Working in a quiescent enclosure at a constant temperature helps to reduce convection to a large extent other than the caveat noted above. Active vibration isolation is also helpful. Marongoni flow is minimized by working at low surface concentrations, typically 5\% of full monolayer coverage. Migration, the transport of ions due to an electric field, is easily eliminated by adding an excess of inert electrolyte to the aqueous subphase. In addition, the amphiphiles studied in this thesis are neutral and therefore unaffected by the presence of an electric field. Most of the work presented in this thesis involves cyclic voltammetry of TEMPO systems.
35. Pfeffer, W., *Osmotische Untersuchungen, Studien zur Zellmechanik*. Nostrand Reinhold: Leipzig, Germany, **1877**.
45. Tabor, D., *J. Coll. Interface Sci.* **1980**, 75, 240; Could lecanomancy have predicted that I would spend five years studying amphiphiles adsorbed at the air/water interface?
46. Pliny the Elder, Natural History. *Book ii. Sect. 234*. Manuscript dates to ca. 78 A.D.
Chapter 2: Experimental and Methods

2.10 Materials

It is important to distinguish between pure and “surface pure.” A compound that is 99.9% pure might still not be surface pure. If the 0.1% impurity has a partition constant that is 1000 times greater than the species of interest (which is quite plausible), then the two species would be represented at an equal level of concentration at the interface. In order to assure that the materials were as surface pure as possible, TEMPO was purified by sublimation. The surfaces of all solutions were aspirated prior to performing voltammetry. This step was found to be very important in assuring reproducibility in both qualitative and quantitative terms in voltammetry. SiO and MgF$_2$ were obtained from Balzars and used with no further purification.

2.11 Synthesis of 4-n-alkano-2',2',6,6'-tetramethyl-1-piperodinyloxy

4-n-alkano-2',2',6,6'-tetramethyl-1-piperodinyloxy free radical (C$_n$TEMPO) derivatives were synthesized as follows. 4-oxo-2',2',6,6'-tetramethylpiperidone (98% Aldrich) was purified by sublimation, then reacted overnight with C$_n$MgBr or C$_n$Li in a dry round bottom flask at –78 °C. The product was then dehydrated with 6 M sulfuric acid at 60 °C for several days, with the progress of the reaction monitored by thin layer chromatography. When the reaction was complete, the resulting mixture was neutralized with baking soda and extracted with ethyl acetate. The extract was concentrated using a rotovap, then dissolved in methanol and placed in a bomb under 50 atmospheres of H$_2$ pressure at 80 °C in the presence of a Pd/C catalyst. After several days, the hydrogenated product was oxidized in a solution containing sodium EDTA, hydrogen peroxide, sodium tungstate, methanol, and water. Final purification was done via column chromatography using a 10:1 mixture of hexanes: ethyl acetate. Excess solvent was removed by rotary evaporation, with the product being left under vacuum for several days to ensure complete removal of the solvent. For C$_6$TEMPO, calculated and found elemental analysis results were C 74.9, H 12.6, N 5.8 and C 74.9 H 12.9, N 5.8, respectively.

2.12 Fabrication of line electrodes

As cleanliness is of the utmost importance, all handling of glass slides and electrodes was done wearing powder free latex or nitrile gloves. Microline electrodes were fabricated as follows. Glass slides (Fisher) were cleaned in either hot chromic acid or hot piranha (4:1 18 M H$_2$SO$_4$:30% H$_2$O$_2$) solution. After ~15 minutes in hot acid solution, the slides were rinsed and dried thoroughly. One of two approaches was then employed to enhance gold adhesion to the glass slide. The slides could treated for 3–4 hours in a self assembly solution of 2% (v/v) 3-mercapto-propyltrichlorosilane (MPS) in 1,2 dichloroethane, followed by subsequent rinses in 1,2 dichloroethane, acetone, isopropanol, and deionized water, then baked at 105–110 °C for 10 minutes. Alternately, a thin (~7 nm) layer of chromium could be vapor deposited onto the glass slides using the same masks that would be subsequently used for gold vapor deposition (VD). Gold was placed in a tungsten boat in a bell jar, which was then evacuated to 5 x 10$^{-6}$ Torr. VD was then carried out by resistive heating of the gold, resulting in melting, then evaporation. The deposition thickness was monitored using a quartz crystal microbalance. Typical deposition thicknesses were ~100 nm.

Following gold VD, the surfaces of the electrodes and slides were rendered hydrophobic by treatment in octadecyl-mercaptan (1 hour self assembly time, saturated solution in ethanol) and octadecyltrichlorosilane (1 hour self assembly time, ~55 mL OTS in 120 mL anhydrous hexadecane), respectively. Each glass slide contained six electrodes of the shape shown in Figure 2.1. The working electrodes for use in the experiment were produced first by scribing the
back side (opposite of the side of gold deposition) of the slide in between electrodes, and breaking along the fracture line. Each electrode was then scribed with a steel pencil (on the opposite side from where the gold was deposited and fractured along the dotted line shown on the central image in Figure 2.1. A straight line for scribing was obtained by using a second glass slide as a straight edge guide. For breaking, electrode was held firmly between both hands, using the thumb and index finger to grip the electrode from the top and bottom. The index finger was placed on the same side as the deposited gold, with the glass between the second and third knuckle, and with the length of the index finger holding the electrode parallel to the scribed line. Pressure was then exerted along the length of the line by pushing down with the tip of the thumb and up with the length of the index finger in contact of glass.

The fracturing exposed fresh, hydrophilic surfaces, creating a sharp gradient of wettability, causing the electrodes to self position themselves at the air/water interface. In theory, two working electrodes were obtained from this fracturing procedure, but in practice, only the first electrode used was found to produce consistent results. This was attributed to a degradation of the quality of exposed gold over time, a phenomenon explained in greater detail in Chapter 3. For the same reason, it was expedient to use the first half as quickly as possible after breaking.

The design of the electrodes consisted of two circular areas that were connected to a band of gold with a width of 1 cm. This width was chosen to ensure that the diffusion profile at the air/water interface was characteristic of linear diffusion and not that of microband diffusion.

### 2.13 Fabrication of barrier electrodes

Two types of barrier electrodes were employed. The first type employed SU-8, an epoxy-based negative photoresist. After the VD of gold onto electrodes in the bell jar, the slides were rinsed with chloroform to remove traces of pump oil. In order to obtain 1 μm barrier films, SU-8 was spin coated at 5000 rpm on a Headway spinner. In order to obtain 100 nm barrier films, SU-8 was diluted with diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) in a 2:3 diacetone alcohol:SU-8 ratio, then spin coated at 5000 rpm. Regardless of thickness, the slides were then heated at 70 °C and the 90 °C for one minute to evaporate the solvent. The baking was followed by a 30 second exposure through a mask using a Quintel Q4000 Mask Aligner, after which the slides were again baked for one minute at 70 °C and then 90 °C to cross-link photoresist in the exposed regions. The slides were subsequently developed in diacetone alcohol to remove unexposed photoresist and baked overnight at 90 °C to create a rigid and non-permeable film.

Because SU-8 is hydrophilic, further treatment was necessary to create the hydrophobic contact region. The slides were coated with Shipley 1818 positive photoresist, and the area targeted for hydrophobic treatment was exposed and developed. The slides were then completely coated with a thin (~10 nm) layer of gold, and the excess Shipley 1818 was removed with acetone. Subsequent treatment with OM created the hydrophobic point of contact necessary to create a self-positioning electrode at the interface. Treatment with OTS was unnecessary.

The final product of this procedure may be seen in Figure 2.2.

An alternate procedure for barrier electrodes was to employ silicon monoxide as a rigid, impermeable film. In this procedure, the electrodes taken from the bell jar following CVD of gold were treated in an MPS self-assembly solution, identical to the one outlined earlier. This step was necessary in order to obtain good adhesion of SiO to the gold electrode. This strategy essentially inverts the process used to adhere gold to glass, as the goal now is to get a glassy substance to adhere to gold. Following MPS treatment, the slides were loaded into the bell jar
Figure 2.1 An illustration of the line microelectrodes used to perform 2D line cyclic voltammetry. The central image is a front view of an electrode prior to fracturing. The dotted line represents the point of fracture. On the left, one sees what the electrode looks like after fracturing and placed in contact with solution, along with some relevant dimensions. On the right is a grossly out of scale cartoon side view, demonstrating the hydrophobicity of the modified face and hydrophilicity of the cross sectional region of glass and gold exposed by the fracture.
Figure 2.2 Front view of an SU-8 barrier electrode. A thin layer of gold is coated over the SU-8 in order to create a hydrophobic point of contact with the solution after treatment with OM. The dimensions are identical to those shown in Figure 2.1. The barrier thickness could be varied from 100 nm to 1 μm.
with masks exposing only the water contacting region of the electrodes. Silicon monoxide was then coated onto the slides using vapor deposition, with the thickness monitored by a quartz crystal microbalance. Alternatively, adhesion for SiO could be improved by depositing a thin layer of chromium over the region targeted for barrier deposition. Improving adhesion with MPS was the preferred method, generally. The final step was the treatment of the electrodes with OTS. In this case, treatment with OM was unnecessary.

Attempts were also made to employ magnesium fluoride as a barrier film, but the challenge of attaining adequate adhesion to gold proved insurmountable. Or rather, it was deemed unnecessary to surmount once a satisfactory method for SiO adhesion was obtained.

2.5 Electrochemical Measurements

Electrochemical measurements were performed using either a CH Instruments 660A or 660B potentiostat with a three electrode setup under computer control. Saturated calomel and platinum were employed as the reference and working electrodes, respectively. When convenient, a copper Faraday cage was employed to minimize noise. Solution pH was adjusted to 3 using perchloric acid in order to minimize the water oxidation background at high potentials. Lithium perchlorate was also used as a supporting electrolyte at 2 mM concentration. Precise positioning of the electrode at the air/water interface was obtained through the use of a Mitutoyo 192 Precision Gauge lifter, capable of reproducing height within 0.1 mm.

2.6 Brewster Angle Microscopy

Brewster angle microscopy (BAM) measurements were performed on an active vibration isolation table (MOD-2, Halcyonics, GmbH, Göttingen, Germany). Enhanced performance of vibration isolation was found when a lead brick was placed on the front end of the table. To minimize air flow disruptions and dust contamination, the microscope was encased in a Plexiglas box in an area with a positive pressure of HEPA filtered air. The microscope (BAM2plus, Nanofilm Technologie GmbH, Göttingen, Germany) is equipped with a 50 mW Nd:YAG laser. No BAM measurements appear in this dissertation, but enough work was performed on BAM to justify its inclusion in the experimental section.

2.7 Surface Tension Measurements

Two methods were employed for surface tension measurements. The tedious, but often more effective method was to employ a DuNoüy tensiometer (model 70535, CSC Scientific Co. Inc.) The ring was a Pt/Ir alloy, and was flamed in between measurements using a methane/air flame to remove impurities.

The other method was the Rame-Hart bubble shape analysis. Air bubbles were deployed through a Teflon tip, and a camera took pictures and calculated the surface tension based off the shape of the drop.

2.8 Electron Structure Calculations

A series of calculations was performed on isolated TEMPO and small (fewer than 5 molecules) TEMPO-water clusters in order to estimate the strength of the TEMPO-water hydrogen bond. Geometries were optimized using the unrestricted Hartree-Fock (UHF) method with the standard 6-31G* basis set. No significant spin contamination was found in the UHF wave functions. Final single point energies at these optimized geometries were then evaluated, including the effect of electron correlations via unrestricted second order Møller-Plesset theory with core orbitals frozen, using the 6-31+G* basis. This level of theory, which may be denoted as UMP2(fc)/6-31+G*/UHF/6-31G* is believed to be sufficient to characterize trends in binding
energies as a function of the number of coordinated water molecules. Calculations were performed by Martin Head-Gordon and Jarrod McClean using the Q-Chem program\textsuperscript{6}.

2.9 Numerical Simulation Parameters

The finite element simulations of cyclic voltammograms were done with COMSOL Multiphysics Software (version 3.3 with the chemical engineering module) run on a Dell Precision workstation 650 using a 2.8 GHz Xenon processor and 2 GB RAM (OS, Red Hat, Linux 8.0). The weak form of the “Transport and Adsorption” model was employed. Simulation domain dimensions of $x_{\text{min}}$, $x_{\text{max}}$, and $y_{\text{min}}$ were set to $x_{\text{min}} = y_{\text{min}} = 6\sqrt{D_{\text{sol}}t_{\text{end}}}$ and $x_{\text{max}} = 6\sqrt{D_{\text{surf}}t_{\text{end}}}$ where $D_{\text{sol}}$ and $D_{\text{surf}}$ are the TEMPO diffusion coefficient in the bulk solution and its maximum expected value at the water surface, respectively; $t_{\text{end}}$ is the duration of the voltammetric scan. A mesh made of unstructured triangles was generated using the default mesh settings and refined in the region near the microband\textsuperscript{7}. More complete simulation details are given in Appendix 1.

