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SURFACE CHARACTERIZATION OF SELF-ASSEMBLED MONOLAYERS FOR APPLICATIONS OF SELECTIVE IONIC TRANSPORT THROUGH NANOPOROUS MEMBRANES

BY

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DISSERTATION

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ABSTRACT

Electrokinetics is the study of ionized particles or molecules and their interactions under an applied electric field. Transport processes include those of colloids and other charged particles in electrolytes, whose motion under applied external electric fields is described in part by fluid mechanics.

In particular, there is growing interest for the application of electromigration through nanoporous membranes to water desalination. For thin double layers, the volumetric flow ratio (VFR) between electroosmosis and pressure driven flow is inversely proportional to $1/r^2$, indicating the advantages of utilizing electrokinetics for systems with small characteristics length scales.

Bare solid surfaces of metal and metal oxides tend to adsorb organic contaminants in order to lower the free energy between the metal and the environment. The adsorbed matter can alter the interfacial properties of microfluidic and nanofluidic systems. The adsorbed matter does not have any specific functional properties; therefore, it is hard to reproduce any physical properties (e.g., thermoconductivity, electroconductivity, hydrophobicity). Self-assembled monolayers (SAMs) provide a unique way to control and functionalize the interfacial properties of metal, metal oxide, and semiconductors for nanoscale devices. The control in functionality can improve the performance of nanoscale devices by improving process precision.

In this dissertation, a focus of interfacial transport phenomena is proposed in order to achieve improved-charge selective nanofluidic systems. There have been numerous studies on the quality of organic SAMs as a blocking mechanism for prevention of ion
adsorption with applications ranging from biosensors to chemical sensing through nanoporous membranes. The applications of these devices are often limited by the quality of the SAM. For transport studies utilizing a SAM on a gold-coated nanoporous membrane, electrochemical impedance spectroscopy (EIS) can be used as a probe to characterize insulative surface properties. Insulation is especially crucial for short length scales found in microchannels and nanopores. A well-grown monolayer can help reduce adsorption of ions on walls of nanopores/nanochannels, which can lead to lower irreversibilities for charge selective systems.

There have been extensive studies, which demonstrate that by making a polymer membrane conductive mostly through a process called electroless gold plating, that charge selectivity can be accomplished by controlling the surface charge of the conductive membrane by applying a range of cathodic and anodic potentials. The membranes are functionalized with SAMs in order to prevent adsorption of ions. Past work has shown that selectivity of ion adsorption can vary, depending on whether anodic or cathodic potentials are applied across the membrane. A second motivation of this work has been to study and characterize the quality of SAMs with the intent to minimize adsorption ions on a membrane surface in order to maximize charge selectivity. By minimizing adsorption, smaller over-potentials can be applied to achieve charge selectivity.

Lastly, the fabrication of a membrane permeate flow cell is described which was then utilized to study the transport of organic analytes through a conductive nano-capillary array membrane (NCAM) by UV absorption spectroscopy. The goals of the transport studies are to demonstrate improved charge selectivity when well-grown SAMs are used over a wide range of potentials applied across a membrane. In addition, the studies are to
further implement chemical separations by applying potentials within the millivolt range (≤±400 mV). This work improves on previous studies of applying potentials across conductive NCAMs by determining the critical voltage range at which potentials can be applied with minimum ion conduction through the SAM.

Future work will also be addressed where it is suggested to explore the idea of competing effects between the contributions of the diffuse layer potential at the membrane surface and nanopore wall.
To my family
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Chapter 1: Introduction

1.1. Charge Selective Systems for Separation Processes

1.1.1. Water Desalination

Most of the earth is covered by water, however; 97% of this water is not consumable by humans. Of the remaining three percent, two percent of the water is found in glaciers and ice caps. The remainder one percent of water is surface and groundwater, which is available for human consumption. The demand for water globally has placed a strain on the available freshwater [1]. The causes have been a combination of increase in world population, industrialization in developing countries, and the inefficiencies in managing wastewater [2]. Desalination is a process for extracting fresh water from saline water. The two main desalination processes are done by thermal and membrane technologies. Thermal technologies use heat to vaporize water and subsequently condense the vapor to attain clean water. Membrane technologies separate feed streams into concentrate and dilute streams by ionic separation processes. The two membrane technologies that exist on the market today are reverse osmosis (RO) and electrodialysis (ED). RO is a membrane process in which a pressure is applied across a selective membrane. The solvent is passed through the RO membrane while the solute is retained. However, 55% of the irreversibilities found in RO systems are a result of large pressure drops associated with the diffusion of water through the RO membrane [3].

The impact of using an electric field to drive ions across a nanoporous membrane can be approximated by the volumetric flow ratio (VFR). The VFR is defined as:
\[ VFR = \frac{\text{flow rate due to electroosmosis}}{\text{flow rate due to pressure}} \]  

where the flowrate due to pressure derives from the Hagen-Poiseuille approximation.

Because the VFR scales to \( \frac{1}{r^2} \), there is an advantage to driving ions across nanoporous membranes using externally applied electric fields in contrast to using hydrodynamic driven flow. ED is an electrochemical process used for separation of ions across permselective membranes. ED uses a DC bias as a driving mechanism to selectively transport ions across membranes. When a DC bias is applied across the membrane stacks, cations migrate towards the cathode and anions migrate towards the anode. This process has been used for the production of drinking water from brackish and seawater. The current efficiency (CE) is a parameter, which can determine the optimum range for ED systems to operate under. CE is the ratio of current carrying contaminant ions to total current, multiplied by the ratio of output clean water flow to input flow. Some of the losses in ED systems can be attributed to non-ideal permselectivity and physical leakage of the membrane. Figure 1.1 demonstrates how a typical ED system operates. The streams that are adjacent to the electrodes are called the concentrate streams. These two streams are where ions migrate across the membrane to be washed away as the concentrated brackish solution. The stream in between two ion-exchange membranes is the dilute stream. It is the location where production of potable water occurs.
There is also ongoing research that demonstrates the energy required for desalination of ED processes can be recovered by utilizing a reverse electrodialysis (RE) process [4-9]. The basic principles are that a considerable amount of energy can be recovered (up to 80%) by taking advantage of the difference in electrochemical potentials between river water and seawater [10].

In this work, nanocapillary array membranes (NCAMs) coated with gold were used to control the surface charge of the membrane. The goal was to study the permselectivity of conductive-coated membranes under an applied electric field. In the absence of functionalizing the Au-coated membrane surface, it was found that the system was limited to small voltage ranges without considerable adsorption of ions on the gold surface or considerable faradaic current. This in turn limited the selectivity of the NCAM. Irreversible changes in charge selectivity can occur by the adsorption of ions on the surface of the Au coated membrane. Functionalizing the membrane with self-assembled monolayers (SAMs) can help reduce irreversibilities at the membrane surface. In our lab, we have electrochemically studied the quality of SAMs under various electrochemical
conditions. Improving the SAM structure on the membrane surface can lead to improved charge selectivity across the membrane.

1.1.2. Ionic Transport Through Nanoporous Membrane

Nanoporous membranes have received great attention in the fields of water desalination, biosensing, and chemical separations [1, 10-24]. There have been numerous studies for separation of biomolecules and analytes based on charge selectivity [25-30]. It has been demonstrated that proteins can be separated by applying potentials across conductive alumina membranes [31]. Cheow et al. developed a platinum coated nanoporous alumina membrane to demonstrate the permselectivity of proteins by applying different potentials across the membrane [32]. The alumina membranes were made conductive by physical sputtering with platinum on each side of the alumina membrane surface. Several studies have also been done demonstrating charge selectivity through nanoporous membranes [2, 5, 33-36]. Studies have included fabrication of ion-tracked polyethylene terephthalate membranes, with the surface terminated with carboxylate terminal groups [12]. The membranes selectively transported cations and prevented migration of anions. Attaching amino moieties on the membranes surface and pore wall proved to reverse the selective properties of the membrane. It has also been demonstrated that functionalizing gold nanotubule membranes with SAMs could alter the pH responsiveness of the membrane [37]. Selective transport through nanopores has also been found to be dependent on the hydrophobic interaction between the analyte and membrane surfaces. Zenglian et al. used an electroless gold-deposited PCTE membrane with a
modified thiol surface which was hydrophobic, to study mass transport experiments of two molecules, and the effects of adding alkyl surfactants [38].

Initially, we performed potentiometric experiments on an electroless gold-coated NCAM using a u-tube permeation cell. This study was followed by an investigation of transport through nanopores under an externally applied electric field across the membrane using UV absorption spectroscopy. Applying low potentials across the membrane (±400 mV range), allows high field strengths to be achieved across the nanopore. The goal in this work is to explore the electrochemical behavior of the membrane system by using electrical-chemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). In the absence of functionalizing the Au coated membrane surface, it was found that the system was limited to small voltage ranges which could be applied with minimum faradaic current. In addition, SAMs with different terminal groups were covalently bonded to the membrane system in order to prevent the adsorption of ions. This enabled a larger potential range, which could be applied across the membrane. In addition, the membrane selectivity improved when a SAM was attached to the membrane surface.

1.1.3. Protein Separations Using Charge Selective Transport

Separation of proteins in microfluidic devices has become a growing and developing field. Because proteins are in the order of nanometers in size, there is a need to develop nanoscale fluidic channels and nanopores. This has lead to more research on the integration of nanofluidic and microfluidic devices on one chip. The introduction of nanofluidic devices has led to the necessity of understanding the transport phenomena of ions at the nanoscale. There are a number of ways in which protein separation processes
are done. One such method is controlling protein charge by adjusting the pH about the protein's isoelectric point. This method is known as isotachophorisis, brings a protein molecule to its isoelectric focus. Manipulating the pH of the buffer solution can control the point at which the protein no longer is dependent on the external electric field applied across the system.

Other techniques include the integration of a nanoporous membrane to act as preconcentrators for proteins. The advantage of using preconcentration techniques includes the lack of complexity for integrating the membrane within a microfluidic chip. One of the challenges in isotachophorisis is the complexity of making buffer solutions with varying pH within the microfluidic system. The motivation of preconcentration of proteins is to be able to collect and detect very small concentrations of

![Figure 1. Cross channel with laser-patterned porous polymer membrane used for the present studies. The channel width and depth are 80 and 20 μm. The membrane thickness is roughly 50 μm.](image1)

**Figure 1.** Cross channel with laser-patterned porous polymer membrane used for the present studies. The channel width and depth are 80 and 20 μm. The membrane thickness is roughly 50 μm.