Simulations not requiring the modeling of adsorption and desorption phenomena were modeled using the DigiSim package (model 3.03aCV, Bioanalytical Systems, Inc., West Lafayette, Indiana).
1. Malec, A. Lateral Diffusion of Amphiphiles Probed by 2D Electrochemical and ESR Methods. UC Berkeley, Berkeley, 2006: It is worth noting that the SiO used for vapor deposition had been sitting in the lab for 25 years. No attempt to deposit newly purchased SiO was made.


Chapter 3: Gibbs Monolayers at the Air/Water Interface: Determination of Lateral Mobility Using 2D Line Voltammetry

3.1 Justification of TEMPO as probe

The selection of the proper probe is of the utmost importance in these experiments. As discussed in the introduction, the probe must not immerse any deeper than the 10:90 region. This is the first essential requirement. Fortunately, MD simulations suggest that the polar group of amphiphiles adsorbed at the air/water interface do not immerse any deeper than the head group\(^1\)\(^-\)\(^3\). This trend should hold especially well with TEMPO, where the polar fragment is heavily shielded by the methyl groups on the adjacent carbons, as can be seen in Figure 3.1.

Another important consideration is the interactions between probe molecules\(^4\),\(^5\). As noted in the introduction, surface monolayers can exist in a number of phases. In order for our results to be interpretable as a representation of the viscosity of the air/water interface, we need to be sure that probe-probe interactions are negligible. For Langmuir monolayers, this assumption holds in the gaseous phase. The same holds for Gibbs monolayers. Additionally for Gibbs monolayers, this assumption holds when the system can be modeled using the Langmuir isotherm. Indeed, one of the fundamental assumptions of the Langmuir isotherm is that interactions between adsorbed species may be neglected. As discussed below, the adsorption isotherms obtained for TEMPO, which forms Gibbs monolayers, can be fit well using the Langmuir-Szyszkowski equation\(^6\).

Satisfied that TEMPO meets these criteria, we found it of interest to quantify the strength of hydrogen bond that may form between TEMPO and water. Ab initio calculations performed by Head-Gordon indicated the strength of the TEMPO-water hydrogen bond to be 8.682 kcal/mol, about 30% stronger than the hydrogen bond found in clusters of two water molecules\(^7\). This value was obtained for TEMPO in the chair conformation. An interesting result found later by McClean gave a slightly more favorable interaction when the piperidine ring was not fully in the chair conformation, calculating the energy to be 8.968 kcal/mol, as seen in Figure 3.2. Apparently the energetic loss due to steric forces within the molecule is more than compensated for by creating greater exposure for the oxygen to allow hydrogen bonding.

Despite the fact that TEMPO-water clusters are lower in energy than water-water clusters, interactions between TEMPO and two water molecules are not as energetically favorable as those between three water molecules. This is because the heavily shielded nature of the polar fragment does not allow it to participate in the network structure formed by large clusters of water molecules. These calculations further suggest that TEMPO/water interactions at the interface are limited entirely to the polar fragment and that TEMPO diffuses at the interface largely unimmersed. It is also possible to hypothesize that TEMPO diffuses hydrogen bound to one water molecule. If this is the case, it is entirely possible that the lateral diffusion coefficient of TEMPO is equal to the lateral diffusion coefficient of water in the 10:90 region.

Having established that TEMPO behaves as ideally for the purposes of this project as we expect any probe to behave, it is worth taking a minute to discuss its “probe-able” features. As a free radical, TEMPO and its derivatives can be studied with ESR to obtain the microscopic lateral diffusion coefficient. As noted in the introduction, experiments with this objective in mind have been performed, with some degree of success.

In addition to its ability to be studied via ESR, TEMPO exhibits reversible and kinetically facile\(^8\),\(^9\) electroactivity, being oxidized to the oxonium cation (TEMPO\(^+\)), as illustrated in
Figure 3.1 A space filling model of TEMPO. The polar fragment is heavily shielded by the methyl groups on the adjacent carbons, minimizing the depth of immersion.
Figure 3.2 Standard chair conformation (top) and twist chair conformation (bottom) for TEMPO. The top conformation is more stable, but the bottom conformation allows for more favorable interactions with water molecules.
Scheme 3.1. Although stable as a radical due to its lack of α-hydrogens, TEMPO does undergo disproportionation at low pH. The rate of disproportionation becomes significant as the pH approaches 1. My research indicated the redox potential of TEMPO to be 0.49 ± .01 V vs. SCE. Experiments performed with a 10 µm diameter gold microdisk electrode indicated the bulk diffusion constant to be $7.7 \times 10^{-6} \pm 0.35 \text{ cm}^2/\text{s}$. 

### 3.2 Physical Properties of TEMPO

The next order of business is to determine the partition constant. Both the ring method and bubble shape analysis are applicable approaches for this measurement. Ring tensiometry has the disadvantage of being tedious, but easier to operate. Bubble shape analysis can be a finicky method. When it works, it works well, but when it doesn’t, you can fight with the instrument all day and not be any closer to having an isotherm than you were in the morning. One concern that I always had with the ring tensiometer is that the surface being measured is exposed to the air. This creates the possibility for impurities to adsorb from the air, as well as for volatile surfactants to evaporate. Because bubble shape analysis introduces a cavity inside the solution, these concerns are minimized and the results obtained from drop shape analysis were used in preference to those from ring tensiometry. The partition constant was found to be 320 M$^{-1}$ using drop shape analysis and 240 M$^{-1}$ using ring tensiometry. The data obtained from the two methods may be compared in Figure 3.3.

Early experiments gave rise to the concern that TEMPO might partition differently in the presence of electrolyte. Experiments performed on the drop shape analysis instrument confirmed the suspicion. TEMPO was found to have a partition constant of $380 \pm 30$ M$^{-1}$ in 2 mM LiClO$_4$ and 1 mM HClO$_4$, which are the conditions typically used in these experiments. This is the value that will be used in simulations to fit the experimentally obtained voltammograms. The maximum surface concentration was found to be 51 Å$^2$/molecule, corresponding to the surface area occupied by one TEMPO molecule on the surface.

These results also have their own intrinsic value, as an understanding of the dynamics of bulk/surface partitioning (in addition to the lateral mobility sought in this study), is essential for the characterization of emulsions and foams. It is claimed that this understanding even shines light on a number of other significant phenomena, perhaps most notably those that take place in the atmosphere.

### 3.3 Experimental Parameter Optimization

In order to minimize voltage losses due to resistance, it is necessary to use an electrolyte. It was also found helpful to maintain the solution at a slightly acidic pH in order to reduce the background signal from water oxidation at high potentials. Because TEMPO is a neutral molecule, migration is not a large concern. The quality and quantity of supporting electrolyte is not a trivial matter, for a variety of reasons. Salts containing chloride are not a possibility, due to the high potentials scanned on a gold electrode—this would lead to the degradation of the electrode. Ultimately LiClO$_4$ and HClO$_4$ were chosen to serve as the electrolytic system.
Figure 3.3 Langmuir-Szyszkowski plots of data obtained with drop shape analysis (upper set, closed circles) vs. ring tensiometer (lower set, open circles). The measurements were taken on same solutions on same day. The partition constant, $K$, is $240 \text{ M}^{-1}$ for the ring tensiometer method, and $320 \text{ M}^{-1}$ for the ring tensiometer.
Scheme 3.1 The reversible oxidation of TEMPO to the TEMPO oxonium cation (TEMPO+).
Unfortunately, even 99.99% LiClO₄ proved to be of insufficient purity. Ring tensiometry measurements confirmed the presence of surface active impurities in the electrolyte. In order to determine whether or not these surface active impurities formed Langmuir or Gibbs monolayers, I performed experiments using the Langmuir trough. After the balance was zeroed, the barriers were compressed and the system was aspirated. This was repeated until there was no residual surface pressure. Then a solution containing 100 mL of 50 mM LiClO₄ was added to the trough (which contains a volume of about one liter) and compressed. The surface pressure was found to be 0.34 mN/m, compared to 0.17 mN/m for the control experiment of adding 18 mΩ water with no added electrolyte. Though generally useful, recrystallization proved to be an impractical approach for removing these impurities, mostly because nobody in the lab seemed to be any good at it. In order to minimize the introduction of these impurities, the concentration of electrolyte was set to be just one order of magnitude above the TEMPO concentration. Even so, there were still some residual effects from the trace impurities.

The residual effect of trace impurities were ultimately removed by aspirating the system prior to making electrochemical measurements. Aspiration had a marked impact on both signal quality and magnitude, as can be seen in Figure 3.4. A suitable procedure for aspiration was as follows: about 100 mL of solution was added to a Teflon trough. The solution was then aspirated thoroughly over the entire surface. This aspiration typically caused the solution level to decrease about 1–3%.

After a thorough aspiration, the trough was covered with a glass cover designed for this system. The cover was necessary to reduce noise from external air currents. The cover had holes in it for the introduction of the working, reference, and counter electrodes. The system was allowed to equilibrate for about 5 minutes, to ensure that TEMPO was able to reach its equilibrium concentration on the surface, and also to allow any other residual impurities to adsorb at the interface, even though I was pretty sure there weren’t any left to worry about. I then aspirated through the hole designed for the introduction of the working electrode, just to be extra sure there were no surface active impurities there. Repeated aspiration between experiments was not found to have an impact on experimental measurements, but I liked to do it every hour or so just to be sure.

3.4 Electrode Signal Decay

3.4.1 Observations on Signal Decay

I spent a lot of my time on this project trying to understand and account for the phenomenon that will be treated for the remainder of the chapter: signal decay of the line electrode voltammogram. A typical result is shown in Figure 3.5. It can be noted that the second peak is about 85% of the first, and the third peak is 90% of the second. Degradation of the signal was not just quantitative, as the shape of the CV changed as the scans progressed. The peak potential shifted to more positive values, and the ratio of the peak current to current at the switching potential approached one. In a number of cases, the switching potential was also the peak potential. Attempts to model the decay using simulations proved unsuccessful.

The following observations were made about the decay of the peak TEMPO signal. Notably, the signal obtained from the 2nd half of a line electrode did not produce signals of the same quality as the half of the line electrode that was used immediately after breaking. Attempts to store the 2nd half of the line electrode in an oxygen free environment proved ineffective at preserving the quality of the 2nd half. These attempts included placing the 2nd half into 18
Figure 3.4 This figure demonstrates the effect of aspiration. Scan 1 was first obtained, then the system was through aspirated and scan E2 was obtained. The solution was then removed completely from the cell and replaced with another sample from the same stock solution. Scan 3 was then obtained, followed by a through system aspiration and obtaining scan 4. All scans were performed at 20 mV/s on a 0.1080 mM TEMPO solution.
Figure 3.5 A typical experiment showing three consecutive cycles recorded with one electrode. The peak current value decays monotonically from scan to scan. The peak current in the second scan has decayed to 85% of the first scan peak value, and the third scan has a peak current that is about 80% of the original peak current. Note that the form of the voltammogram changes, becoming more sigmoidal in shape. These scans were performed at 20 mV/s on a 0.0992 mM TEMPO solution.
Figure 3.6 These two voltammograms are the averages obtained from: 1. The second scan obtained on a solution of TEMPO (2\textsuperscript{nd} scan) and 2. The first scan obtained after touching the electrode to solution and waiting 45 seconds (the duration of a full cycle at 20 mV/s) before starting the scan (45 s wait). These scans were performed at 20 mV/s on a 0.1000 mM TEMPO solution.
Figure 3.7  Eight scans obtained over a fifteen minute interval on a single electrode. The electrode was placed in contact with solution and allowed to sit for five minutes prior to performing any voltammetric scans. Among the scans shown here, the seventh scan performed exhibited the greatest current, while the fourth scan exhibited the least, indicating that the variation in current is due to random fluctuations and not any systematic change in signal amplitude over time. These scans were all performed at 20 mV/s on a 0.1060 mM TEMPO solution.
OMΩ water, in a small chamber ventilated with house nitrogen, and a chamber ventilated with an argon tank. Signal decay was dependent primarily on the amount of time an electrode had been in contact with solution, and not on the number of scans performed, as can be seen in Figure 3.6. As can be seen in Figure 3.7, decay was typically complete in about 5 minutes. No treatment was found to restore electrodes to their virgin state. Copper under-potential deposition (UPD) experiments, which provide information about the molecular surface area of the microband, exhibit no decay, indicating that the exposed microband retains its electrochemical activity.