![Figure 2. Membrane schematic and background-corrected images of protein concentration. Microchannel edges have been drawn for clarity: HV, high voltage; PV, pinch voltage (PV = 0.45 HV); GND, ground. (a) Schematic. S denotes sample, W waste, B buffer, and SW sample waste. (b) Before loading. (c) After loading. (d) During injection.](image2)

**Figure 2.** Membrane schematic and background-corrected images of protein concentration. Microchannel edges have been drawn for clarity: HV, high voltage; PV, pinch voltage (PV = 0.45 HV); GND, ground. (a) Schematic. S denotes sample, W waste, B buffer, and SW sample waste. (b) Before loading. (c) After loading. (d) During injection.

**Figure 1.2.** Images of the protein concentration device in which the membrane was fabricated between a cross channel of microchips. Samples of proteins were loaded in the section of the device labeled S. Reprinted with permission from Analytical Chemistry, 76, 4589-4592, Song S. et al., Electrophoretic Concentration of Proteins at Laser-Patterned Nanoporous Membranes in Microchips.
protein molecules in an electrolyte solution. Preconcentrating the proteins increases the
signal to noise ratio. Song et al. fabricated a protein concentration device in which the
membrane was fabricated between a cross channel of microchips. Samples of proteins
were loaded in the section of the device labeled S shown in figure 1.2 [39]. A range of
voltages were applied between the sample and sample waste reservoirs. A pinch voltage
was applied to the buffer and waste membrane to reduce diffusion-related losses of protein
concentration at the membrane surface

1.2 The Promise and Challenges of SAMs for Applications to
Nanoscale Devices

Bare solid surfaces of metal and metal oxides tend to adsorb organic contaminants
in order to lower the free energy between the metal and the environment. The adsorbed
matter can alter the interfacial properties of metals and metal oxides. These contaminants
can alter the electrochemical properties of a nanopore or nanochannel. The adsorbed
matter does not have any specific functional properties; therefore, it is hard to reproduce
any physical properties (e.g. thermoconductivity, electroconductivity, hydrophobicity).
SAMs provide a unique way to control and functionalize the interfacial properties of metal,
metal oxide, and semiconductors. SAMs can be used to control the surface charge,
hydrophobicity, and electrical properties of nanoscale devices. Therefore, in addition to
the isotachophoresis study mentioned in section 1.1.2, SAMs can be used to control the
interfacial properties at the solid-liquid interface as a mechanism to control electrokinetic
transport in nanochannels and nanopores.
1.2.1. SAMs Used for Biosensing

The remarkable specificity and catalytic power of enzyme proteins have attracted investigators to immobilize enzymes on electrodes and harness them to collect or supply electrons to and from entities in solution [22, 23, 40, 41]. This idea forms the foundation of enzyme electrode biosensors. For instance, glucose oxidase (GOD) has been used as a sensor for glucose. Proteins (enzymes) generally denature upon contact with metal. Denaturing of the protein can lead to a loss of its electrochemical activity. Redox species in solution that couple directly to the metal can be a source of redox interference. SAMs can act as a promoter to provide an adsorption surface for enzymes (positive or negative charged terminal groups are possible). The SAM can prevent direct contact of solution with metal, thus reducing the redox interference. Lowering the interaction of enzymes with bare metal surfaces decreases background current interference. Figure 1.3 shows a biosensor application in which superoxide reacts with cytochrome-c for biodetection. This thesis will address how improving the quality of the monolayer can affect the improvement of signal-to-noise ratio for biosensing detection using electrochemical methods. With the proper terminal group, a SAM may be able to bridge the enzyme redox center buried deep within the enzyme. This can promote tunneling through the monolayer, which can increase the signal-to-noise ratio. A suitable promoter, with appropriate terminal group may be able to
**Figure 1.3.** Depiction of Cytochrome-c (cyt-c) held at oxidized potentials in order for cytochrome c (cyt c) to be able to react and act as a reducing agent for superoxide.

Bridge the enzyme redox center buried deep within the enzyme. Successive electron hops facilitate this process with the proper terminal group. The promoter may reduce electrode capacitance, decreasing charging current. Mixed SAMs can modify surface properties and enhance adsorption of enzyme. Covalent binding of enzyme to promoter is possible with suitable chemistry.

**1.2.2. SAMs Used for Chemical Sensing**

Membranes have been used for chemical sensing. Past studies have shown that detection of analytes can be achieved by interactions with the membrane surface/pore wall [42-44]. If specific adsorption of a molecule occurs on the membrane surface, then the detection limit will be degraded by the loss of interaction between the membrane surface
and analyte. If the selectivity can be improved, then detection can be improved for a specific molecule of interest. Achieving selectivity at lower voltages results in minimizing faradaic currents. This can play an important role for improving signal-to-noise (S/N) ratios. Redox currents typically increase the background current noise. If detection can be accomplished with low voltages, then faradaic currents can be minimized, thus improving S/N ratio (e.g. superoxide detection). Martin and many others authors have used the electroless gold deposition process to gold Nano Capillary Array Membranes for applications of chemical sensing [45-48]. The first process consists of sensitization by immersing the membrane in a tin solution. The second step consists of activation, by immersing the membrane in a solution of silver. The third step consists of Au particles galvanically replacing silver particles, secondary to gold being more noble than silver. The fourth step is the electroless deposition of gold. Figure 1.4 shows an SEM image of gold nanotubes, which was fabricated as part of my PhD work. The gold nucleation sites, which have already formed on the surface, act as catalytic sites for the oxidation of formaldehyde and the reduction of Au$^+$ ions. The reaction is as follows:

$$2\text{Au}^+ + \text{CH}_2\text{O} + 3\text{OH}^- \rightarrow \text{HCOO}^- + 2\text{H}_2\text{O} + 2\text{Au} \quad (1.1).$$

More discussion regarding the electroless deposition process will be discussed in Chapter 4.
1.3. SAMs Used for Microprocessor Cooling

An important research area in thermal management of microprocessor packaging is the improvement of the Thermal Interface Material (TIM). Figure 1.5 shows a typical processor package, such as TIMs, which can constitute over 30% of the thermal budget. A key challenge in improving the performance of the TIMs is reducing the contact resistances between the TIM and the package. As such, the improvement of the interfacial thermal conductance is critical. A previous study concentrated on measuring the interfacial thermal conductance of self assembled monolayers (with different head and tail groups) and suggested that the conductance was dependent on the bond energy between the headgroup of the SAM and the substrate (SiO$_2$) [23]. A mixture of monolayers with thiol
and methyl-terminated headgroups was used to grow a SAM on the gold substrate to investigate its thermal conductance properties. The methyl-terminated SAM was bonded to a gold substrate through physisorption, which is a bond from Van Der Waals forces between the methyl terminated SAM and the gold substrate. The thiol-terminated SAM is chemisorbed, or covalently bonded to the gold to form a thiolated bond. Gold-thiol bond

**Figure 1.5.** Typical microprocessing package which shows that TIMs make up a big part of the thermal budget. Reprinted by permission: Employing the Latest Innovative Technologies in Present and Future Electronic Products, Ahmed, R. et al., SemiTherm 2004 Short Course.
strengths are typically 126 kJ/mol or 1.30 eV. These bond strengths are typically an order of magnitude larger than bonds due to van der Waals force attractions. The bonding strength of the monolayer to the gold substrate can increase the interfacial conductivity by 80%. The studies demonstrated that low surface coverage of the SAMs on substrate could lead to lower interfacial conductivities. This could be attributed to the inadequate growth time of the SAM or the micro-roughness of the substrate. The micro-roughness (1-10 nm) of the substrate can influence the quality and structure of the SAM [45]. Some of the challenges for SAMs include the quantification of the SAM’s pinhole density (or number of defects) that might affect the interfacial thermal conductance. The pinhole density may be quantified by several methods including atomic force microscopy (AFM), scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS) [46-55]. Several factors including some of the parameters for growing the SAM (annealing of substrate, temperature of thiol solution, immersion time of substrate in monolayer solution) on the substrate may lead to an overall improved monolayer structure. The equipment required to measure the thermal conductance of SAMs can be implemented by time-domain thermoreflectane (TDTR). Figure 1.6 shows the dependency of thermal conductance as a function of the concentration of thiol molecules within the monolayer mixture. As the thiol molecular concentration is increased, the interfacial conductance increases.
The Objective and Scope of the Dissertation

My research was focused on demonstrating how thiol monolayers can act as electrical insulators for reduction of adsorption of ions on gold-coated membrane surfaces. The goal of this work is to minimize the irreversibilities associated with selective transport through nanoporous membranes by reduction of adsorbed analytes on the membrane surface.

The first part of my dissertation (Chapters 2-3) focuses on surface characterization of monolayers on gold surfaces in order to understand the electrochemical properties associated with ionic transport through monolayers. The goal of this work was to develop
and understand the intrinsic properties of SAMs when potentials are applied across the surface. This research includes using electrochemical impedance spectroscopy (EIS) as a means of finding the insulative behavior of SAMs. The work also addresses how SAMs are affected by temperature, applied potentials, and the surface roughness of the substrate in which the SAM are grown on.

In Chapter 2, the idea behind SAM quality quantification is discussed. In addition, a discussion is presented on how the dependency of intrinsic properties of SAMs varies with the ionic strength of the electrolyte. Based on these basic principles, the performance of SAMs is further investigated under different electrochemical environments. In chapter 3, the electrochemical properties are investigated under a range of cathodic and anodic potentials. Chapter 3 focuses on how the role of van der Walls interactions from the molecular chains of SAMs can affect the quality of SAMs. In chapter 4, a background on electrokinetics is discussed with applications for studying ionic transport through nanopores. The governing equations of electrokinetic flow as well as some of the applications associated with electrokinetic phenomena are addressed. In addition, methods to characterize and measure surface charges within nanochannels are discussed.

Lastly, the fabrication of a membrane permeate flow cell is described with the aim of subsequently studying the transport of naphthalene and methyl viologen through a conductive nano-capillary array membrane (NCAM) by UV absorption spectroscopy. The membrane was made conductive by sputter coating gold on the PCTE membrane surface. In particular, the voltage range that can be applied to the Au-coated membrane without getting a considerable faradaic current; the role of naphthalene disodium disulfonate
(NDS\textsuperscript{2-}) and methyl viologen (MV\textsuperscript{2+}) in redox reactions; and the procedure for the preparation of Au coated membranes are carefully outlined.

1.5. References


Chapter 2: Insulative Behavior of Thiolated Monolayers on Gold

2.1. Introduction

Electrodialysis (ED) is an electrochemical process used for the separation of ions across perm-selective membranes. ED was first introduced during the 1950’s [1]. The most significant application of ED is production of potable water from brackish water. ED has also been used in the electroplating industry for the removal and recovery of metal ions—which can include nickel, zinc, and tin—from plating bath solutions. ED processes are also used in the food and biological industries. Some of these processes may include demineralization of cane sugar juice, deacidification of fruit juices, and desalination of cheese whey used in ice cream, sauces, and infant formulas [2]. High purity water is needed in the power industry for supplying supercritical boilers. Special attention is paid in removing silica to avoid mechanical failure in the steam systems.

For concentrations less than 5000 ppm, ED is a more economical process than reverse osmosis. ED plants in the United States were first developed and commercialized during the late 70’s. Today, there are more than 2000 plants in the U.S., which can produce 1,000,000 m$^3$ of potable water each day. ED is not an economical process for purifying dilute water because of the high resistance across the membrane that develops from concentration polarization (CP).

The current efficiency (CE) of the ED process can be expressed as:

$$CE(\%) = \frac{2FQ_f (C_i - C_o)}{NI} \times 100$$  \hspace{1cm} (2.1),
where z is the valency of the ion, F is the Faraday constant (96,485 C/mol), $Q_f$ is the dilute flowrate, N is the number of membrane stacks, and I is the current required to drive the ions across the membrane stacks. CE is an important parameter that can determine the optimal range for the ED process to operate. The energy cost associated with ED can be from the large current required to drive ions across ED membrane stacks. Large overpotentials are required for ED processes to overcome large solution resistances across the unstirred diffusion boundary layer (DBL) and the electrodes. This chapter addresses the idea of using conductive nano-capillary-array membranes (NCAMs) to reduce the potential required to drive ions across a membrane. This voltage reduction is achieved by applying smaller potentials across the NCAM in conjunction with creating high field strengths across the nanopore to selectively transport ions.

As mentioned in section 1.1.2, some of the losses that affect the current efficiency are found from the permselectivity of the membrane and membrane leakage, which leads to back diffusion. Back diffusion occurs as a result of counterions diffusing back from the concentrated ED cell to the dilute cell. Adsorption of anions on gold can reduce the selective properties of conductive NCAMs [3]. Our studies aim to demonstrate how thiol monolayers on gold can be used to improve selectivity of ions through conductive NCAMs. We report the characterization of such monolayers on gold-coated microscope slides. This lays the groundwork for using SAMs to reduce the adsorption of ions on the NCAM in order to improve charge selectivity. In this work, electrochemical impedance spectroscopy (EIS) is used to measure the characteristics of gold (Au)-coated membranes and their inherent limitations. The fabrication of a membrane permeate flow cell is described with the aim of subsequently studying the transport of ions through a conductive polycarbonate
track etched membrane (PCTE), coated by hydrophilic Polyvinylpyrrolidone (PVP), by interrogating the system using EIS and CV measurements. In particular, we would like to ascertain the voltage range that can be applied to the Au-coated membrane without getting considerable faradaic current, the difference between platinum and Au electrode, and the effects of different electrolyte concentrations for a range of applied DC potentials.

2.2. Electrodialysis

Figure 2.1 is a schematic of the operation of a typical ED cell. The streams that are adjacent to the electrodes are the concentrate streams. These two streams are where ions migrate across the membrane to be washed away as the concentrated brackish solution. The stream in between two ion-exchange membranes is the dilute stream. This stream is where production of potable water occurs. When a DC bias is applied across two membranes, cations migrate towards the cathode and anions migrate towards the anode.

**Figure 2.1.** Schematic of a typical ED cell which consists of anion exchange membranes (AEM) and anion exchange membranes (CEM) in series.
At the electrodes, hydrogen and oxygen gas are formed due to water electrolysis. As a result of these reactions, hydronium ions will accumulate at the anode and hydroxide ions will accumulate at the cathodes affecting the local pH at the electrode-electrolyte interface.

2.3. Current Efficiency and Limitations For ED

For electrodialysis processes, concentration polarization can play a critical role for the separation rate of ions. Some of the parameters that can affect CP effects, include applied current density, feed flow rate, and the characteristics of the surface of the membrane. When counterions are transported across a permselective membrane, a depletion of ions occurs at the interface of the dilute cell and enrichment occurs at the interface of the concentrated cell. As time increases, the concentration of counterions continues to decrease as a result of more ions migrating across the membrane to the concentrated ED cell. An increase in resistance leads to a higher energy consumption per unit of salt. As the concentration of ions within the diffusion boundary layer at the dilute membrane interface approaches zero, the current density reaches a plateau. The maximum current is known as the limiting current density, which is the current density that occurs when mass transport across the membrane reaches a maximum. CP is a result of concentration gradients, which are formed at the membrane-electrolyte interfaces. A schematic of CP can be observed in Figure 2a. As can be visualized, the CP zone, also referred to as the unstirred layer, develops due to local concentration gradients between the interface of the membrane and the bulk solution. The limitations of ED results are secondary to lower current efficiencies, which are achieved when the voltages applied
exceed the limiting current density. This leads to an increase in resistance across the unstripped layer or boundary layer. The limiting current can be found by plotting the resistance $(E/I)$ of the membrane stack with respect to the inverse measured current $(I^{-1})$ [4]. Higher current densities can be achieved beyond the limiting current density. One way of decreasing the thickness of the unstripped layer is by use of vigorous stirring [5]. Larger current densities can also be achieved by applying higher field strengths across the membrane stacks as shown in Figure 2b. It has been proposed that applying higher potentials to achieve current densities larger than the limiting current can be a result of oscillating currents within the diffusion boundary layer [6, 7]. However, it is not recommended for ED processes to operate under conditions above the limiting current density due to the effects of water electrolysis. The increased hydroxyl and hydroxide ions lead to problems associated with scaling of the membrane surface and rupturing of the permselective membranes [4].

**Figure 2.2.** Plot of concentration polarization zone due to depletion of cations. The goal of this work is to reduce the amount of potential required to separate ions. This in turn can reduce the amount of faradaic current at the electrodes, which can lead to smaller diffuse boundary layers at the membrane interface. Reprinted with permission from Journal of Separation Science, 30, 1398-1419, Holtzel, A., Tallerek, U., Review, Ionic conductance of nanopores in microscale analysis systems: Where microfluidics meets nanofluidics, Copyright 2007, John Wiley and Sons.
2.4. Concentration Polarization

In membrane processes, concentration polarization (CP) affects almost all membrane separation processes and can be the cause of a substantial reduction in the separation factor and flux [8-11]. Theoretical models have been developed to describe distribution of concentration in the boundary layer on the surface of membrane. [12, 13]. Additional studies have been done to find the relationship between CP zone and electroosmotic flow at the membrane interface [14]. In addition, the effect of CP on the performance of electroosmotic pump was studied by observing the propagating of CP in an EO system [15].

Computational studies have been done to study parameters, which can minimize the CP zone. Pak et al. studied the prediction of the growth rate of the concentration polarization boundary layer and effect of Reynolds number along the length of tubular membranes [16]. Ahmad et al. concluded according to their CFD simulations that CP tends to increase for narrow membrane channels and smaller wall shear stresses at the membrane-solution interface [17]. Santiago and coworkers studied concentration polarization both experimentally and computationally [18-20]. A computational model was able to accurately predict the existence of CP with propagating enrichment and depletion shocks in a microchannel-nanochannel system on the basis of separately determining the zeta potential and ion mobility. Kim et al studied the depletion region in order to investigate the effects on CP [21]. It was found that ion depletion occurs even at high buffer solution concentrations and the electrical field strength and nonlinear
electrokinetic mixing affect the diffusion length. The thickness of boundary layers depend on the interactions with the solute and the surface. Studies have shown that boundary layer thickness can range from a subnanometer to several hundred nanometers [22]. Theoretical studies in nanofluidics have furthermore speculated on the consequences of combining different boundary phenomena, such as liquid slip with electroosmotic flow, or liquid slip with diffusion-osmosis [9–11].

2.5. The Use of Self-Assembled Monolayers for Reduction of Concentration Polarization

One of the major challenges of microfluidics and nanofluidics are the charged surfaces formed when in contact with a solution, which promote organic molecules to adsorb on the surface. The main contributions to specific adsorption of molecules are due to hydrophobic, electrostatic, and van der Waals forces. In the present study, the effects of PEG for adsorption of organic analytes were studied on a glass surface. In addition to alkane SAMs, it has been shown that polyethylene glycol (PEG) can help reduce adsorption of proteins by up to 80% [23]. The structure of PEG includes hydroxyl groups at both ends of the molecule (HO(CH₂CH₂O)ₙCH₂CH₂OH). PEG is highly soluble in water due to its similarity in molecule structure, resulting in strong hydrogen bonding. When a protein approaches a surface coated with PEG, repulsive steric forces act on the protein, which results in a loss of conformational freedom from the PEG chains [24]. The second repulsive effect comes from osmotic effects at the membrane interface [24].

PEG can reduce the CP zone by reducing the number of molecules that adsorb on the membrane surface. In the literature, there have been two primary methods in forming a
thin layer of PEG on a glass surface. The first involves a covalent coupling technique, which is done by reacting PEG with silicon tetrachloride using a catalyst (triethylamine) [24]. This reaction leads to the formation of PEG-OSiCl$_3$. The hydrolysis of this molecule at the glass surface results in a Si-O-Si bond. The second method involves the reaction of PEG with an end alcohol group, which forms a Si-O-C bond on a silica layer [25]. In our method, a methoxy-based silane was attached directly to the SiOH surface. Prior to coating the surface with PEG, our surfaces were immersed in a piranha solution to remove all the organic contaminants. When coating the surface with PEG, all work was done in an anhydrous environment under a chemical hood. PEG solution was prepared by dissolving powdered PEG in a 100% anhydrous ethanol at room temperature. After several hours, the glass surfaces were removed from the PEG solution and rinsed with ethanol. Subsequently, PEG-coated glass surfaces were placed in an oven for several hours for polymerization to occur.