This type of decay has no basis in theory. Simulations predict that repeated cycling will result in the second voltammogram having a peak current that is ~90% of the first scan due to depletion of the analyte in the vicinity of the electrode. Further scans result in a quasi-steady state, displaying virtually no decrease in signal with repeated cycling. Furthermore, the scans should maintain the same qualitative features. The nature of signal degradation is consistent with characteristics observed when resistance increases, as well as when segments of an electrode become deactivated. The fact that UPD experiments exhibit no decay, and that the signal reaches a minimum that corresponds roughly with the expected bulk signal, imply that the decay mechanism is one that erodes the integrity (or perhaps even the existence) of the electrochemical activity at the triple phase line.

3.4.2 Hypotheses for Decay Mechanisms

Various hypotheses were proposed as a mechanism for signal decay. I shall list them, then treat them in the order listed. Possible mechanisms include: 1.) Degradation of the thiol monolayer in such a manner as to block current at the triple phase line; 2.) Oxidation of gold surface; 3.) Adsorption of TEMPO to the electrode and/or thiol monolayer; 4.) and adsorption of amphiphilic impurities leading to a rise in the meniscus and the disappearance of an electrochemically active triple phase line.

3.4.2.1 Variation of the Self-Assembled Monolayer

The hypothesis that the degradation of the self-assembled OM monolayer could be responsible for decay led to a systematic study of the effect of the length of the alkane chain on electrode performance. The results can be summed briefly: only octadecyl mercaptan was found to yield reproducible results consistent with theory. Shorter chains did not exhibit sufficient hydrophobicity, and were not held tightly enough by dispersion forces to remain adhered to gold when the potential was scanned to high voltages. A meniscus that rose from scan to scan was observed whenever chains shorter than fourteen carbons were used. I would have tried a chain longer than 18 carbons if Aldrich offered one, but they don’t.

An especially notable failure was the use of perfluorononanethiol. Fluorinated compounds are noted for exhibiting both hydrophobic and lipophobic character. This is commonly attributed to a low polarizability of the molecule. Whatever the reason is, voltammograms obtained with monolayers of perfluorononanethiol were of especially poor quality.

Interesting results were obtained with tert-tetradecyl alkane thiol (tC14SH). The bottle obtained from Aldrich was a mixture of alkyl thiols, but all containing fourteen carbons with the thiol group attached to a tertiary carbon. Initial work with tC14SH showed remarkable stability, reproducing the same current quantitatively and qualitatively after a large number of scans. Unfortunately, these results proved to be irreproducible, and later tC14SH monolayers exhibited decay greater than or equal to that seen on electrodes made with OM. I tried very hard to get tC14SH to work, and assembled the monolayer under a variety of conditions. None of them proved successful.
Ultimately, it was conclusively demonstrated that the thiol monolayer was not responsible for signal degradation. Normally, the glass was rendered hydrophobic by treatment with OTS in a dry atmosphere. This was typically done after OM treatment, but this order was not imperative. Contact angle measurements indicated that when the self-assembly was performed under dry conditions, OTS formed monolayers only on glass. It was possible to render the gold surface hydrophobic by treating the electrodes with OTS in a humid environment. Decay was still observed in the absence of any thiol monolayer over the gold.

This raised the possibility of OTS being responsible for electrode decay. In order to control this factor, a batch of electrodes was made by first treating the glass with OTS, then depositing gold over the OTS, thereby ensuring that only OM was coated over gold. The signal obtained from these electrodes decayed over time, too.

### 3.4.2.2 Gold Oxidation

The next hypothesis to treat is that of gold oxidation. Under this hypothesis, oxygen in the air and/or dissolved in solution cause various parts of the electrode to become electrochemically inactive, effectively reducing the line length. This hypothesis has the merit of providing an explanation for the appearance of resistive effect in the voltammograms, as well as the degradation of the electrode in air, but falls short in almost every other measurable way. Under this hypothesis, slow scan rates would provide superior results to fast scan rates because slow scan rates allow for a thicker diffusion layer to form, thereby “averaging out” the inactive parts of the electrode and giving the appearance of a uniformly active line. This is not observed. Furthermore, this effect is not generally observed with other applications of gold electrodes at air/water interfaces, notably the horizontal touch method, and even more notably, in SU-8 barrier electrodes described in the methods section as well as in the following chapter.

Removing oxygen from the system by deaerating the solution and maintaining a nitrogen atmosphere on the electrodes resulted in accelerated decay of the peak current, seen in Table 3.1. Finally, if gold oxidation were the problem, it should be possible to restore the electrode to a virgin state by scanning to reducing potentials, a phenomenon which is not observed.

### 3.4.2.3 TEMPO Adsorption at the Electrode

The next hypothesis to treat is that of the adsorption of TEMPO at the line electrode. This hypothesis predicts that higher concentrations of TEMPO should produce higher decay rates. The fact that decay occurs on line electrodes that simply sit exposed to air for one minute should be enough to indicate that this is not likely the primary source of decay. Nonetheless, it is worth taking the time to investigate every possibility, just to be sure. Solutions made of varying concentrations of TEMPO, up to one order of magnitude greater than the typical working concentration, all gave similar decay rates to solutions of TEMPO under the standard working conditions of 0.1 mM concentration. Therefore, it seems reasonable to discard this hypothesis.

### 3.4.2.4 Meniscus Rise Due to Amphiphilic Impurities

The final hypothesis mentioned will receive the most thorough treatment. Again, this hypothesis is that amphiphilic impurities, either in water or from electrolyte, absorb at the face of the electrode, causing the meniscus to rise and eliminate the triple phase line. This hypothesis is not without merit. For example, it explains why no decay is seen when line electrodes are used to measure solutions containing no surface active components. Unfortunately, this hypothesis does not explain a wide variety of observed phenomena governing decay.

One observation that is not explained by this hypothesis is the degradation of electrodes sitting in air. It seems implausible that such amphiphilic compounds would be found to any substantial extent in air. The ineffectiveness of experiments designed to eliminate or reduce this
<table>
<thead>
<tr>
<th>Condition</th>
<th>Percent decay</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mM LiClO₄</td>
<td>24</td>
<td>6</td>
</tr>
<tr>
<td>50 mM KClO₄</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>10 mM KClO₄</td>
<td>22</td>
<td>4</td>
</tr>
<tr>
<td>5 mM KClO₄</td>
<td>19</td>
<td>3</td>
</tr>
<tr>
<td>1 mM KClO₄</td>
<td>22</td>
<td>7</td>
</tr>
<tr>
<td>0.5 mM KClO₄</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>0.1 mM KClO₄</td>
<td>19</td>
<td>2</td>
</tr>
<tr>
<td>0.03 mM KClO₄</td>
<td>23</td>
<td>10</td>
</tr>
<tr>
<td>1 mM H₂SO₄</td>
<td>17</td>
<td>4</td>
</tr>
<tr>
<td>1 mM TEMPO</td>
<td>24</td>
<td>5</td>
</tr>
<tr>
<td>0.5 mM TEMPO</td>
<td>21</td>
<td>5</td>
</tr>
<tr>
<td>Nitrogen stream</td>
<td>35</td>
<td>4</td>
</tr>
</tbody>
</table>

**Table 3.1** In order to pinpoint a cause for the decay, a number of system parameters were varied. Presented in this table are results obtained from varying 1) the electrolyte used; 2) the concentration of electrolyte; 3) the concentration of TEMPO; and 4) with nitrogen blowing into the electrochemical cell. The baseline conditions are using 50 mM LiClO₄ and 1 mM HClO₄ with a 0.100 mM TEMPO solution. In other words, what ever condition is not explicitly varied in the table has the value given in the preceding sentence. All scans were performed at 20 mV/s.

The first column indicates the parameter that was varied. The second column gives the percent decrease of the peak current from the first to the second scan, with the third column representing the 95% confidence interval for the value of the decay.
Figure 3.8 Plots showing peak potential, peak current, and decay as a function of varying electrolyte concentration. It seems clear that the only graph with a justifiable trend is the plot of peak potential. The increasing value of peak potential is attributed to decreasing solution conductivity. All scans were performed at 20 mV/s on 0.1000 mM TEMPO solutions.
mechanism of decay also indicate (to me, at least) that this is not the mechanism governing signal degradation.

The first significant effort to understand and hopefully control this phenomenon was to vary the electrolyte, in the hopes that we could find a purer electrolyte that did not contain a significant number of trace contaminants. Three electrolyte systems were chosen for study: recrystallized KClO$_4$, H$_2$SO$_4$, and LiClO$_4$. The results are summarized in Table 3.1. The only statistically significant increase in decay rate came when a nitrogen atmosphere was maintained in the cell, as described above. As a side note, scans performed with sulfuric acid as the supporting electrolyte differed both qualitatively and quantitatively in ways that we were unable to predict with theory. For that reason, sulfuric acid was discontinued as a system for study.

Although the statistical significance in the difference of the rate of decay between systems of LiClO$_4$ and KClO$_4$ was low, the better performance of KClO$_4$ systems induced a more systematic investigation of the effect of perchlorate concentration. The results are summarized in Figure 3.8. As the data show, there is no discernable effect of electrolyte concentration on the decay rate or peak current. There is a clear trend of increasing peak potential with decreasing electrolyte, attributable to increasing solution resistance. After this set of experiments, our recrystallized KClO$_4$ supply (which was obtained from another lab, as no one in our lab could recrystallize effectively) ran out, and so the electrolyte used from then on was LiClO$_4$. To minimize the impact of impurities in the electrolyte while also keeping the conductance high, 2 mM solutions of LiClO$_4$ were employed from this point on.

Because nothing from the electrolyte experiments could be used to refute or confirm the meniscus rise hypothesis, other approaches were necessary to explore the idea further. One significant effort to eliminate this effect was the roughening of the gold surface. It is well known that roughened surfaces exhibit a greater degree of hydrophobicity than smooth surfaces$^{18, 19}$. If the problem is caused by the rise of the meniscus, then increasing the water/gold contact angle should prevent the disappearance of the electrochemically active triple phase line.

A variety of techniques were employed to roughen gold, including oxidizing gold electrodes then reducing the gold from solution back onto the electrode, “polishing” the gold with fine sandpaper, and using a hydrofluoric acid based etching cream to roughen the glass side prior to gold deposition. The first method generally resulted in a lovely pink solution of gold nanoparticles and non-functioning electrodes. The second method generally resulted in scratching off substantial parts of the electrode. The third method proved highly successful at roughening the gold surface and increasing the gold/water contact angle from its typical value of ~110° to ~135-140°. Roughened gold electrodes exhibited nearly identical current decay characteristics of non-roughened electrodes.

Despite these results, the meniscus rise hypothesis was still not discarded. Although attempts to eliminate the effect had proved futile, the possibility of accelerating the affect was then probed. Specifically, various experiments were carried out that introduced amphiphilic impurities into the system to measure their impact. The first such experiment simply consisted of spreading a monolayer of 1-octanol over the surface and measuring the resultant current. This had the surprising result of completely eliminating all electrochemical signal whatsoever. This was a surprise because previous experiments have successfully measured the bulk current when a monolayer of stearic acid was spread over the surface$^6$, and it was anticipated that 1-octanol would only impact the surface current.

Undaunted, I pressed on with other ways of introducing 1-octanol into the system. Using the ring tensiometer, I measured the partition constant of 1-octanol to be 530 ± 50 M$^{-1}$, and then
made a solution containing TEMPO and 1-octanol at concentrations that corresponded to equal surface concentrations for both species, with both being at 5% of a monolayer. The signals obtained from these solutions decayed at exactly the same rate as the runs performed under all the conditions listed heretofore in this dissertation, although they did start with a peak current that was 80% of the value obtained for identical solutions not containing 1-octanol. This can be attributed to the increased viscosity of the air/water interface due to the increased concentration of surface species, an effect demonstrated by Johnson et al.

To give this hypothesis all the possibilities to succeed that it could, experiments were then designed to incorporate amphiphiles directly into the self assembled monolayer as much as possible. Two different techniques were used to introduce amphiphiles into the monolayer. In the first technique, chloroform solutions were made containing alcohols with long carbon chains. The length of the chain was varied from eight to fourteen carbons. Drops from this solution were then deposited onto electrodes, and the chloroform was allowed to evaporate. This had no discernable impact on the decay rate. The other technique was to introduce the amphiphiles in the thiol self-assembly process to give them the maximum opportunity to integrate themselves into the monolayer. The contact angle of water on the gold of electrodes treated in this fashion was identical to those treated with pure octadecyl-mercaptan, and there was no difference in the decay rate for electrodes treated in this fashion. In light of the information provided by the experiments in this section, I feel confident in considering this hypothesis discredited. I acknowledge that my research advisor does not share this conclusion with me.

3.4.2.5 Summary and Directions for Future Study

The phenomenon of signal decay was and remains the most frustrating part of my graduate career. All proposed hypotheses have been discredited, and I have no others. I spent at least a year and a half working on this problem, and although I have successfully ruled out all the hypotheses enumerated in this dissertation, I do not have any new hypotheses to test.

Still, in light of what has been learned, it seems reasonable to assert that the phenomenon of decay is related to degradation of signal at the triple phase line, resulting in a shortening of the electrochemically active portion and eventually in its elimination. The presence of signal decay does not render the experimental results completely worthless, however. The relevant question to ask is in what ways the decay can be compensated for. Three main options exist for handling the decay seen in the signal:

1. Take multiple scans with the same electrode and try to fit the decay to a first order reaction, then project the peak current at “zero exposure time.”
2. Perform the scans at as fast a scan rate as possible to minimize the amount of time the electrode is exposed to solution before the peak current is reached.
3. Ignore the results from these scans and develop a new geometry that doesn’t exhibit electrode signal decay. This approach is the subject of chapter four, and will be treated fully there.

All three of these approaches were employed, and I’ll now discuss their relative merits. The extrapolated currents obtained fitting the decay to a first order process give about 105 nA currents at time equal to zero. Fitting these currents yields surface lateral diffusion constants that are physically unrealistic, on the order of $10^{-3}$ cm$^2$/s. The basis for labeling this value as physically unrealistic is because it would require treating TEMPO as though it had no interaction with water, and behaved as a two-dimensional gas, in accordance with the Enskog theory of dense gasses. The peak value of 105 nA is also inconsistent with other measurements made on the system, including. Although a first order model for decay appears to fit the data well, no
Peak Currents (nA)

<table>
<thead>
<tr>
<th></th>
<th>simulated</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mV/s</td>
<td>76</td>
<td>84.2</td>
</tr>
<tr>
<td>20 mV/s</td>
<td>67</td>
<td>67.3</td>
</tr>
<tr>
<td>10 mV/s</td>
<td>61</td>
<td>56.5</td>
</tr>
</tbody>
</table>

_**Table 3.2**_ This table illustrates the effect of scan rate on peak current, as well as the signal decay. The simulated values were obtained by fitting voltammograms obtained from 20 mV/s scans in the COMSOL numerical simulation program. The values obtained for $k_{\text{des}}$ and $D_{\text{surf}}$ were then used to carry out simulations at 10 mV/s and 50 mV/s, all with 0.100 mM TEMPO. It is for this reason that the simulated and experimental values for 20 mV/s are in such good agreement, and not because 20 mV/s represents the ideal scan rate.

As can be seen, the simulated current at 50 mV/s is lower than experimental value, while the simulated current for a 10 mV/s scan is greater. This is attributed to decay of the electrochemical signal at the triple phase line. The peak potential is reached in less than 9 seconds for a 50 mV/s scan, in 22 seconds for a 20 mV/s scan, and in 44 seconds for a 10 mV/s scan. For this reason, faster scan rates are preferred.
more than three consecutive scans were measured for this approach, and it’s easy to get a nice fit when you don’t have a lot of data points. Furthermore, there is no theoretical justification for assuming a first order decay rate, because we don’t know what is even causing the decay. This approach was abandoned shortly after the initial application yielded physically unrealistic results. Nevertheless, it would be interesting to see if the peak current extrapolated at “zero time” is consistent when scan rates are varied, as well as to take more than three consecutive voltammograms and see if a first order model still fits well.

The second approach was utilized to a substantial extent. The scan rate was switched from the traditional 20 mV/s to 50 mV/s in light of the experimental results summarized in Table 3.2. The predicted values were obtained by fitting the results obtained from 20 mV/s scans to the numerical simulations described below, then adjusting the scan rate in the numerical simulator to 50 and 10 mV/s. It is for this reason that the predicted and measured currents match for 20 mV/s. As can be seen, scanning at 50 mV/s gave higher current than anticipated, and scanning at 10 mV/s gave lower current than anticipated. This is explained in terms of signal decay: the faster the scan, the less time the electrode spends in contact with solution before the peak is reached. The scan rate was not brought above 50 mV/s due to physical limitations imposed by the system. The method used to analyze these data is treated in the following section. The lack of understanding of the decay mechanism means that these results must be treated with caution, and cannot be confidently cited as evidence for the value of the lateral diffusion coefficient.

Given that the decay introduces a systematically low bias, the results obtained by fitting these data can perhaps be treated as a lower bound value—presumably the lateral diffusion constant is at least as great as the value needed to fit these curves.

3.5 Theoretical Description and Results

In our system, as is typical of electrochemical systems, the current at the electrode is determined by the flux of the redox species at the electrode. Figure 3.9 illustrates a side view diagram of the electrode in contact with solution. Mass transport to the electrode in the solution is governed by Fick’s second law:

\[
\frac{\partial C(x, y, t)}{\partial t} = D_{\text{sol}} \left( \frac{\partial^2 C(x, y, t)}{\partial x^2} + \frac{\partial^2 C(x, y, t)}{\partial y^2} \right)
\]  

(3.1)

where the concentration is expressed as a function of \(x, y,\) and \(t,\) with \(D_{\text{sol}}\) being the diffusion constant of TEMPO in the bulk phase. This equation describes flux at \(y = 0\) and \(0 < x < w.\) Mass transport at the interface is described by Fick’s second law adjusted for two dimensions and modified by additional terms for the adsorption and desorption of TEMPO\(^{11} \).

\[
\frac{\partial \Gamma(x, t)}{\partial t} = D_{\text{surf}} \frac{\partial^2 \Gamma(x, t)}{\partial x^2} + k_{\text{ads}} \Gamma_\phi(x, t)C(x, t) - k_{\text{des}} \Gamma(x, t)
\]  

(3.2)

where \(D_{\text{surf}}\) is the lateral diffusion coefficient for TEMPO, \(k_{\text{ads}}\) and \(k_{\text{des}}\) are the adsorption and desorption rate constants, and \(\Gamma_\phi\) expresses the number of free surface sites available for adsorption. Similar expressions govern the mass transport of the oxonium cation generated from the redox reaction. The equations were solved with the typical assumptions of semi-infinite diffusion boundary conditions. Briefly, the assumptions are as follows. Denoting the concentrations of TEMPO and TEMPO+ with the subscripts \(T\) and \(T+,\) respectively, we have for time equal to zero:

\[
C_T(x, y, 0) = C_{\text{init}}, \text{ for } -\infty < x < \infty, \text{ and } -\infty < y < 0
\]

\[
C_{T^+}(x, y, 0) = 0, \text{ for } -\infty < x < \infty, \text{ and } -\infty < y < 0
\]

54
\[
\Gamma_t(x,0,0) = \Gamma_{\text{init}}, \text{ for } w \leq x < \infty
\]
\[
\Gamma_{T+}(x,0,0) = \Gamma_{\text{init}}, \text{ for } w \leq x < \infty
\]

For time greater than zero, the governing assumptions are
\[
\frac{C_{T+}(x,y,t)}{C_t(x,y,t)} = \exp \left[ \frac{F}{RT} (E - E^0) \right] \text{ for } 0 < x < w
\]
\[
\frac{\Gamma_{T+}(x,t)}{\Gamma_t(x,t)} = \exp \left[ \frac{F}{RT} (E - E^0) \right] \text{ for } x = w
\]

These are coupled with the semi-infinite condition that at all times
\[
\lim_{x \to \infty, y \to \infty} C_t(x,y,t) = C_{\text{init}}
\]
\[
\lim_{x \to \infty} \Gamma_t(x,t) = \Gamma_{\text{init}}
\]

Equations 3.3 assume rapid kinetics of electron exchange at the electrode, with equations 3.4 asserting that the solution far from the electrode is unperturbed by the experiment \(^{23}\).

Finally, setting the length of the electrode as \(l\) and denoting Faraday’s number with the usual letter \(F\), the surface (\(i_{\text{surf}}\)) and bulk (\(i_{\text{sol}}\)) contributions to the current can be expressed with the following equations:
\[
i_{\text{surf}} = FID_{\text{surf}} \left[ \frac{\partial \Gamma_t(x,t)}{\partial y} \right]_{x=w}
\]
\[
i_{\text{sol}} = FID_{\text{sol}} \int_0^w \left[ \frac{\partial C_t(x,y,t)}{\partial y} \right]_{y=0} dx
\]

With this set of governing equations, the total current is a function of two unknown parameters: \(D_{\text{surf}}\) and \(k_{\text{des}}\), as all other relevant experimental parameters can be independently determined. I’ll repeat those values again, just to bring them all together. For our measurements, \(D_{\text{sol}} = 7.7 \times 10^{-6}\) cm\(^2\)/s, \(w = 100\) nm, \(l = 1\) cm, scan rate \(\nu = 50\) mV/s, \(K = 380\) M\(^{-1}\), and \(\Gamma_{\text{max}} = 3.2 \times 10^{-10}\) mol/cm\(^2\). Typical working concentrations for TEMPO solutions were 0.1 mM, corresponding to 3.6% of a monolayer coverage, which give 1400 Å\(^2\)/molecule, plenty of room for them to diffuse without bumping into each other much. The surface pressure given by the Langmuir-Szyszkowski equation is 0.3 mN/m, which is approximately a 0.4% decrease in the surface tension of water. Under these conditions, we assert that the lateral diffusion of TEMPO molecules will be unaffected by the presence of other TEMPO molecules, and that surface pressure gradients will be negligible, eliminating concerns of Marongoni flow.

As noted at the beginning of the previous paragraph, we have two unknown and independent parameters, \(D_{\text{surf}}\) and \(k_{\text{des}}\). The whole point of this research is to figure out \(D_{\text{surf}}\), but to do so, it is necessary to determine \(k_{\text{des}}\). It is not unreasonable to assume a desorption rate constant on the order of \(10^2\) s\(^{-1}\). For comparison, the desorption rate constants for the following surfactants have been reported in the literature: decanol, 220 s\(^{-1}\);\(^{24}\) pentanol, 115 s\(^{-1}\);\(^{25}\) heptanol 110 s\(^{-1}\).\(^{25}\) Abbot and coworkers have reported a desorption rate constant of 45 s\(^{-1}\) for decanol using MD simulations\(^{26}\).

As it turns out, desorption rate constants greater than 1 s\(^{-1}\) have a significant impact on the time scale of our experiments. Glandut and coworkers demonstrated that for \(k_{\text{des}}\) less than 1 s\(^{-1}\), the bulk and surface contributions to the current can be treated as independent of each other\(^{21}\). This was done by comparing the bulk and surface currents obtained via numerical simulation in the COMSOL program with those obtained by simulating the two components
separately in DigiSim, a commercially available package created to model electrochemical processes. DigiSim is not powerful enough to include perturbations from partitioning between bulk and interfacial species. Excellent agreement was obtained when comparing results from DigiSim to those obtained by COMSOL when $k_{\text{des}}$ was set at 0.01 s$^{-1}$.

However, as $k_{\text{des}}$ increases, there begins to be interchange between the bulk and the surface species. As the surface species is depleted by oxidation, material from the bulk partitions to the interface, thereby enhancing the surface contribution to the total current. The effect on the return sweep is especially interesting. TEMPO+ is able to completely desorb from the interface, and so the surface component of the voltammogram has no cathodic component. The easiest way to represent the impact of these physical constants is by looking at the voltammograms and concentration profiles obtained by varying the systems parameters. Figure 3.10 contains a demonstration of the impact that varying $k_{\text{des}}$ and $D_{\text{surf}}$ have, both independently and in conjunction with each other. It is noteworthy that identical peak currents can be obtained for $D_{\text{surf}}$ values that range over orders of magnitude by varying the value of $k_{\text{des}}$ as well. Figure 3.11 shows the impact of $k_{\text{des}}$ on the concentration profile. When $k_{\text{des}}$ is low, depletion in the bulk has hemicylindrical symmetry about the microband. For high values of $k_{\text{des}}$, the symmetry is distorted by enhanced depletion on the side of the microline as material from the bulk adsorbs onto the interface to replace the oxidized TEMPO species.

In light of the previously mentioned points, it is not possible to determine $D_{\text{surf}}$ from the measurements made at line electrodes. In the first place, the decay renders uncertain the value obtained for the peak current. Even without concerns of electrode signal decay, the best that can be done is to create a calibration plot, where $D_{\text{surf}}$ is obtained as a function of $k_{\text{des}}$. On this curve lie the number $D_{\text{surf}}$ and $k_{\text{des}}$ couples that provide the experimentally measured current. The calibration plot obtained for microline electrodes is shown in Figure 3.13 and a comparison between simulated and experimental voltammograms is shown in Figure 3.12. It bears noting that the fit for the anodic sweep is excellent, but the fit for the cathodic sweep is fair. This may be due to inaccurate assumptions governing the dynamics of the TEMPO+ generated in the experiment. The fact that the forward sweep matches suggests that are assumptions governing the dynamics of TEMPO are accurate, however, and that is what we are interested in.