Several glass samples were immersed in 100 ppm of a fluorescent-tagged polystyrene-based molecule in potassium phosphate buffer (PB, pH 7.4) for one hour. Samples were then rinsed several times with deionized water for removal of non-adsorbed colloids and salts. A fluorescence microscope was used to observe the amount of fluorescent molecule adsorbed. As seen from Figures 3 and 4, there is a reduction of adsorbed PBS when a glass surface is pretreated with PEG. The amount of adsorbed PBS will be a strong function of how well the monolayer is formed on the SiOH surface. Therefore, there is a motivation to study the quality of a well-formed SAM. In the following sections, we explore by EIS, how to determine the quality of a SAM grown on a
substrate using EIS. Further studies also investigate how to improve on the quality of the monolayer by growing the SAM under different incubation times.

Figure 2.3. A fluorescent image of glass surfaces without PEG coating.
Figure 2.4. A fluorescent image of glass surface pretreated in PEG solution.
2.6. Introduction to Self Assembled Monolayers

Bare solid surfaces of metal and metal oxides tend to adsorb organic contaminants in order to lower the free energy between the metal and environment. The adsorbed matter can alter the interfacial properties of microfluidic and nanofluidic systems. The adsorbed matter does not have any specific functional properties; therefore, it is hard to reproduce any physical properties (e.g. thermoconductivity, electroconductivity, hydrophobicity). SAMs provide a unique way to control and functionalize the interfacial properties between metal, metal oxide, and semiconductors for nanoscale devices. The control in functionality can improve the performance of nanoscale devices by improving the signal-to-noise ratio.

SAMs typically range in thickness from 1-3 nanometers (nm). As the size of a system decreases, and the characteristic length of a material is reduced to a nanoscale dimension, a high surface:volume ratio forms [26-28]. Because atoms on a surface are not bonded to neighboring atoms, they experience different surface energies, electronic states, and structures in the nanoscale regime [29]. SAMs are formed on many different metal-coated substrates including glass, silicon, colloids, and nanoporous membranes. Several spectroscopic measurements—including X-ray photon spectroscopy (XPS), mass spectroscopy, atomic force microscopy (AFM), and scanning tunneling microscopy (STM)—are used to characterize the structure of SAMs [28, 30-33]. Usually a small thin film is deposited on the substrate before gold is deposited. This layer is usually 1-5 nm thick. An adhesion layer is added to promote bonding between the gold and the substrate. Because gold is a noble metal, it does not readily form an oxide layer, which prevents good adhesion to the substrate. The formation of an oxide layer on the metal is important since most of the substrates usually form oxide layers (e.g. glass or silicon). Adhesion layers also
aid in providing a smoother surface when gold or other metals are deposited. Titanium, chromium, and nickel are some examples of adhesion layers that are used. Although chromium is commonly used for adhesion layers, they are known to diffuse through the metal film. Furthermore, chromium layers may not be suitable for bioapplications, as they are known to be harmful to biomolecules. In our experiments, we chose to use titanium as an adhesion layer between the silica surface and the thin gold layer. Titanium is known to have less effect for contaminating organic molecules. In our experiments, a 200-nm thick gold film was used. Studies have shown that alkane thiols on gold are stable in phosphate buffer for several weeks [34]. Gold is commonly used as a substrate for SAMs because it does not react readily with O₂ in the atmosphere. Avoiding oxidation on a metal is crucial when studying the insulative behavior of SAMs, or studying ionic transport through nanopores/nanochannels. Mercury is another candidate for studying electron transport through monolayers, since atomically it has a smoother surface than gold. However, Hg is not appropriate for biouse or for assembly of stable surfaces due to its toxicity and liquidity.

The formation of a thiolated monolayer on a gold surface requires activation energy for bonding between thiol and gold to occur. Techniques to find the activation energy usually include temperature-programmed desorption in which the substrate is heated up (few degree per second) to an optimum temperature at which desorption of molecules occur [35-40]. The activation energy for desorption can be measured, which is related to the heat of adsorption when the process is assumed reversible. The thiol-terminated SAM is chemisorbed, or covalently bonded to the gold to form a thiolated bond. During the bonding process of disulfide, it is thought that hydrogen is lost and forms dihydrogen (H₂) [26]. These bond strengths are typically 126 kJ/mol or 1.30 eV, which are typically an
order of magnitude larger than bonds formed from lateral bonding forces [27]. The forces between the disulfide and gold are strong enough to prevent desorption of disulfide at room temperature. At higher temperatures, formation of disulfides from the thiol monolayer is kinetically possible. The organization of the monolayer occurs through three main processes. The first step is the formation of the disulfide or thiol gold bond. The second process involves lateral bonding between the molecular chains of SAMs from Van Der Waals (VDW) forces. These forces dictate the densities of the sulfur atoms on the surface and the molecular arrangement. The third step includes tilting of the molecular chains to maximize the VDW forces. The kinetics for the latter two steps of organization of the monolayer structure are orders of magnitude lower than the covalent bonding process, which occurs within minutes. The rate-limiting steps are therefore the organization of the monolayer structure after covalent bonding at the gold substrate has occurred. More discussion of the kinetic process of SAM formation will be addressed in Chapter 3.

2.7. Electrochemical Impedance Spectroscopy

The impedance of a membrane is one of the factors that determine how much energy is expended during the ED process. Electrochemical impedance spectroscopy (EIS) is a non-invasive way to study the electrochemical properties of nanoporous membranes [41-45]. EIS is a tool that can identify mechanisms occurring for an electrochemical system by simultaneously monitoring the phase and impedance characteristics of the system, while scanning over a wide frequency range. Fouling, which is a challenge when using membrane systems for separation processes, has also been studied using EIS by
studying the capacitive change of the double layer at the interface between the surface of the membrane and electrolyte solution [41].

EIS measurements are done by applying an AC potential (with known amplitude) over a range of frequencies and measuring the current response of the system. By measuring the current of the electrochemical cell, the overall impedance may be determined by dividing the phasor voltage by the phasor current. The impedance may be represented as a real and imaginary part as shown in equations 2.2:

\[
Z = \frac{E_t}{I_t} = \frac{E_0 \sin(wt)}{I_0 \sin(wt+\theta)} = Z_0 \frac{\sin(wt)}{\sin(wt+\theta)}
\]  

(2.2)

The real and imaginary part describes the Ohmic and capacitative nature of the system respectively. Figure 2.5a-c demonstrates a Bode plot, Nyquist plot, and an equivalent linear circuit model used to fit the mechanistic behavior of the electrochemical system being studied. The Bode plot demonstrates the behavior of an electrochemical system over a range of frequencies. At low frequencies, the two plots exhibit that the system’s impedance is real as a result of ion conduction through a SAM or redox reactions at the working electrode. At higher frequencies, the phase of the system approaches a value of -90°, displaying the capacitative component of the system. This capacitative nature of the system is a result of the double layer charging at the surface of the electrochemical system. Figure 2.5c is a Randles circuit, which models an electrochemical system in which the solution resistance is in series with an RC circuit. The model is used when a SAM is
considered to be a “nonperfect” insulator to ion conduction. More detail is discussed in Chapter 3 using linear circuit modeling for EIS measurements.

**Figure 2.5.** The plots above are examples of common EIS plots and circuit models used for analyzing EIS data [46]. Figure (a) is a Bode plot, which displays the magnitude of the impedance and phase of the system. Figure (b) is a Randles circuit model, which is used to fit EIS data when the system contains exhibits a resistive behavior either from ion conduction through a monolayer or redox reactions at the surface of the working electrode. Figure (c) is an example of a Randles circuit, which can be used to linearly fit EIS data.

Additional electrolytic systems may show mass transfer impedances (also called the Warburg impedance) at low frequencies and high DC potentials, which promote facile kinetic reactions at the working electrode. The Nyquist plot provides a good indication of limiting current by displaying a 45° angle as seen figure 2.6a. The circuit model, which is similar to a Randles circuit, adds a Warburg impedance to account for the impedance from
mass transport limitations at lower frequencies. At higher frequencies, the mass transfer impedance is too low, since the time scale is too small for any diffusion to occur.

(a)

Figure 2.6. Figure a is a Nyquist plot, which shows a line of 45° at low frequencies, which is an indication of mass transport limitations [46]. Figure b is a linear circuit model, which uses a Warburg impedance to account for mass transport effects at low frequencies.
2.8. Electrochemical Instrumentation and Measurements

Electrochemical measurements were performed using a Gamry Reference 600 (Gamry Instruments, Warminster, PA), which is shown in figure 2.7.

Figure 2.7. Image of the electrochemical cell where EIS experiments were performed. All test solutions were initially purged with nitrogen for 15 minutes prior to experiments to prevent redox reactions with oxygen.

Employing a three-electrode cell: the monolayer-coated gold surface acted as the working electrode, an Ag/AgCl wire in 3 M NaCl (Bioanalytical Instruments, West Lafayette, IN) as the reference, and a gold wire as the counter electrode. Gold wire counter electrodes (Alfa Aesar, Ward Hill, MA) were used for the impedance measurements. Gold-coated microscope slides were mounted in a custom-designed cell. The gold layer was used as the working electrode as shown in figure 2.8. All potentials are reported with respect to the Ag/AgCl electrode. Phosphate buffer (PB) solutions were prepared as a ratio of mono- and dihydrogen potassium phosphate salts (Sigma-Aldrich, St. Louis, MO) in DI
water. A pH=7 was used for all electrolyte solutions, with concentrations ranging from 1 mM – 50 mM.

Figure 2.8. Schematic of the electrochemical cell used to perform EIS experiments. The working, reference, and counter leads were connected to the gold substrate Ag/AgCl reference electrode, and gold wire.