In order to determine $D_{\text{surf}}$, it is necessary to either determine $k_{\text{des}}$ independently, or vary the system geometry to create a different calibration curve and look for where the two curves intersect. Collaborative efforts have been initiated to apply the former approach. Results obtained from the latter approach form the basis for chapter four.
Figure 3.9  A side view of a microline electrode in contact with the air water interface. The microband width is 100 nm. The total flux to the electrode is the sum of the bulk solution and surface components.
Figure 3.10 Theoretical voltammograms obtained from COMSOL show the impact of varying $D_{\text{surf}}$ and $k_{\text{des}}$, demonstrated on nine pairs of $D_{\text{surf}}$ and $k_{\text{des}}$ values. The green curve shows the signal due to electrooxidation at the microline, while the red curve shows the signal arising from the bulk component. The black curve is the sum of the two, giving the total current. Note that identical peak currents can be obtained by varying both of these parameters independently of each other over several orders of magnitude. All scans are simulated at 20 mV/s, with 0.1000 mM TEMPO.
Figure 3.11 Two TEMPO concentration profile plots obtained from COMSOL at $E = E^0 + 0.25$ V, the switching potential for the scan. When $k_{\text{des}}$ is small (upper plot), the depletion of TEMPO around the microband has hemicylindrical symmetry, as seen in the top diagram. When $k_{\text{des}}$ is large (lower plot), the symmetry is distorted on the side of the microband as material from the bulk adsorbs at the interface to replace TEMPO that has been oxidized. In both cases, the electrode is positioned at the center of the profile, at point (0,0). The initial TEMPO concentration is 0.10 mM, and the scan rate is 20 mV/s.
Figure 3.12 A comparison of voltammograms obtained from experiment (thick red line) and COMSOL simulation (thin black line) for the 2D microline experiment. The concentration of TEMPO is 0.0850 mM, and the scan rate is 20 mV/s.
Figure 3.13 Calibration plot obtained on the basis of COMSOL simulations and fitting the total current to the average current obtained from TEMPO electrooxidation at a line microelectrode. The error bars represent 95% confidence intervals obtained on the basis of fifteen experiments performed on 0.1 mM TEMPO solutions.
Chapter 4: Gibbs Monolayers at the Air/Water Interface: Determination of Lateral Mobility Using Barrier Electrodes

4.1 Introduction: Theory of Barrier Films

As noted in the previous chapter, in the absence of any independent means of determining the desorption rate constant for TEMPO, it is impossible to pinpoint the value of the lateral diffusion coefficient. This is due to the dynamic exchange of surface and bulk species on the time scale of the experiment, which substantially enhances the signal due to surface adsorbed species when the rate constant is greater than $1 \text{ s}^{-1}$, which is the most likely case, given that most surface active species have rate constants on the order of $10^2 \text{ s}^{-1}$.\(^1\)-\(^3\)

The key idea in this chapter is the introduction of a rigid, impermeable film, of controllable and variable thickness, over the face of the gold electrode. This barrier prevents direct electrooxidation of TEMPO at the 2D line microelectrodes. This does not mean that the surface adsorbed species have no impact on the total current. As TEMPO is depleted by electrooxidation in the solution phase, the diffusion layer eventually grows beyond the width of the barrier, which is varied from ~100 nm to ~1.5 \(\mu\)m. Once the diffusion layer reaches past the barrier, surface adsorbed species desorb to maintain equilibrium at the interface. A diagram of the barrier electrode may be seen in Figure 4.1, and the simulated concentration profiles are found in Figure 4.2. It is especially interesting to note that the presence of the barrier inverts the effect on the bulk concentration profile due to the partitioning of the solute, as can be seem from comparing Figure 4.2 to Figure 3.10.

The replenishment of TEMPO in the bulk solution will enhance the current to a degree dependent on the thickness of the barrier, the lateral diffusion coefficient, and the desorption rate constant. This will enable the creation of an independent calibration curve, one that should ideally intersect the curve obtained with no barrier. In fact, an independent curve will be created for every thickness. Thus, by creating a range of thicknesses of barrier films, a great number of calibration plots can be made, allowing us to assert with greater confidence the location of the $D_{\text{surf}}$ and $k_{\text{des}}$ intersection. In theory, at least. In practice, we may find that making more than two calibration plots will remind us of the adage, “He who has one watch knows what time it is. He who has two is never sure\(^4\)”

4.2 Barrier Material Requirements

I will now discuss the requirements necessary for a successful barrier film experiment. The first requirement is that the barrier film must adhere well to the surface of the gold electrode. This is simple and obvious enough, but still merits stating. Barriers with low adhesive quality will not be able to withstand the experimental conditions of high electrode potentials and will delaminate upon contact with solution. The second requirement is that the barrier film must be hydrophilic, but possible to render hydrophobic. Barrier film experiments still rely on a sharp gradient of contact between the electrode and solution. If the barrier film is hydrophilic, then the adhesion of water on the barrier will result into uncertainty as to the location of the interface relative to the electrode, and it will not be possible to simulate the results. A third requirement is that the barrier film be impermeable to both charge and the electroactive species. Like the first requirement, this is simple and obvious, but merits mention. A permeable or semi-permeable film would not constitute a barrier at all, and a conducting film would simply recreate the microline experiment described in tedious detail in Chapter 3. A fourth requirement is that the barrier be rigid and break in a uniform and reproducible fashion. If the barrier film swells, oozes or shatters, the results will be highly imprecise, and it will not be possible to model the electrode...
Figure 4.1 Front and side views of a barrier electrode. As with the microline electrodes, the electrode is scribed and fractured along the dotted line, and then touched to the solution. The side view shows the increasing size of the diffusion layer as the experiment progresses.
Figure 4.2 TEMPO concentration profiles obtained for barrier electrodes. Parameters are identical to those in Figure 3.10 (20 mV/s scan rate and 0.100 mM TEMPO), with barrier electrodes used in place of line electrodes ($k_{\text{des}} = 0.01$ for top plot, $k_{\text{des}} = 100$ for lower plot). The isoconcentration lines correspond to TEMPO concentrations of 0.058 mM (inner line) and 0.065 mM (outer line). The initial TEMPO concentration is 0.100 mM and the scan rate is 50 mV/s.
Figure 4.3 Calibration curves obtained by fitting electrodes with varying gold and SU-8 thicknesses. In the legend, the first number denotes the thickness of the barrier, and the second number the thickness of gold electrode. Error bars reflect 95% confidence intervals, and were obtained by simulating for the upper and lower bounds of 95% confidence for the voltammetric signal. The green curve was obtained by fitting the current obtained from a microline electrode, with no barrier. Although these curves clearly do not intersect in a point, it is possible to identify an “intersection region,” beginning around log \( k_{\text{des}} \) = 4. The lateral diffusion coefficient can be approximated as \( 8 \pm 2 \times 10^{-5} \text{ cm}^2/\text{s} \).
geometry accurately. Finally, it must be possible to apply the barrier film in a uniform and precise manner, with thicknesses ranging from 100 nm to 10 µm. Barriers larger than 10 µm do not allow the diffusion layer to grow to the point where the surface component can contribute to the total current. If the barrier is not uniformly thick over the face of the electrode, the geometry of the system is difficult to impossible to determine, and cannot be simulated. Ideally, the fabrication procedure should be simple, but this is not a requirement.

4.3 SU-8 Barrier Films: Results and Discussion

My initial work with barrier electrodes followed closely in the steps of the work of Glandut\(^5\), who used barrier films made from SU-8 photoresist. For that reason, I report here the findings made by Glandut and coworkers about the features of these barrier electrodes. The details of electrode fabrication may be found in Section 2.4 of this dissertation. Although the fabrication procedure is tedious, this barrier met all the requirements listed in the previous paragraph. There have been concerns about the rigidity of this polymer, but no systematic investigation was conducted into whether or not the polymer oozed after breaking. This could most easily be done by doing control experiments with 4-OH TEMPO and Cu UPD and seeing if the current obtained from 4-OH TEMPO matched simulated result for a microband with the thickness given from the Cu UPD experiments. It was demonstrated that the polymer did not swell when in contact with water. The variation in thickness was less than 5% across the face. Voltammograms performed with SU-8 barrier films over the gold surface (no breaking of the electrode) yielded current densities that were reduced by over three orders of magnitude from those performed on clean gold surfaces, demonstrating the impermeability of the film\(^5\). These scans performed with these electrodes did not decrease in signal over time, either in air or at solution, providing further evidence that the reason for signal decay in 2D line microelectrodes is due to loss of signal at the triple phase line. Furthermore, the results obtained with electrodes from a single slide tended to have very high precision. The primary improvement of my work over that of Glandut was the introduction of aspiration of the system prior to making measurements.

The calibration curves obtained from SU-8 barrier electrodes are shown in Figure 4.3. Although an intersection point cannot be identified, it is possible to identify an intersection region. This intersection region begins as \(k_{\text{des}}\) approaches \(10^4\) s\(^{-1}\), and there is no reason to exclude any of the \(k_{\text{des}}\) values in excess of this value as part of the intersection region. The range of \(D_{\text{surf}}\) values can be interpreted as the highest and lowest points of complete overlap of the 95% confidence intervals. That is to say, the upper value of \(D_{\text{surf}}\) is the upper limit on the first error bar of the bottom curve that overlaps with the lower limit of the error bar on the top curve, and vice versa for the lower value. Under this interpretation, these curves yield a \(D_{\text{surf}}\) of \(8 \pm 2 \times 10^{-5}\) cm\(^2\)/s.

These results are comparable to those obtained by Glandut with SU-8 barrier electrodes\(^5\). Also unable to obtain intersection in a single point, his results are systematically lower than mine, especially those obtained from the microliner. I attribute this to the lack of aspiration in his experiments. He reports a \(D_{\text{surf}}\) value of \(4.4 \pm 1.2 \times 10^{-5}\) cm\(^2\)/s and a lower bound of \(k_{\text{des}}\) as \(2 \times 10^4\) s\(^{-1}\).

The values obtained for the lateral diffusion coefficient are eminently reasonable and supported by MD simulation work. The values obtained for \(k_{\text{des}}\) are several orders of magnitude higher than those that have been experimentally measured. Glandut uses the work of Garrett et al\(^6\) to provide a theoretical justification for this values of \(k_{\text{des}}\). The approach of Garrett and coworkers is as follows: recognizing that desorption of surfactants into the aqueous phase is an
activated process, they apply transition state theory to obtain an expression for the expected desorption rate constant. Grote-Hynes theory, which allows for molecules to recross the activation barrier, was combined with the following expression for $k_{\text{des}}$:

$$k_{\text{TST}} = \frac{kT}{hQ^R(T)} \exp \left[ -\frac{[W(z^+) - W_{\text{surf}}]}{RT} \right]$$

(4.1)

From this expression Glandut obtained a theoretical range of $3 \times 10^5$ to $2 \times 10^7$ s$^{-1}$. He estimated $Q^R(T)$ (a unitless parameter) as 25-50, with the activation energy, $W(z^+)$, approximated as 5 kJ/mol, and the free energy of desorption, $W_{\text{surf}}$, calculated as -15.4 kJ/mol. I have been unable to replicate the calculations of Glandut. Analyzing decanol, Shin and Abbot use $W(z^+) = 9$ kJ/mol and $W_{\text{surf}} = 39$ kJ/mol, and from that obtain a $k_{\text{des}}$ value of 45 s$^{-1}$. Comparing these values to the ones used for TEMPO, it is easy to see that the value Shin and Abbot use for $[W(z^+) - W_{\text{surf}}]$ is triple the value of that used for TEMPO in this calculation, but the resulting desorption constant is nearly four orders of magnitude greater. My understanding of this system suggests that TEMPO should have a $k_{\text{des}}$ value of about $10^3$ s$^{-1}$ based on a comparison of TEMPO’s thermodynamic values to those of decanol.

### 4.4 SiO Barrier Films: Results and Discussion

#### 4.4.1 Characterization

Reconciling the data obtained from SU-8 barrier electrodes with theoretical results became moot when the bottle of SU-8 ran out. Financial constraints and concerns about the rigidity of SU-8 barrier films obligated the exploration of new barrier materials, preferably ones fabricated from cheap materials. Two solid materials that could be vapor deposited in the bell jar were considered: SiO and MgF$_2$. Efforts to create magnesium fluoride barriers failed due to poor adhesion of MgF$_2$ to gold. Attempts to improve adhesion through modifications to the electrode were unsuccessful.

Silicon monoxide did not adhere well to gold directly, but could be made to adhere well with the modifications mentioned in section 2.4. Having solved the problem of silicon monoxide adhesion, SiO barrier electrodes were characterized to see to what extent they satisfied the other requirements of barrier electrodes. Scans performed on gold electrodes coated with SiO exhibited current densities that were about half the value obtained from clean gold electrodes, but once the surface was rendered hydrophobic via OTS treatment, current densities plummeted to values similar to those obtained for SU-8 barrier films. On the basis of the ease of coating uniform layers of SiO onto gold electrodes, the strength of the adhesion, and the ease of rendering the barrier hydrophobic, SiO was deemed to be a suitable material for making barrier electrodes.