The electrolyte solutions were bubbled for 15 minutes with nitrogen to remove oxygen prior to electrochemical characterization. All experiments were done within a Faraday cage to eliminate any external noise while performing experiments as shown in figure 2.8.

2.9. Preparation of Monolayer Surfaces

Self-assembled monolayer (SAM) formation on gold requires a very clean gold surface free of contaminants and subsequent exposure of a pristine gold surface to monolayer-forming molecules. Not all cleaning procedures can be carried out on every
substrate because of substrate limitations, in which case a selected set of procedures have to suffice. The cleaning procedure depends on what the substrate can endure. For example, mechanical polishing can be done on bulk gold electrodes, but would be too harsh for a thin gold substrate 100 nm thick.

10-undecanethiol and 10-undecanol were purchased from Sigma-Aldrich, and dissolved in absolute ethanol (Pharmaco-Aaper, Shelbyville, KY) at a concentration of 1 mM. SPR-quality glass slides (GenTel Biosciences, Madison, WI) coated with evaporated titanium (5 nm) and gold (100 nm) thin films were washed in a heated SC-1 bath (100 mL of DI water/25 mL of H₂O₂/2 mL of NH₄OH) and rinsed thoroughly with DI water (resistivity 18 MΩ-cm) and ethanol.

The clean gold surfaces were incubated in a sealed Petri dish for immersion times ranging from 48 hours to several weeks. The monolayer gold-coated substrates were first electrochemically polished. Electrochemical polishing was done as follows: 0.1 M NaOH was de-aerated with nitrogen gas for 15 minutes, with two cycles being required. The first was a wide and fast sweep from -1.2 to +1.5 V vs. Ag/AgCl at 1 V/s (21 segments). Secondly, without removing the electrode from solution, another (narrow and slow) sweep from -0.8 to 0.6 V vs. Ag/AgCl at 0.05 V/s (21 segments) was performed. The voltage range chosen was based on previous studies, which ensure a monolayer formation of gold oxide [47, 48]. The peak shown in figure 2.9 represents the formation of the gold oxide. The reductive peak represents the stripping of the gold oxide from the gold layer. The number of sweeps was determined by observing that the cyclic voltammogram (CV) plots overlapped. In addition, the pH level was chosen to ensure that there was no oxidation of gold ions into the solution, as shown in Figure 2.10. Figure 2.10 is a Pourbaix diagram,
which provides information on the different electrochemical phases at different pH levels and applied potentials. The advantage of using a basic electrolyte solution is the prevention of oxidation at the titanium adhesion layer.

![Cyclic voltammogram](image)

**Figure 2.9.** Cyclic voltammogram (10th sweep) of a bare gold 100 nm Au substrate. The gold substrate was swept at 1 V s⁻¹ in 0.1 M NaOH

After electrochemical polishing, gold substrate was rinsed with ethanol, which aided in the removal of any remaining oxide layer contributed to by the polishing. Studies have shown that Au₂O₃ can be reduced by reaction with ethanol to form acetaldehyde [49]. The gold oxide layer can impede the formation of a monolayer by preventing coalescing of the SAM to form the most densely packed monolayer. Studies have shown that there can be up to 30% more monolayer coverage when gold substrate is immersed in ethanol solution for thirty minutes.
Not much is known about the effects of the presence of oxygen in solution during the formation of SAMs. Some studies have shown that degassing the solvent before preparing the thiol solution may help in improving the formation of SAMs on the substrate. It is also reported that placing the thiol solution in an inert atmosphere can improve the conditions for SAMs formation. Reducing the concentration of oxygen in solution may help prevent the oxidation of thiols to sulfonates.

2.10. Determination of Electrochemical Surface Area

A method for determining the active area of the gold substrate was done by an oxygen adsorption measurement. The process involves scanning the gold electrode to anodic potentials for an oxide layer formation on the gold surface. It is assumed that the

Figure 2.10. Porbaix diagram, which shows the electrochemical equilibrium phases of within an aqueous environment for gold [1].
monolayer of oxide formed on the gold surface is at a ratio of 1:1. The amount of oxygen necessary for complete surface coverage has been estimated to be 677 µC cm$^{-2}$ for polycrystalline gold [47]. This is based on the thickness of the monolayer, atomic weight, and average density of polycrystalline gold. We wanted to find the microscopic surface area of the Au-substrate by cyclic voltammetry. 100 mM PB was used as the electrolyte solution at pH = 7.

![Graph](image)

**Figure 2.11.** Cyclic voltammogram of a bare gold 100 nm Au substrate. The shaded area under the curve is the oxide peak area, which is integrated to find the total charge. The gold substrate was swept at 50 mV s$^{-1}$.

The Au substrate was SC1 cleaned for 30 minutes with 100:20:1 of DI water, H$_2$O$_2$, and NH$_4$OH. The solution was de-aerated with nitrogen for 15 minutes. Two CV scans were done between -0.061 V and 1.239 V (vs. Ag/AgCl) with a scan rate of 50 mV s$^{-1}$. The total charge was then calculated by integrating the oxide peak area (Figure 2.11). The electrochemical area was calculated to be 0.60 cm$^2$. 
2.11. EIS Experiments

Figure 2.12 is the impedance spectrum of 100 nm Au substrate immersed in 1 mM undecanethiol solution for 48 hours at 0 DC V with respect to Ag/AgCl. As can be seen, the phase angle decreases as electrolyte concentration is increased. This indication shows that there are minor pinhole defects within the monolayer.

![Impedance spectrum (Bode plot) for an undecanethiol SAM formed by 48-hour immersion in various phosphate buffer concentrations. The applied DC potential was 0 V with respect to Ag/AgCl. The magnitudes at 1 Hz (lowest frequency) were 53, 41, and 29 kΩ for 1 mM (■), 10 mM (●), and 50 mM (▲), respectively, while the phases were: -80.75°, -83.13°, -84.07° for 1 mM (■), 10 mM (●), and 50 mM (▲).](image)

The magnitude Bode plot show that as the system is scanned to lower frequencies, the magnitude of the impedances do not overlap because the impedance of the system is not completely capacitive. The change in phase between 1 mM and 50 mM is approximately 5%. Evidence of a “defect free” monolayer can be seen in Figure 2.13. The phase magnitude varies less than 1.5% between 1-50 mM. A brief discussion of a small inductance at high frequencies will be demonstrated in Chapter 3. It is reported that the structure of SAMs do not change significantly when exposed to a 1 mM solution for 12-18
hours [26]. However, evidence has shown that immersion times of 7-10 days can reduce the number of pinholes in the SAM and cause the conformational defects in the alkane chain to decrease. Thus, for applications such as the study of electron transport via tunneling through monolayers or preparation of surfaces—which need to be well insulated from solution redox species—longer immersion times for improved monolayer regularity and stability are needed.

Figure 2.13. Bode phase plot for an undecanethiol SAM formed by immersion in thiol solution for 12-days in various PB concentrations. The applied DC potential was 0 V (vs Ag/AgCl). The phase angles at a frequency of 1 Hz for 1mM (■), 10mM (●), and 50mM (▲) were: -87.3°, -88.3°, and -88.64°, respectively.

EIS can demonstrate more subtle effects that are not clearly seen in a cyclic voltammogram. Boubour and Lennox have shown that below a critical potential, the monolayers no longer act as ionic insulators, and a significant change in phase angle is associated with ion penetration in the low-frequency region. They found that critical potential is dependent on chain length (-0.25 V vs. Ag/AgCl for n=11; -0.35 V for n≥15) [50, 51]. The critical
potentials associated with ionic conduction through the SAMs were at more anodic potentials than the desorption potentials found for alkanethiols (-1.0 to -1.4 V). In fact, it may be within the potential window that is normally taken to be within the double-layer charging potential of the monolayer. The changes to the monolayer can be observed in EIS when the phase angle at 1 Hz begins to deviate from -88° (almost purely capacitive) and begins to have some resistive component. They further found that potential-induced defects are reversible for hydrophobic SAMs but are not reversible for SAMs terminated with hydrophilic groups (-COOH and -OH). This is borne out in our experiments with undecanethiol with a lower phase shift at -0.5 V bias (see Figure 2.14). The effect can also be seen in the Nyquist plot, at the transition where the plot is purely capacitive (straight line) to that region where it becomes semi-circular in nature. The equivalent circuit of the SAM changes from a constant phase element (CPE) in series with solution resistance (a “defect-free” SAM) to a more complicated circuit composed of SAM capacitance, SAM resistance (which reflects ion/water migration), phase transfer resistance (in transporting an ion from the solution to the gold substrate), and defect capacitance, all of which reflect the ability of the SAM to store ions.
Figure 2.14 Bode plot for monolayer formed over 12 days. Impedance spectra were measured in 10 mM phosphate buffer at pH 7, with an applied DC potential. The applied potentials across the monolayer were -0.5 V (♦), -0.2 V (▼), 0 V (▲), 0.2 V (●), and 0.5 V (■).
To develop models for categorizing SAMs into those that are defect-free or those having induced defects, the corresponding impedance data were fitted to equivalent circuits using the algorithms built into the Echem Analyst software package (Gamry, Inc.). Models were constructed using the built-in Model Editor. In the following plots, the solid lines are the fits to the data (symbols). All fitted data are for the 12-day incubation in ethanolic thiol solution, and the electrolyte is 50 mM phosphate buffer. Figure 2.15 shows the equivalent circuits used to model the monolayer in electrolyte solution. Equivalent circuit A is a series combination of a resistance in series with a CPE, which represents the monolayer impedance (Tab. 1). Y represents the admittance parameter for a CPE. It has the unit siemens-second^a (S*s^α).

![Equivalent Circuits](image)

**Figure 2.15.** Equivalent circuits of the thiol monolayer: (A) CPE in series with a solution resistance (equivalent circuit I in [28]), indicative of a “defect-free” SAM. (B) and (C) are equivalent circuits of a SAM with potential induced defect. B) is equivalent circuit II in [28], while (C) is similar to a Randles circuit.
The constant $a$ can range from values of 0-1. When $a=1$, as it is for an ideal capacitor, the unit is equivalent to Farads. The impedance of the CPE model is given as:

$$Z_{CPE} = \frac{1}{Y_o(j\omega^a)} \quad (2.3)$$

where $Y_o$ is the capacitance (F), $\omega$ is the frequency of the applied electric field, and $a$ is the constant which represents the ideality of the capacitor. $R_s$ is the series solution resistance between the working and reference electrodes.