Evidence presented below indicates that SiO barriers do not exhibit uniform breaking. As can be seen in Figure 4.4, the fit of simulated and experimental SiO voltammograms is excellent. However, it was noted in early experiments that the current obtained from SiO barrier films was on the order of 30% greater than anticipated on the basis of the results obtained from SU-8 films. The relationship between peak current and lateral diffusion coefficient is not even linear, so fitting voltammograms obtained from SiO barrier electrodes by using the same treatment that had been applied to data obtained from SU-8 electrodes required increasing the diffusion constant to about $1 \times 10^{-3}$ cm$^2$/s, an almost physically unrealistic number, even when treating TEMPO diffusion as taking place entirely in the gas phase, in line with Enskog-
Figure 4.4 Average cyclic voltammogram of TEMPO at a SiO barrier electrode compared to COMSOL simulation. The width of the gold electrode is 100 nm, and the width of the SiO barrier is 200 nm. SiO has been treated as an oxidizing surface in the simulation. The TEMPO concentration is 0.1040 mM and the scan rate is 20 mV/s for both theory and experiment.
Figure 4.5  Cyclic voltammograms obtained on 0.100 mM TEMPO solution with barrier electrodes featuring 100 nm of SiO deposited over 100 nm of Cr.  No gold is present in the electrodes. The features are indicative of a high resistance, although it does appear there is some onset of oxidation, perhaps of water, at potentials greater than 0.65 V vs SCE. The scan rate is 50 mV/s.
Chapman theory. However, because of the excellent qualitative fit, it was of great interest to find the source of the discrepancy.

Because the first SiO barrier electrodes were made using ~8 nm of chromium between gold and SiO in order to improve adhesion, it was suspected that perhaps the presence of this thin chromium layer was having a disproportionate effect enhancing the current. This theory was tested by creating barrier electrodes with 100 nm of chromium and no gold in them whatsoever. As can be easily seen in Figure 4.5, the current obtained at barrier electrodes made in this fashion is an order of magnitude lower than those typically obtained in these experiments and shows no features indicative of facile and reversible electrooxidation of much of anything. In light of the information gained in this experiment, it seems unlikely that 8 nm of chromium placed over 100 nm of gold is responsible for increasing the current by 30%.

Despite the implications that there should be no problem using chromium between gold and SiO to improve adhesion, I searched for an alternative method of SiO barrier electrode fabrication, and ultimately found that MPS coated on gold was successful in getting SiO to adhere. Although the results obtained from electrodes made in this fashion were identical to those obtained using chromium, I preferred to use MPS for adhesion because I knew that it had zero impact on the current, as opposed to the very slight and in all likelihood negligible contributions from chromium.

In order to have a control experiment for the bulk solution contribution to the current in the absence of partitioning, 4-OH TEMPO was employed. This molecule is a TEMPO derivative modified to include a hydroxyl functional group on the carbon opposite the nitroxy group. This increases the solubility substantially, and 4-OH TEMPO is found not to partition to the interface. Voltammograms performed on SiO barrier electrodes on solutions of 4-OH TEMPO yielded currents that were about 5% higher than those predicted by theory. I found that there was excellent agreement between theory and experiment if I treated the SiO barrier as a region where electrooxidation could occur.

4.4.2 Probing the Conductivity and Electroactivity of SiO Films

The hypothesis that SiO was a semiconducting material where redox reactions could take place seemed promising initially for a substantial number of reasons. First, it had been observed that non-silanized SiO barriers were very poor insulators, and the SiO exposed when breaking the electrode would have been untreated. Second, because of the logistical setup of the bell jar where gold and SiO were deposited onto the glass slides, it was observed that there were traces of gold depositing onto the SiO contained in the deposition boat, making it reasonable to hypothesize that the SiO was gold doped, which would presumably enhance its conducting properties. Third, a substantial body of literature exists that probes the conductivity of vapor deposited SiO, including crystal structure and mechanism. Finally, as noted above, the currents obtained when experiments were performed on TEMPO were 30% greater than anticipated, in contrast with the 5% greater observed for the non-partitioning species. If SiO was an electroactive surface, not only would this increase the effective width of the electrode, but it would also decrease the effective width of the barrier to an almost negligible amount. A decrease in barrier thickness coupled with an increase in electrode thickness was necessary to account for such a substantial increase in current. Simulations performed that treated 100 nm of gold and 100 nm of SiO barrier as 199 nm of conducting material and 1 nm of insulating material (1 nm approximated the thickness of the silanized surface) yielded excellent agreement between simulation and experiment, with lateral diffusion values on the order of \(10^{-4} \text{ cm}^2/\text{s}\). All that remained was to demonstrate that SiO was an electroactive surface.
Attempts to do so failed at all levels. The simplest experiment to do was the one used to rule out chromium as the source of the high current: 100 nm of SiO was deposited onto a glass slide using the same masks used to make gold electrodes. A typical example of a resulting voltammogram is shown in Figure 4.6, with a voltammogram taken on a piece of glass for comparison. The curves clearly demonstrate that TEMPO is not oxidized with facile, reversible kinetics at an SiO electrode.

This experiment did not rule out the possibility that SiO in proximity to gold was able to carry charge to TEMPO, or that TEMPO might be able to permeate the hydrophilic region of SiO exposed after the fracturing step. In order to test this hypothesis, a mild modification was made to the electrode fabrication process. A thin strip of aluminum was placed over the masks during the gold deposition step, causing the initial electrode to consist of two pieces of unconnected gold. Silicon monoxide was then deposited in its usual manner, covering the gold and the gap between the two parts. A diagram of this electrode design may be seen in Figure 4.7.

The electrode could be broken in two different ways, leading to three types of experiments that could be performed with these electrodes. One option was to break at the point where only the SiO film would be exposed to water. This would create two equivalent electrodes, and electrooxidation of TEMPO could only occur to the extent that SiO was able to carry the charge from gold to the water surface, or that TEMPO could permeate the barrier. The other option was to break the electrode at a point that would expose both gold and SiO. This would create two different electrodes, one identical in nature to the standard SiO barrier electrode, and the other having the gold exposed at the air/water interface having no direct connection to the gold contact pad. In the latter experiment, electrooxidation of TEMPO could occur only to the extent that SiO was able to serve as a conductor to bridge the gap. The results obtained from electrodes that exposed gold connected to the contact pad and SiO to the air/water interface yielded results identical to electrodes made in the standard fashion. The results obtained from electrodes that exposed only SiO to the air/water interface, as well as those that exposed gold with no direct connection to the contact pad are shown in Figure 4.8. For all practical purposes, the curves obtained from the latter two experiments are identical to each other and show nothing but noise. This pretty much put the nail in the coffin of SiO as a conductor idea.

If the experiments of the previous paragraph are the nail in the coffin, the results shown in Figure 4.9 are the hammer that pounded it firmly into place. Despite two slightly outlying pieces of data, the overall trend is clear and unmistakable, especially when the margin of error is taken into account: the thicker the SiO barrier, the lower the current obtained at the electrode. This result is not predicted by a model allowing permeability to TEMPO or electrical conductivity. SiO clearly functions as a barrier, so something else must be contributing to the increased current. Further complicating the picture is an heretofore unmentioned aspect of SiO barrier electrodes: in contrast with SU-8 barrier electrodes, the signal obtained at SiO barrier electrodes decreases with successive scans. Signal decay even happens in scans performed on 4-OH TEMPO, although these quickly reach a stable value, typically after the 3rd scan. This gave birth to the hypothesis that perhaps there was some trace electroactive contaminant in some component of the electrode system that was oxidized more or less to completion on the first scan, making a substantial contribution to the observed current in the initial scan, but not later scans. Even more intriguingly, if this was the case, the oxidation of the contaminant was irreversible.

In order to investigate this hypothesis, electrodes were made with just about every permutation possible in the fabrication procedure. There were three components that had to be
Figure 4.6 A voltammogram obtained on an “electrode” created by depositing 100 nm of SiO onto a glass slide (upper blue curve). The lower (red) curve is the signal obtained when a sweep cycle is performed on a piece of glass. Clearly, this is not a surface where electron exchange happens easily. As usual, the TEMPO concentration is 0.1000 mM. The scan rate is 20 mV/s.
Figure 4.7 A “gap” microelectrode. The gap in the gold was created by placing a thin strip of aluminum over the electrode masks during gold deposition. The two pieces of gold are connected by the SiO film. The electrode can be fractured on the gap, exposing no gold, or at a region where both gold and SiO are exposed in the cross section. Breaking in the latter manner would create one electrode where the gold in contact with water had a direct connection to the circular contact pad, while the other electrode would only be able to oxidize material that permeated that SiO barrier.
Figure 4.8  Typical voltammograms obtained from gap electrodes where 1) only SiO was in contact with the air/water interface (lower curve) and 2) both SiO and gold were in contact with the air/water interface, but there was no direct connection of the gold to the circular contact pad (upper curve). Neither curve indicates an electroactive surface. The scan rate was 50 mV/s and the solution was 0.100 mM in TEMPO.
Figure 4.9 Plot correlating peak current to SiO barrier thickness. All scans were performed with 100 nm gold electrodes on a solution containing 0.1 mM TEMPO, 1 mM HClO₄, and 2 mM LiClO₄. The blue curve (diamonds) corresponds to scans performed at 50 mV/s, and the magenta curve (squares) corresponds to scans performed at 20 mV/s. Error bars represent 95% confidence limits, with the number of scans varying per data point, but in no case fewer than six experiments.
present in every barrier electrode: the glass slide, gold, and SiO. There was no reason to suspect glass or gold as being the source of contamination, and it also seemed improbable that SiO was the source, due to the vaporization step in the deposition of SiO onto gold, and also because thicker SiO layers resulted in lower current—the opposite of what you would expect if SiO was contaminated with an electroactive species. There remained two main components of the system to be investigated: the material used to adhere gold to glass and SiO (Cr and/or MPS), and the material used to render the surface hydrophobic (OTS and/or OM).

Chromium can be eliminated from electrodes by using MPS to adhere gold to both glass and SiO. Typically, OTS would then be used to render the slide hydrophobic, but OTS could be eliminated from the fabrication procedure by assembling another layer of MPS on the SiO, then depositing a thin layer of gold over the SiO, and rendering the gold hydrophobic with OM. In shorthand, the chromium free electrodes with OTS as the hydrophobic layer may be referred to as MPS/Au/MPS/SiO/OTS electrodes, with the OTS free electrodes referred to as MPS/Au/MPS/SiO/MPS/Au/OM electrodes. Similarly, electrodes were made with the following schemes: Cr/Au/Cr/SiO/OTS, Cr/Au/Cr/SiO/Cr/Au/OM. In addition, the effect of the thickness of the glass slide was also probed by fabricating electrodes on microscope cover slips, which are about 15% as thick as microscope slides. All of these electrodes gave a higher current than predicted by theory, with more or less identical results regardless of fabrication procedure.

I mention the permutations in electrode fabrication only for the sake of being thorough in my dissertation. I could have saved time and space by simply stating in a sentence that a systematic investigation of the impact of individual components of the electrode failed to provide any insights into the source of high current.

4.4.3 Determining the Effective Electrode Length and Width

Ultimately, the only thing that electrodes with high current had in common was the presence of an SiO barrier. While the earliest analysis of curves obtained with an SiO barrier suggested the presence of a larger electroactive surface than that provided by the cross section of exposed gold, all experiments designed to probe the electroactivity of SiO had indicated that it was not an electrochemically active interface. This led to the hypothesis that more gold was being exposed than the geometric cross section. Two mechanisms could be responsible for an increase in effective gold surface, with neither mechanism being at all exclusive of the other. One possibility was that the roughness of the interface created when the glass slide was broken effectively increased the length of the microline. This effect would be more significant at fast scan rates than at slow scan rates, and would require the line to be 30% longer than the geometric cross section. The other possibility was that SiO does not fracture in a uniform fashion, and that its adhesion to the gold surface is not strong enough to prevent small shards from “flaking off” along the length of the line, effectively increasing the width of the microelectrode. In order to account for the unexpectedly high current, this mechanism would have to result in exposing about 800 nm of gold, effectively increasing the surface area by an order of magnitude. Because of the hemi-cylindrical geometry of the system, the voltammetric signal rises directly in proportion to the increase of the length of the microline, but the increase in signal due to increasing the width is nowhere near as pronounced.

Again, as noted above, these two mechanisms of increasing the exposed surface area are not mutually exclusive. It is also possible to postulate that roughness at the microscopic level is responsible for 50% of the current increase, with an effectively greater width being responsible for the remainder of the current increase. A diagram of the possible outcomes for the resulting microband when SiO barriers are used is shown in Figure 4.10. It is vital to know which
proportion of the current increase to assign to which effect, because of the implications for the modeling of the system. Any increases in current due to increased electrode length will also result in an increase from the surface component, but increases due a greater width result in no increase of current due to the surface component.