Figure 2.16 shows the Bode plot of a “defect-free” SAM, while Figure 2.17 is that of the same SAM, but with potential-induced defects. Indeed, the fitting shows that the model appropriate to a defect-free SAM is that of a CPE in series with solution resistance. The monolayer CPE/capacitance value obtained is higher (1.2—1.31 $\mu$F cm$^{-2}$) than that reported for a similar thiol (1.11 $\mu$F cm$^{-2}$) in the same buffer concentration. This seems to be reasonable due to the CPE factor being closer to unity than reported [52], implying a well-formed blocking SAM.
Figure 2.16 Bode plot of a “defect-free” undecanethiol SAM in 50 mM PB. The applied potential was 0 V. Solid line is the fit to equivalent circuit A in Figure 2.15.

For the monolayer with -0.5V bias induced defects, we tried to fit the equivalent circuit B [29] using both the simplex and Levenberg-Marquardt method. While appearing to converge, the parameter values we obtained for $C_d$, $C_m$ and $R_m$ (Figure 2.15 B) have error values that are of the same magnitude as the calculated values, indicative of a poor fit. We used a Randles equivalent circuit, whose fit is shown in Figure 2.17. This resulted in values of solution resistance and capacitance that are close to the solution resistance and CPE of the defect-free monolayer, but with the added element of a parallel resistance across the membrane of 135 KΩ. This resistance represents the “leakage resistance” of a SAM with induced defects.
**Figure 2.17.** Bode plot for an undecanethiol SAM with potential-induced defect, in 50 mM PB. Applied voltage was -0.5 V. Solid line is the fit to the Randles equivalent circuit (C in Figure 2.15).

<table>
<thead>
<tr>
<th>Equivalent circuit A (CPE + Rs)</th>
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<tr>
<td>E/V</td>
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<td>0</td>
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*Table 2.1. Fitting parameters obtained from “defect-free” SAM.*

<table>
<thead>
<tr>
<th>Equivalent circuit C (Randles)</th>
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<tr>
<td>E/V</td>
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<tr>
<td>-0.5</td>
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*Table 2.2. Fitting parameters obtained from SAM with potential-induced defects.*

EIS experiments were also performed on a hydroxyl-terminated thiol, as shown in Figure 2.18. We wanted to investigate the applicability of using a hydrophilic SAM due to
the hydrophobic properties of the molecule 1,5 naphthalenedisulfonic acid disodium salt (NDS\(^2^-\)). The number of sulfonates per aromatic ring for NDS\(^2^-\) is 1 [53]. This ratio means that the molecule can exhibit both hydrophobic and hydrophilic behavior. Thus, it is important to understand how the migration behavior of NDS\(^2^-\) changes when exposed to a hydrophilic or hydrophobic surface. An EIS experiment was done on both mercaptoundecanol- and undecanethiol-coated gold using various applied bias voltages. Figure 2.20 summarizes the EIS results for the two monolayers terminated with hydroxyl and methyl groups. It can be seen from the upward inflection of the phase plot that the critical voltage of the mercaptoundecanol was exceeded at ±0.2 V, while the undecanethiol monolayer showed no change at either of these voltage extremes. This clearly demonstrates that the lower critical voltage is exhibited from SAMs with hydroxyl terminated groups (hydrophilic) compared to SAMs terminated with methyl terminated groups (hydrophobic).
**Figure 2.18** Comparison of the insulating behaviors of methyl and hydroxyl terminated SAMs. Insulating behavior of hydroxyl terminated SAM is only found at 0 V, whilst insulating behavior for methyl terminated SAM is found at anodic and cathodic potentials.

This is ascribed to the interaction of the hydrophilic functional groups with the electrolyte ions causing ion penetration of the monolayer at much lower potentials [49].

### 2.12. Conclusions

The use of thiol–modified gold as a blocking mechanism to ion conduction under an externally applied electric field to the membrane surface was demonstrated, with the purpose of studying the potential range on a gold-coated glass substrate-solution interface. The range of voltages and quality of the SAM aided in determining the minimization of Faradaic activity and the prevention of adsorption on the electrode surface. Comparisons of CV and EIS measurements for determination of the quality of a SAM were compared and was determined that EIS can show more subtle effects that are not clearly seen in a cyclic voltammogram. This lays the groundwork for the application of thiol-modified
membranes for the study of ion-selective transport through charged Au-coated membranes. As such, it is important to understand the stability of thiol monolayers used in this application. We also investigated the effect of immersion time on the quality of the monolayer formed, and found that longer immersion time improves the insulating properties of the monolayer, as demonstrated by EIS. The present work has laid the groundwork for finding the limits of applied potentials across the membrane with minimal faradaic currents. In Chapter 5, studies of ionic transport through gold-coated nanoporous PCTE membranes will be addressed.

2.13. References


Chapter 3: Study of Insulating Properties of Alkanethiol SAMs Under Prolonged Incubation Using Electrochemical Impedance Spectroscopy

3.1. Introduction

The electrochemical interfacial properties of a well-ordered, self-assembled monolayer (SAM) of 1-undecanethiol (UDT) on evaporated gold surface have been investigated by electrochemical impedance spectroscopy (EIS) in electrolytes without a redox couple. Using a constant phase element (CPE)-series resistance model, prolonged incubation times (up to 120 h) show decreasing monolayer capacitance approaching the theoretical value for 1-undecanethiol. Using the CPE exponent $\alpha$ as a measure of ideality, it was found that the monolayer approaches an ideal dielectric ($\alpha=0.992$) under prolonged incubation, which is attributed to the reduction of pinholes and defects in the monolayer during coalescence and annealing of SAM chains. The SAMs behave as insulators until a critical potential $V_c$ is exceeded in both cathodic and anodic regimes, where electrolyte ions are believed to penetrate the monolayers. Using a Randles circuit model for these cases, the variation of the capacitance and charge transfer resistance with applied DC potential show decreased permeability to ionic species with prolonged incubation time. The EIS data shows that UDT (methylene chain length n=10), incubated for 120 h, forms a monolayer whose critical voltage range extends from -0.3 to 0.5 V (vs. Ag/AgCl), previously attained only for alkanethiol at n=15. At low frequencies where ion diffusion occurs, almost pure capacitive phase (-89°) were attained with lengthy incubation.
3.2. Background

Interfacial transport at the micro and nanoscale plays a crucial role due to high surface area to volume ratio of micro and nanosystems [1]. SAMs provide a unique way to control and functionalize the interfacial properties at a solid/liquid interface. There have been numerous studies on the quality of organic self-assembled monolayers (SAMs) as a blocking mechanism for prevention of ion adsorption [2-7], with applications ranging from biosensors to nanoscale transport. Studies on charge selectivity have been done on electroless gold-coated polycarbonate track etched membranes (PCTE) [8]. An alkanethiol was used to prevent anion (e.g., chloride ions) adsorption to the gold surface. The membrane was immersed in 1 mM thiol solution for 24 hours. However, it was observed that an irreversibility of charge selectivity occurred due to the poor quality of the monolayer over the gold-coated membrane surface. In addition to prevention of ion adsorption, the diffuse layer potential at the monolayer surface can act as a screening mechanism for nanoscale transport applications [9]. The model of a SAM-covered electrode-electrolyte interface includes the following features: a potential of the metal ($\phi_m$), a potential drop across the monolayer (assumed to be linear); a potential at the surface of the monolayer ($\phi_s$); and, a potential drop in the diffuse layer, all relative to some remote point in the solution ($\phi_{ref}$) [5]. For a smooth surface, the zeta potential should be close to, if not coincident, to the diffusive double-layer potential [10]. As the ionic strength is increased, the diffuse-layer potential becomes a linear function of the applied potential. A calculation of diffuse layer potential for HO(CH$_2$)$_{14}$SH monolayer coated Au electrode in 1 mM electrolyte resulted in a range of roughly ±40 mV. Results from ±300 mV of applied
potential, as shown in figure 3.1, shows the measurement of the diffuse layer potential for a methyl and hydroxyl terminated SAM [5].

Additional studies have shown the surface charge density of alkane monolayers to be dependent on the pH of the electrolyte solution [11, 12]. The diffuse layer potential decreases for the same applied potential as the ionic strength is increased, due to the compaction of the diffuse layer.

The applications of SAMs are often limited by the quality of the monolayer. In the biosensor arena, SAMs on a metal electrode allow the direct electron transfer of an enzyme immobilized on the monolayer, facilitating the investigation of enzyme kinetics using electrochemical techniques [13-18]. Ideally, the catalytic current through the enzyme is detected as increased tunneling current through the monolayer at the enzyme’s Nernst potential, but conduction through pinholes (areas where metal is exposed to solution due to absence of monolayer) and collapsed sites may affect the outcome. Figure 3.2 is a schematic of a biosensor used to detect superoxide (SO). A SAM is used to act as a

Figure 3.1. Measure of Diffuse Layer Potential for thiol monolayers terminated with methyl and hydroxyl groups. Reprinted with permission from Langmuir, 23, 9083-91, Diffuse Layer Properties of Thiol-Modified Gold Electrodes Probed by Direct Force Measurements, Rentsch et al., Copyright 2007, American Chemical Society.
promoter for cytochrome-c. SAMs can prevent direct contact of solution with a metal, reducing redox interference. A suitable promoter, with an appropriate terminal group may be able to bridge the enzyme redox center buried deep in the enzyme. Successive electron hops can be facilitated with the proper terminal group. The promoter may reduce electrode capacitance, decreasing charging current. Mixed SAMs can modify surface properties and enhance adsorption of enzymes. Covalent binding of enzymes to SAMs is possible with suitable chemistry. Cytochrome-c (cyt-c) is used as a model protein for electrode work. It is a small protein whose structure has been characterized extensively; it is relatively small and soluble in aqueous solutions and takes part in electron transfer in the mitochondria. Mixed SAMs formed from mercaptoundecanol and mercaptoundecanoic acids have been shown to improve cyt-c adsorption and activity.