Fortunately, it is fairly easy to assess the relative contribution from each proposed mechanism, and in fact, there really was no reason to ever assign any of the increase to an increased length. Why not? Because this effect had never manifested itself until the introduction of SiO barrier electrodes. Never in microline or SU-8 barrier electrodes were there discrepancies between theory and experiment that could only be explained by postulating an increase in the length of the microline. To postulate so at this point would be to hold the monolayer of SiO accountable for increasing the roughness of the fracture, which seems to be an unreasonable thing to do. Nonetheless, because of the simplicity of treating the electrode system if effective length increases were responsible, as well as the fact that postulating a 30% increase in effective surface area appears more enticing than postulating an order of magnitude increase in surface area, this phenomenon was investigated with the aid of copper underpotential deposition (Cu UPD).

Cu UPD is a powerful tool for measuring the atomic surface area of a gold electrode. Because of the energy of adsorption associated with copper depositing onto a gold surface, it is possible to deposit a monolayer of copper on gold at potentials below those required to produce copper deposition on a copper surface. This monolayer can then be anodically stripped, and the resulting current can be integrated to obtain the charge, which is directly proportional to the number of adsorbed copper atoms, and hence the surface area of the gold. This technique is best employed with slow scan rates and at monocrystalline gold (111) surfaces. Under such conditions, the amount of charge density is 420 µC/cm². Unfortunately, our electrode fabrication procedure does not result in the formation of (111) gold surfaces. While such surfaces can be created by heating the gold, as done by others, our glass slides are unable to withstand the temperatures needed to form this crystalline state. The solution to this problem was to calibrate our system using macroscopic electrodes made from vapor deposited gold, and assume a similar current density for the microelectrodes created by fracturing the glass. The macroelectrode for this experiment simply consisted of using the circular contact pad in an unfractured electrode. A typical UPD scan is shown in Figure 4.12. The average current density was found to be 240 ± 30 µC/cm².

With the system calibrated, UPD was then performed on both microline and SiO barrier electrodes. The resulting voltammograms may be seen in Figure 4.12. SiO barrier electrodes exhibit nearly a factor of ten more charge than microline electrodes. Similarly with the results obtained on TEMPO, there was a very low degree of precision in the Cu UPD measurement of the gold surface area. This is easily attributable to the irreproducibility of the fracturing process. Indeed, it seems unreasonable to expect high precision when the shattering of glass is involved. This result confirms what was initially expected: the increase in current is due to an effective increase in width of the microline.

This increase in microline width cannot be due a wider cross sectional area of gold. The gold is 100 nm thick, and that is all there is to that. The increase in effective width must be due to additional gold being exposed on the face of the electrode. The model for this system is that shown in Figure 4.13. Because the exposed SiO and gold are hydrophilic, the SiO still maintains its full thickness as a barrier, and TEMPO adsorbed at the surface must still desorb and diffuse.
Figure 4.10 A diagram of possible breaking patterns for SiO barrier electrodes. On the left is the case of a rough microband, but no additional gold exposed on the face of the electrode. This effectively increases the length, but not the width of the electrode. On the right is the case of a smooth microband with SiO flaking off. This increases the effective width of the electrode, but not the length. In the center is a model with rough breaking and SiO flaking off, increasing both the effective width and length of the electrode.
Figure 4.11 Copper underpotential deposition experiment obtained on 0.196 cm$^2$ vapor deposited gold electrode. Potential is plotted vs. SCE. The scan rate was 10 mV/s and the solution contained 1 mM CuSO$_4$ and 1 mM H$_2$SO$_4$. The charge density is 240 µC/cm$^2$ for the cathodic sweep.
Figure 4.12 Copper underpotential deposition experiment obtained on 500 nm SiO barrier electrode (red, large curve) and traditional microline electrode (blue, small curve). Potential is plotted vs. SCE. The scan rate was 10 mV/s and the solution contained 1 mM CuSO₄ and 1 mM H₂SO₄. The total integrated current (charge) is about 8 times greater for the barrier electrode, indicating 8 times more gold area exposed.
Figure 4.13 Model used to simulate current at SiO barrier films. The effective amount of gold exposed on the electrode face is obtained by performing experiments on 4-OH TEMPO, a non-partitioning electrolyte. The gold face height is adjusted in the simulation file until the peak height matches that for 4-OH TEMPO. Simulations are then performed to match peak height of TEMPO voltammograms as a function of $D_{surf}$ and $k_{des}$. 
the full length of the barrier in order to make a contribution to the voltammetric signal. This means that although it is unreasonable to assume that the amount of gold face exposed by SiO flaking off is uniform along the length of the electrode, it is reasonable to treat the additional area as an average exposed area along the face.

4.4.4 Normalization of Current to Effective Electrode Width

Ideally, the increased width of the electrode could be measured by an internal, non-partitioning standard analyte in solution with TEMPO. This would allow the effective width of each electrode to be ascertained individually and in conjunction with the TEMPO signal it produced. A variety of redox species were employed to this end, but all proved dissatisfactory for different reasons. As Tolstoy said, “Happy families are all alike, but each unhappy family is unhappy in its own way.” Like wise, the perfect internal standard must completely meet a minimal set of requirements. The peak arising from its voltammetric signal must not overlap with that of TEMPO. This eliminated 4-OH TEMPO from the list of acceptable internal standards. It also must have a redox potential high enough so that there is no interference from proton reduction in the acidic media. This eliminated a wide array of metal ions. It must also have facile and reversible kinetics. This eliminated Fe(CN)$_6^{3-}$, which requires large amounts of Cl$^-$ ion to be present for facile kinetics, a requirement incompatible with the gold electrodes employed in our system.

One molecule that displayed a fair amount of promise was Ru(NH)$_6^{3+}$Cl$_3$. The kinetics and thermodynamics of this redox couple have been well studied. The redox exchange Ru(NH)$_6^{3+} + e^- \rightarrow$ Ru(NH)$_6^{2+}$ occurs at about –0.12 V vs. SCE, so overlap with proton reduction is not a concern. Overlap with oxygen reduction is a problem, however. Normally, this problem is solved easily by deaerating the solution for 15 minutes prior to performing potential sweeps. Unfortunately, this did not prove to be an easy resolution for our system, for two main reasons. The first reason is that deaeration, either by bubbling of nitrogen or argon, resulted in a decrease of the voltammetric signal obtained from TEMPO. This may presumably be attributed to TEMPO’s high volatility, and the air bubbles carry TEMPO out of solution and into the vapor phase.

This obstacle would perhaps have been surmountable by calibrating the solution with a microdisk electrode to measure the decrease in TEMPO signal, and assuming a proportionate decrease in TEMPO concentration when performing the numerical simulations. Even if this approach of controlling for the TEMPO concentration had been effective, another problem with the system proved insurmountable. At least, I never surmounted it. The problem was that performing experiments so near the interface allowed for the rapid readsorption of oxygen into the deaerated system. Even when maintaining a gentle and steady nitrogen flow over the surface of the solution, it proved impossible to eliminate entirely the oxygen background.

This is rather unfortunate, because the experiments I performed with Ru(NH)$_6^{3+}$ present showed great promise if this background could be eliminated. When the TEMPO signal from each electrode was normalized to the area of gold exposed as indicated by the internal standard, the relative standard deviation of the measurements dropped by a factor of five, providing further evidence for the validity of the hypothesis of additionally exposed gold. Unfortunately, the presence of the oxygen background burdened the results with a systematic positive error.

In order to avoid this systematic error, I employed the technique that finally brought my research in this group to its conclusion. My idea is based on the premise that SiO fracturing will be relatively equal within a batch of slides. From each slide, half the electrodes can be used to obtain the voltammetric signal due to a solution containing 4-OH TEMPO. This signal will be
used to give the average exposed amount of gold face per electrode. The remaining electrodes will then be used to perform experiments on a solution containing TEMPO, and the resulting curves will be modeled using the thickness obtained from an analysis of the 4-OH TEMPO experiment. This experiment has the advantage of using 4-OH TEMPO as the standard, a molecule that diffuses and oxidizes in a manner as identical to TEMPO as can be expected from a non-partitioning molecules. It has the drawback of adjusting electrode gold exposure using an average value obtained from experiments that are imprecise, in contrast with the high precision obtained from calibrating electrodes individually using an internal standard. As a consequence the uncertainty in the measurement is a bit higher than desired, but it really isn’t all that bad.

4.5 Results and Discussion

The resulting calibration curves are shown in Figure 4.14. Please turn to the figure and reflect on its relevant features before continuing on with the text in this dissertation. Figure 4.14 should be compared to Figure 4.3. The error bars in Figure 4.14, it is worth noting, are substantially larger than those in Figure 4.3. This is the result of the inherent imprecision that comes in the fracturing process. Error bars were not placed on the 400 nm curve because they were so large, they were off the chart, in part a consequence of relatively few runs being performed with 400 nm SiO barrier electrodes.

With the bad features out of the way, let us turn our attention to the good features. The intersection region begins where \( k_{des} \) is equal to about 500 s\(^{-1}\), and continues on until \( k_{des} \) is equal to 10\(^4\) s\(^{-1}\) where the curves end. The maximum value of mutual overlap shown on the graph is 1.2 \(\times\) 10\(^{-4}\) cm\(^2\)/s, with a minimum value of 2\(\times\) 10\(^{-5}\) cm\(^2\)/s, with the curves for the 100 and 800 nm SiO barriers crossing at about 7 \(\times\) 10\(^{-5}\) cm\(^2\)/s. The value obtained for \( D_{surf} \) here is remarkably well in line with my earlier work with SU-8 barrier electrodes, while the intersecting value of \( k_{des} \) has dropped by an order of magnitude, bringing it much more in line with theoretical predictions.

In light of the experiments performed at the microline, SU-8 barrier electrodes, and SiO barrier electrodes, it seems eminently reasonable and justifiable to assert that the lateral diffusion constant for TEMPO adsorbed at the air/water interface is 7 \(\pm\) 3 \(\times\) 10\(^{-5}\) cm\(^2\)/s, approximately one order of magnitude greater than the bulk diffusion coefficient. These results appear to agree quite well with the theoretical results obtained by Wilson and Pohorille\(^{24}\), who performed MD simulations on a system containing TEMPO adsorbed at the air/water interface and found the lateral diffusion coefficient to be 4.2 \(\pm\) 1.5 \(\times\) 10\(^{-5}\) cm\(^2\)/s. However, it is important to note that their MD simulations also give a bulk diffusion coefficient of 1.2 \(\times\) 10\(^{-5}\) cm\(^2\)/s for TEMPO, about 50\% greater than our experimental value. Additionally, their simulations report 5.7 \(\times\) 10\(^{-5}\) cm\(^2\)/s as the value for the self-diffusion constant of water, double the accepted value of 2.3 \(\times\) 10\(^{-5}\) cm\(^2\)/s\(^{24}\). In light of these facts, it seems reasonable to adjust the value of the lateral diffusion coefficient obtained from these MD simulations downward by 25–50\%, meaning that the experimentally determined value is more than double that obtained from the simulations. Clearly, future work remains to be done to determine the source of the discrepancy between the experimentally and theoretically obtained results.

Finally, it is interesting to use this information to make some assertions as to the viscosity of the air/water interface. Determining the viscosity of a two-dimensional system is a difficult problem. It turns out that there is no solution for the linearized Navier-Stokes equations in two dimensional systems\(^{25}\). Because of this, some have asserted that the concept of a two-dimensional viscosity should not be considered\(^{26}\). Others, being more pragmatic and presumably interested in publishing, have analyzed the forces resulting on a two dimensional system from
the neighboring phases. Pioneering work was done in this field by Saffman and Delbrück, who considered three approximations that could be made to find solutions to the Navier-Stokes equations\(^{27}\). These included giving the 2D layer a finite size, taking into account the viscosity of the outer liquid, and solving the equations for a system not at equilibrium. Later, Hughes and coworkers expanded this work for more general systems, including accounting for the viscosity of both bounding regions of the 2D layer\(^{28}\). Their paper is long and complicated, and I do not ever expect to fully understand it, though I think I could if I really wanted to. Prior work done by Anvar and Charych aided greatly in helping me interpret this paper\(^{29, 30}\). All I need is the equation they use to relate diffusion coefficients to viscous drag.

\[
D = \frac{kT}{4\pi\eta h} \left[ \ln\left(\frac{2}{\varepsilon}\right) - \gamma + \frac{4\varepsilon}{\pi} - \frac{\varepsilon^2}{2} \ln\left(\frac{2}{\varepsilon}\right) \right]
\]

(4.2)

where \(k\), \(T\), \(\varepsilon\), and \(\pi\) all have their usual meaning, \(\eta\) is the viscosity of the 2D membrane or layer, \(h\) is the height of the object diffusing within the layer, \(\gamma\) is Euler's constant and has the value 0.5772, and \(\varepsilon\) is a dimensionless constant characteristic of a 2D system bounded by different phases. It is expressed as

\[
\varepsilon = \frac{\eta_1 + \eta_\infty}{\eta_{2D}} \frac{r}{h}
\]

(4.3)

Where \(\eta_1\) and \(\eta_\infty\) are the viscosities of the lower and upper bounding phases, respectively, \(r\) is the particle radius, \(h\) is the particle height, and \(\eta_{2D}\) is the viscosity in the two dimensional region, as illustrated in Figure 4.15. In many systems, including ours, the viscosity of the upper and lower phases differ by more than an order of magnitude, and the viscosity of the upper phase may therefore be discounted in calculating this parameter.