Figure 3.2. A schematic of superoxide attaching to cytochrome c with the support of a monolayer.
Studies have been performed to characterize how the temperature of the thiol solution can affect the growth of the monolayer on a gold substrate. Using STM measurements, it has been demonstrated that the vacancy island area does indeed change over a wide-range of temperatures, but the overall defect fraction area does not change [19, 20]. As the temperature is increased, the number of vacancy islands decreases, but the area of each vacancy island increases as shown in Figure 3.3. This is a result of the Ostwald ripening process, in which larger vacancy islands grow at the expense of smaller gold islands [21, 22]. Some of the contributions that dictate how well a monolayer is grown can be determined by the roughness of the SAM on the substrate.

Figure 3.3. The plot demonstrates that the number of vacancy islands varies, as the temperature of the thiol solution is changes, but the percentage of vacancy islands does not change due to Ostwald ripening. Reprinted with permission from Langmuir, 16, 5523-5525, Effect of Temperature on Structure of the Self-Assembled Monolayer of Decanethiol on Au(111) Surface, Yamada, R. et al., Copyright 2000, American Chemical Society.
Douglass Jr. et al. studied the roughness factor for electrodes that had dodecanethiol grown on a gold substrate [23]. The study determined how the roughness of the gold substrate could affect the overall capacitance (per unit area) of the system. It was determined that the macroroughness (≥10nm) of the substrate influenced the capacitive nature of the system, while the microroughness (1-10 nm) had a larger effect on the quality and structure of the SAM. In addition to monolayers containing defect sites (pinholes), monolayers may include collapsed sites that are present on the substrate. Studies have been done to distinguish the properties of SAMs when defected or collapsed sites are present. The electron rate constant for a monolayer with collapsed sites was found to be two orders of magnitude smaller than that for a defect site [24]. This is evidence that tunneling effects occur for regions within the monolayer that contain collapsed sites. The investigation of pH on the variation of charge transfer resistance (R_{ct}) and the apparent rate constant have been done using EIS [25]. Furthermore, EIS measurements that are done over a range of potentials, give insight to the permeability of the monolayer to penetration by solution ions. Ion penetration into the monolayer manifests as a parallel conduction path from solution to the electrode, necessitating a shift in the model from the series Constant Phase Element (CPE)-resistor to a Randles circuit composed of two resistors, one of which is in parallel with a capacitor. The positive and negative potential limits where the shifts occur are termed as the critical voltages V_{c}. Studies have shown that the critical voltage range can be dependent on the length of the alkane chain [26]. Boubour and Lennox studied the critical voltages for linear chain alkane thiols [26], where it was found that the critical voltage range was chain length dependent. For an alkanethiol of chain lengths n=7 to 15, the V_{c}
ranged from -0.15 V—0.3 V, but \( V_c \) for chain lengths below \( n=15 \) were all less than -0.3 V. The greater impermeability of longer chains may be ascribed to increased chain-chain interactions [27]. These attractive lateral interactions, driven by van der Waals forces, generally increase with chain length [28]. The use of EIS to study the quality of a monolayer for different immersion times has been done to explore the evolution of SAMs over different time scales. Daio et al. studied self-assembled monolayers of octadecanethiol (ODT) on gold by electrochemical impedance spectroscopy (EIS) with a redox couple, in order to make a quantitative analysis of the change of the fractional coverage, pinhole size and separation as a function of incubation time [29]. The range of incubation times in that study was from five seconds to 24 hours. Their results showed that the defective monolayers exhibited Warburg impedances at low frequencies with a redox couple in solution, an indication that the ions were mass transport limited, while diffusing through the defect sites. Monolayer formation kinetics were characterized by an initial fast step (chemisorption) followed by a slow step of surface coverage (through lateral bonding), and the size of the pinholes remain the same, but the number density decreases over time. However because redox species were used, it is difficult to understand the insulative behavior of a monolayer when charge transfer resistance is always present, due to tunneling effects. In another investigation utilizing EIS, experiments were performed without a redox couple in the electrolyte to study the quality of a monolayer for different incubation times of a gold electrode immersed in dodecanethiol (\( \text{CH}_3(\text{CH}_2)_{11}\text{SH} \)) solution [30]. A minimum of 40 hours were found necessary to achieve phase shifts \( \phi \geq -88^\circ \). For an ideal insulating (capacitive) monolayer, \( \phi = -90^\circ \) is expected. The EIS measurements for the monolayers incubated at various times were done at a single applied potential of 0 V vs.
Ag/AgCl. Because ion penetration is exacerbated at anodic and cathodic potentials, it is important to understand how the monolayer incubation time can affect the insulative properties of a monolayer over a range of voltages [2, 3]. Furthermore, as the applied potential approaches the PZC, a field can induce a torque on the headgroup, resulting in conformational changes in the SAM [31]. A torque is formed at negative applied potentials due to the vectors of the dipole moment and electric field almost pointing in nearly opposite parallel directions as shown in Figure 3.4b. The dipole moment vector always points away from the surface due to the large electronegativity of the sulfur group at the gold substrate. These conformational changes can lead to a lower barrier for ion penetration through the monolayer to occur. It is therefore imperative to understand the incubation time of a SAM. This work explores how incubation time on growing the monolayer can affect the critical voltage range.

**Figure 3.4:** Schematic of a SAM grown on a gold-coated membrane surface. When anodic potentials are applied, the vectors of the electric field and dipole moment are nearly parallel (a). At cathodic potentials, a torque is formed, which can make a conformational change within the SAM, making it easier for ion conduction through the SAM to occur (b).
3.3. Preparation of Monolayer Surfaces

Preparation of monolayer surfaces was described as in Section 2.9. 1-undecanethiol was purchased from Sigma Aldrich, and dissolved in absolute ethanol (Pharmaco-Aaper, Shelbyville, KY) at a concentration of 1 mM. SPR-quality glass slides (EMF Corp., Ithaca NY), coated with evaporated titanium (5 nm) and gold (100 nm) thin films, were washed in a heated SC-1 bath (100mL of DI water/25 mL of H₂O₂/2 mL of NH₄OH) and rinsed thoroughly with DI water (resistivity 18 MΩ-cm) and ethanol. Electrochemical polishing, followed by rinsing with ethanol, followed the chemically cleaned substrates. The clean gold surfaces were incubated in a sealed Petri dish for immersion times ranging from three hours to five days.

3.4. Surface Characterization

AFM measurements of bare gold substrates were made under ambient conditions using an Asylum MFP-3D (Santa Barbara, CA). AFM probe tips were used from Budget Sensors (Sofia, Bulgaria). Images were obtained in intermittent contact mode. Roughness was calculated by using the built-in software, Igor Pro from Wavemetrics (Portland, OR). Samples were prepared as described in section 2.2.
3.5. Results and Discussion

3.5.1. AFM Measurements

AFM measurements provided information on surface topography of the gold substrate. The main parameter used in quantitative analysis of the surface was the \textit{rms} roughness. The \textit{rms} roughness was measured to be 1.7-nm for electrochemical-polished substrates. The peak-to-peak values (maximum height difference) were 14-nm, as shown in Figure 3.5. These values are consistent with those found in previous studies for gold-coated glass slides with a titanium adhesion layer [34], which were also used as substrates for monolayer formation.

\textbf{Figure 3.5.} AFM measurement of bare gold substrate obtained in intermittent contact mode. The scan area shown is 1 μm by 1 μm.
In addition, AFM images were obtained for monolayers grown only from 30-120 seconds. A short amount of time was chosen in order to be able to observe “patches” of the monolayer that formed on the gold substrate. Using this method, it is easier to distinguish between the gold surface and the monolayer. Figure 3.6 shows images of a monolayer grown on a gold substrate from 30-120 seconds. As can be seen, the kinetics of initial monolayer coverage is facile. Eighty to ninety percent of monolayer formation on gold occurs within minutes. The AFM can image the increase of monolayer coverage (and decrease of pinhole density) over a small time interval. This confirms that the initial kinetic step for monolayer coverage is facile. However after several minutes, the kinetics significantly decreases, due to the second step related to the van der Waals force attractions having to overcome entropy effects.

Quantitative measures of pinhole density through electrochemical means (CV and EIS) have been attempted [29]. However, their models have not been corroborated by surface imaging studies that can map pinhole area and density such as STM, a non-trivial measurement, due to the possibility of the STM altering the surface under study. The figure of merit used for these studies is the constant phase element (CPE) exponent for a well-grown SAM. Our data supports the findings of Diao et al., in that:

1. The CPE exponent (alpha value) tracks the diameter and number of defects; and
2. Increased immersion times lead to dramatic improvement in alpha values (and hence a decrease in size and number of pinholes). Moreover, the immersion times in the present study show marked improvements not achieved in previous work.
Figure 3.6. AFM images a, b, c, are SAMs grown on evaporated gold substrates for incubation times of 30, 60, and 120 seconds.

3.6. EIS and CV measurements

Self-assembled monolayers of alkanethiols on gold have been shown to strongly block electrochemical oxidation of gold as well as electron transfer with redox couples in solution. The behavior of the SAMs has been ascribed to their ability to limit access of solution-phase molecules (water, electrolyte ions and redox molecules) to the electrode surface. The insulating abilities of thiol monolayers on gold were demonstrated in studies
that used methyl-terminated alkanethiols (11, 13, 15 and 17 methyl groups) could suppress gold oxide anodic stripping by 3-5 orders of magnitude [4, 24]. The present study has confirmed that cyclic voltammetry of bare gold surfaces in electrolyte containing no redox species shows the peaks where gold oxidation and reduction of the oxide occurs, as well as the double layer region where there is only charging current. The CVs compare well with bulk gold and gold sputtered on glass microscope slides. Upon the adsorption of thiol monolayers on the gold surface, gold oxide formation and reduction is suppressed, as evidenced by the lack of peaks in the CV seen in Figure 3.7; this compares two CV experiments between a bare gold polycrystalline surface and of a gold substrate with a monolayer grown for several days at a scan rate of 1 V·s⁻¹. A faster scan rate was used in order to obtain higher charging currents, which made it easier to measure the capacitance (C_{dl}=I/(dv/dt)) in the absence of artifacts due to electrochemical cell time constant (R_uC_{dl}). Slower scan rates would be needed if cell time constant limitation comes into play, which is sometimes seen as rounding of the edges in the CV at the switching potential. The CV of an ideal capacitance results in a rectangular shape CV centered at the current axis. Barring any artifacts due to cell time constants, the differential capacitance, is assumed to be independent of scan rate.
Incubation time studies using CV experiments were not done using CV because CV studies only provide a qualitative demonstration on the blocking mechanism of monolayers. Previous studies have already demonstrated the blocking of redox species by SAMs. The reduction in redox current however, has not been quantitatively tied to the quality of SAMs.