At this point, it is necessary to postulate a geometry for the diffusing particle in order to solve this equation. It has been established that TEMPO's immersion depth is negligible, and that it has strong interactions with water. Because the viscosity of the vapor phase is negligible, the only forces that need to be taken into account are those acting on molecules in the 10:90 region. From this, I hypothesize that the diffusing particle may be treated as a water/TEMPO couple, with TEMPO in the vapor phase of negligible viscosity, and the water to which it is hydrogen bound in the substantially more viscous interfacial region. Molecular dynamics simulations performed by Wilson and Pohorille indicate that TEMPO hydrogen bonds to an average of 1.8 water molecules, which can also be interpreted to mean that surface species of TEMPO spend at least 90% of their time hydrogen bound to two water molecules, as shown in Figure 4.16. The water molecules can be approximated as spheres with a radius of 1 Å, a length slightly greater than that of an oxygen-hydrogen bond. Pairing the two water molecules together creates a cylinder (consider a spherical cow, uniformly filled with milk. . .) with both a height and radius of 2 Å. Using these values and solving for \(\eta\) as expressed in equation 4.2 gives a value of 0.38 \(\pm\) 0.1 cP at 298 K, about 36% of the bulk value for the viscosity of water. Assigning a particular value to the viscosity of the air/water interface requires making some assumptions that, although reasonable, there is no experimental justification for at this point in time. Regardless of the assumptions made to treat this system mathematically, it is unambiguously clear that TEMPO's rate of lateral diffusion at the interface is on 8–12 times higher than its diffusion in bulk water, implying that the high degree of structure at the air/water interface does not impede motion there, consistent with the findings of molecular dynamics simulations. One of the most exciting developments of this research is the ability to measure desorption rate constants greater than \(10^3\) s\(^{-1}\). The general utility of this approach is
unfortunately limited to electrochemically active species. Additionally, it is possible that these results will aid in the refinement of MD models.$^{31}$
**Figure 4.14** Calibration curves obtained from SiO barrier electrodes. The blue, magenta, and yellow lines correspond to experiments performed on 100 nm, 500 nm and 800 nm SiO barriers, respectively. The experiments used to obtain these data were performed with 50 mV/s scans on 0.100 mM TEMPO solutions.
Figure 4.15 Model used by Hughes et al for diffusion of a cylinder with radius $r$ in a two-dimensional phase of height $h$ and viscosity $\eta$. The 2D region is bounded by upper and lower regions of viscosities $\eta_u$ and $\eta_l$, respectively.
Figure 4.16  TEMPO hydrogen bound to two water molecules. The two water molecules are approximated as a cylinder.
4. Attributed to Lee Segal
5. Glandut, N., Monson, C., Majda, M., Electrochemistry of TEMPO in the Aqueous Liquid/Vapor Interfacial Region: Measurements of the Lateral Mobility and Kinetics of Surface Partitioning”. *Langmuir* **2006**, 22, 10697–10704. 5b. I can not deny that I am unsure that the equations were accurately applied
31. Or it may not. The finest application I can see this information being used for is in obtaining my doctorate in philosophy. I’d like to thank Maitland Jones for inspiring me to say whatever I wanted in my footnotes, which no one ever really looks at. Guess who had the last turn with the proofs?
Appendix: Geometry and parameters for COMSOL finite element method simulations

The following variables were defined under the “Constants” setting

<table>
<thead>
<tr>
<th>Variable Name</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ne</td>
<td>Electrons transferred</td>
<td>1</td>
</tr>
<tr>
<td>Faraday</td>
<td>Faraday’s number</td>
<td>96485.3</td>
</tr>
<tr>
<td>IGC</td>
<td>Ideal Gas Constant</td>
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<tr>
<td>Temp</td>
<td>Temperature</td>
<td>298.15</td>
</tr>
<tr>
<td>ff</td>
<td>Faraday/Temp/IGC</td>
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<tr>
<td>alpha0</td>
<td>Forward transfer coefficient</td>
<td>0.5</td>
</tr>
<tr>
<td>alphar</td>
<td>Reverse transfer coefficient</td>
<td>1-alpha0</td>
</tr>
<tr>
<td>k0</td>
<td>Rate constant</td>
<td>Variable</td>
</tr>
<tr>
<td>v</td>
<td>Scan rate</td>
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</tr>
<tr>
<td>length</td>
<td>Length of microline</td>
<td>0.01</td>
</tr>
<tr>
<td>Dsol</td>
<td>Bulk diffusion constant</td>
<td>$7.7 \times 10^{-10}$</td>
</tr>
<tr>
<td>Dsurf</td>
<td>Surface lateral diffusion constat</td>
<td>Variable</td>
</tr>
<tr>
<td>E0</td>
<td>Redox potential of TEMPO</td>
<td>0</td>
</tr>
<tr>
<td>Eini</td>
<td>Initial system potential</td>
<td>Eini-0.2</td>
</tr>
<tr>
<td>RangeE1</td>
<td>Length of forward sweep</td>
<td>0.45</td>
</tr>
<tr>
<td>Erev</td>
<td>Switch Potential</td>
<td>Eini+rangeE1</td>
</tr>
<tr>
<td>RangeE2</td>
<td>Length of reverse sweep</td>
<td>RangeE1</td>
</tr>
<tr>
<td>Eend</td>
<td>Final system potential</td>
<td>Erev-rangeE2</td>
</tr>
<tr>
<td>tend</td>
<td>Time duration of experiment</td>
<td>$(2*Erev-Eini-Eend)/v$</td>
</tr>
<tr>
<td>CsolStarTEMPO</td>
<td>Initial bulk TEMPO concentration</td>
<td>0.1</td>
</tr>
<tr>
<td>CsolStarTEMPOPlus</td>
<td>Initial bulk TEMPO⁺ concentration</td>
<td>$1 \times 10^{-18}$</td>
</tr>
<tr>
<td>CsurfStarTEMPO</td>
<td>Initial surface TEMPO concentration</td>
<td>0.035*CsurfMaxTEMPO</td>
</tr>
<tr>
<td>CsurfStarTEMPOPlus</td>
<td>Initial surface TEMPO⁺ concentration</td>
<td>$1 \times 10^{-18}$</td>
</tr>
<tr>
<td>CsurfMaxTEMPO</td>
<td>Full monolayer TEMPO concentration</td>
<td>$3.16 \times 10^{-6}$</td>
</tr>
<tr>
<td>kdesTEMPO</td>
<td>TEMPO desorption rate constant</td>
<td>Variable</td>
</tr>
<tr>
<td>kadsTEMPO</td>
<td>TEMPO adsorption rate constant</td>
<td>0.38*kdesTEMPO</td>
</tr>
<tr>
<td>CsurfMaxTEMPOPlus</td>
<td>Full monolayer TEMPO⁺ concentration</td>
<td>CsurfMaxTEMPO</td>
</tr>
<tr>
<td>kdesTEMPOplus</td>
<td>TEMPO⁺ desorption rate constant</td>
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</tr>
<tr>
<td>kadsTEMPOplus</td>
<td>TEMPO⁺ adsorption rate constant</td>
<td>0.01*kdesTEMPO</td>
</tr>
</tbody>
</table>

Table A.1 Defined constants in the COMSOL numerical simulation program. This table is presented just as it is entered in the program, which is why there are no units in the table. All units are in the m/kg/s system, so concentration units are mol/m³ and diffusion constant units are m²/s.
Figure A.1 The COMSOL simulation geometry for reference with expressions given in the appendix. The height of the simulated cell is 1 mm, and the width is 2 mm. The gold electrode is 100 nm thick, and the barrier thickness was varied between simulations. The gold electrode was placed 1/3 of the distance from the glass end of the cell. All non-labeled borders are constant concentration boundaries.
The following expressions were defined for the simulation points, boundaries, and subdomains:

**Point Expressions**
None

**Boundary Expressions**
At air/water interface boundary
Variable: react_surfTEMPO
Expression: \(k_{adsTEMPO} C_{solTEMPO} (C_{surfMaxTEMPO} - C_{surfTEMPO} - C_{surfTEMPOplus}) - k_{desTEMPO} C_{surfTEMPO}\)

Variable: react_surfTEMPOplus:
Expression: \(k_{adsTEMPOplus} C_{solTEMPOplus} (C_{surfMaxTEMPOplus} - C_{surfTEMPO} - C_{surfTEMPOplus}) - k_{desTEMPOplus} C_{surfTEMPOplus}\)

**Subdomain Expressions**
None

The following expression was defined as a boundary integration variable:
At the gold electrode
Variable: Courant
Expression: \(n \epsilon F_{araday} \times length \times ndflux_{CsolTEMPO\_di}\)

Expressing the adsorption and desorption of TEMPO required a multiphysics model that combined the weak form with the transport and diffusion model. The following boundary conditions were defined under the weak form setting

**Boundary Settings**
At the air/water interface
Weak terms: \(D_{surf} (-C_{surfTEMPO_{Tx}\_test} C_{surfTEMPO_{Tx}} - C_{surfTEMPO_{Ty}\_test} C_{surfTEMPO_{Ty}}) + C_{surfTEMPO_{test}} \times react_{surfTEMPO} \)

and: \(D_{surf} (-C_{surfTEMPOplus_{Tx}\_test} C_{surfTEMPOplus_{Tx}} - C_{surfTEMPOplus_{Ty}\_test} C_{surfTEMPOplus_{Ty}}) + C_{surfTEMPOplus_{test}} \times react_{surfTEMPOplus}\)

dweak terms: \(C_{surfTEMPO_{test}} C_{surfTEMPO_{time}}\)

and: \(C_{surfTEMPOplus_{test}} C_{surfTEMPOplus_{time}}\)

Init terms: Set \(C_{surfTEMPO}(t_0)\) at: \(C_{surfStarTEMPO}\)
Set \(C_{surfTEMPOplus}(t_0)\) at: \(C_{surfStarTEMPOplus}\)
Set \(C_{surfTEMPO_{t}(t_0)}\) at: 0
Set \(C_{surfTEMPOplus_{t}(t_0)}\) at: 0

No other boundary, point or subdomain expressions were used in the weak form. The following expressions were defined in the diffusion and transport model setting:

**Point settings**
None

**Boundary Settings**
Outer Boundaries
  Condition: Concentration
  Set CsolTEMPO at: CsolStarTEMPO
  Set CsolTEMPOplus at: CsolStarTEMPOplus

Glass and Barrier Boundaries
  Condition: Insulation

Electrode boundary
  Condition: Flux
  Set N_0 for TEMPO at: -k_0*(CsolTEMPO*exp(alphao*ne*ff*(-abs(v*t-Erev+Eini)+Erev-E0))-CsolTEMPOplus*exp(-alphar*ne*ff*(-abs(v*t-Erev+Eini)+Erev-E0)))
  Set k_c for TEMPO at: 0
  Set c_b for TEMPO at: CsolStarTEMPO

  Set N_0 for TEMPOplus at: -k_0*(CsolTEMPO*exp(alphao*ne*ff*(-abs(v*t-Erev+Eini)+Erev-E0))-CsolTEMPOplus*exp(-alphar*ne*ff*(-abs(v*t-Erev+Eini)+Erev-E0)))
  Set k_c for TEMPOplus at: 0
  Set c_b for TEMPOplus at: CsolStarTEMPOplus

Air/water interface boundary
  Condition: Flux
  Set N_0 for TEMPO at: -react_surfTEMPO
  Set k_c: 0
  Set c_b: CsolStarTEMPO

  Set N_0 for TEMPOplus at: -react_surfTEMPOplus
  Set k_c: 0
  Set c_b: CsolStarTEMPOplus

Subdomain Settings
  For both TEMPO and TEMPOplus
  Set δ_t at: 1
  Set D(isotropic) at: 1
  Set R at: 0

Solver Parameters
Analysis: Transient
Solver: Time dependent
Times: 0:0.1:tend
Relative Tolerance: 0.001
Absolute Tolerance: 0.00001
Linear System Solver: Direct (UMFPACK)
Matrix symmetry: Nonsymmetric