Cyclic voltammetry of alkanethiol monolayer-coated electrodes in electrolyte solutions show that the charging current drops dramatically in comparison to the bare metal electrode and becomes constant with electrode potential. This constant potential is consistent with the presence of a low dielectric constant between electrode and electrolyte. Equation 1 is an expression for the differential capacitance $C_d$, which is modeled by a series combination of two capacitances: the monolayer capacitance $C_m$ (which replaces the
Helmholtz capacitance $C_H$ of the bare metal), and the diffuse layer capacitance $C_D$ [35]. Monolayer capacitance is a property of the spacer length, while the diffuse layer capacitance is a function of the electrolyte concentration and applied potential with a minimum at the potential of zero charge ($E_{pzc}$), such that

$$\frac{1}{C_d} = \frac{1}{C_D} + \frac{1}{C_m}$$

(3.1).

To account for the Faradaic currents, investigators postulated that electron transfer could occur at pinholes (sites exposed to electrolyte due to the absence of adsorbate) in the monolayers. Pinholes are thought to occur mainly at grain boundaries, steps and kinks in polycrystalline gold. Even then, at these sites, the gold surface may be partially protected by a collapse of the monolayer, producing a defect in the monolayer where molecules and ions can approach the electrode surface at a distance shorter than the distance of the SAM. The presence of pinholes and defect sites is evidenced by the departure from perfect blocking behavior. Potential dependent background currents are observed for gold-monolayer-electrolyte systems, even in the absence of redox species. Such currents are explained by ion migration through pinhole defects in the monolayer film or charge transport, through the monolayer phase [2]. Even in the absence of pinholes and defects, tunneling through the full width of the monolayer contributes to a current. However, it is not easy to assess quantitatively the fraction of the surface that is composed of pinholes or defects [7]. Electrochemical impedance spectroscopy is used to determine the resistive and capacitive nature of a system over a set of frequencies. It has been used to characterize ionic transport through nanoporous membranes [36]. EIS has been applied to the detailed
analysis of through-film and at-defect electron transport paths in thiol-modified gold electrode in a solution containing a diffusing redox species [3, 6]. Several studies used EIS to show that a defect-free monolayer obeys the Helmholtz ideal capacitor exhibiting a phase shift ≥ 80° [28, 37-42]. Further, the impedance spectra can be fitted to an equivalent circuit of a solution resistance \( R_s \) in series with a constant phase element (CPE), which accounts for double-layer capacitance and SAM capacitance. Equation 2 is impedance of the CPE model expressed as

\[
Z_{CPE} = \frac{1}{Y_0(\omega^\alpha)}
\]

(3.2),

where \( Y_0 \) is the capacitance (F), \( \omega \) is the frequency of the applied electric field, and \( \alpha \) is the constant, which represents the ideality of the capacitor. The constant-phase element (CPE) is analogous to a distributed capacitance—with \( \alpha \) being a measure of variation of the dielectric coating thickness—since we assume that the monolayer formation has no effect on gold electrode surface roughness [31]. Several theoretical models have demonstrated that the roughness, or the degree of disorder of a monolayer, can be estimated by the CPE exponent \( \alpha \) [43-47]. The proof of the presence of the SAM can be observed from Table 1. The capacitance of the bare gold substrate is approximately 1.4 to 60 times greater than the capacitances for SAMs grown from three hours to 120 hours. In addition, as shown in Table 1, the \( \alpha \) value increases as incubation time of monolayer growth increases. An ideal capacitor has \( \alpha=1 \), while \( \alpha>0.88 \) suggests an adequately smooth gold surface. As mentioned above, a CPE model fits better than a simple series RC model. For alkanethiol SAMs with \( n=9 \) (1-dodecanethiol), a CPE of 1.36 to 1.67 \( \mu \)F/cm\(^2\) was reported over the range -0.2 to 0.4 V (vs. Ag/AgCl). [48]. Above \( 10^2 \) M electrolyte concentration, the
diffuse layer capacitance is greater than 10 µF/cm\(^2\), so \(C_m\) dominates the interfacial capacitance.

### Table 3.1. Model data for at applied potential of 0.0 V vs. Ag/AgCl at various incubation times.

<table>
<thead>
<tr>
<th>Immersion Time (Hours)</th>
<th>(R_s) (Ω (\cdot) cm(^2))</th>
<th>CPE (µS (\cdot) s(^α) cm(^2))</th>
<th>(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (Bare Gold)</td>
<td>282</td>
<td>95 ± .002</td>
<td>0.940 ± .009</td>
</tr>
<tr>
<td>3</td>
<td>269</td>
<td>68 ± .008</td>
<td>0.944 ± .001</td>
</tr>
<tr>
<td>15</td>
<td>277</td>
<td>1.73 ± .02</td>
<td>0.986 ± .004</td>
</tr>
<tr>
<td>48</td>
<td>280</td>
<td>1.6 ± .02</td>
<td>0.992 ± .004</td>
</tr>
<tr>
<td>120</td>
<td>281</td>
<td>1.58 ± .02</td>
<td>0.995 ± .004</td>
</tr>
</tbody>
</table>

The capacitance of the bare gold substrate is approximately 1.4 to 60 times greater than the capacitances for SAMs grown from three hours to 120 hours. In addition, as shown in Table 1, the \(\alpha\) value increases as the incubation time of monolayer growth increases. An ideal capacitor has \(\alpha=1\), while \(\alpha>0.88\) suggests an adequately smooth gold surface. As mentioned above, a CPE model fits better than a simple series RC model. For alkanethiol SAMs with \(n=9\) (1-dodecanethiol), a CPE of 1.36 to 1.67 µF/cm\(^2\) was reported over the range -0.2 to 0.4 V (vs. Ag/AgCl). [48]. Above \(10^{-2}\) M electrolyte concentration the diffuse layer capacitance is greater than 10 µF/cm\(^2\), so \(C_m\) dominates the interfacial capacitance.

Figure 3.8 is a Bode phase plot that shows the insulative behavior of monolayers for two different immersion times. For the monolayer grown for 48 hours, the EIS data shows that the phase angle peaks between 1-10 Hz at -68 to -75 degrees for the electrolyte concentrations of 1 mM and 10 mM. The dependency is due to the contribution of the diffuse layer capacitance, which is strongly dependent on concentration.
Figure 3.8. Phase angle plot of undecanethiol SAMs formed at different immersion times, with an applied potential of -0.2 V. The phase angle at low frequencies of the 48-hour grown monolayer exhibits a phase angle less than -88 degrees, for 1mM and 10mM concentrations. The substrate immersed in thiol solution for 5 days shows a phase angle of -88°, an indication of a monolayer without defects for 1mM and 10mM concentrations.

The model used here is from Gouy-Chapman theory, where the capacitance of the space-charge between the electrolyte and the electrode is at a minimum at the potential of zero-charge and rises at higher and lower potentials. At the minimum, at 25° C with a z:z electrolyte, this capacitance is

$$C_{GC} (\mu F/cm^2) = 228 z c^*^{1/2}$$  \hspace{1cm} (3.3),

where $c^*$ is bulk electrolyte concentration in mol L$^{-1}$ [35]. For a 1:1 electrolyte at 50 mM concentration, the double-layer capacitance is calculated to be 50 µF cm$^{-2}$. This relatively high capacitance is characteristic of the gold-solution interface when
it is not blocked from electrolyte by a monolayer, which corresponds to pinhole areas in a SAM.

The monolayer-covered gold/solution interface forms a second kind of interfacial capacitance. This capacitance (neglecting charge on the head group) is dominated by the monolayer capacitance $C_m$, determined by the relative permittivity of the alkanethiol chain and the film thickness $\delta$ of the monolayer, such that

$$C_m = \frac{\varepsilon_0 \varepsilon_r}{\delta}$$  \hspace{1cm} (3.4).

For a well-ordered monolayer, characterized by a permittivity value of around 2 expected for hydrocarbon chains and thickness $\delta \leq 2$ nm, $C_m$ values in the range of 1 to 1.8 $\mu$F cm$^{-2}$ are expected, with longer chain thiols having lower capacitance due to the higher thickness [49]. Since $C_m < C_{GC}$ in the series capacitance model of the Guoy-Chapman-Stern (GCS) model, the impedance of the smaller capacitance $C_m$ dominates as the frequency approaches zero (DC), and the measured CPE can be ascribed to $C_m$.

Therefore, for defect-free monolayers, the phase shift should be independent of concentration due to the monolayer capacitance exhibiting behavior similar to the Helmholtz capacitance, which is independent of electrolyte concentration. A similar gold surface incubated for 5 days exhibited at $-88^\circ$ phase shift at 1 Hz shown in Fig. 3.8. At this frequency, the phase angle varied less than 1.2% between 1 and 10 mM for the Au-substrate immersed for several days. This is evidence of a monolayer that has minimal pinholes and defects, due to the improved ordering of the monolayer, afforded by prolonged incubation in thiol solution. It has been reported that the structure of SAMs do
not change significantly when exposed to a 1 mM solution for 12-18 hours [28]. However, evidence has shown that immersion times of seven to ten days can reduce the number of pinholes in the SAM and the conformational defects in the alkane chain to decrease [28]. Thus, for applications such as the study of electron transport by tunneling through monolayers or preparation of surfaces that need to be well-insulated from solution redox species, longer immersion times for improved monolayer regularity and stability are needed. It is also important to note that an inductance was present at higher frequencies above 10k Hz for the EIS experiments with 1 mM electrolyte concentration. A survey of the literature was made as to find the causes of inductance in a circuit with only capacitances and resistances. These effects have been divided into inductances that appear at low frequencies (<10 Hz) and those that appear at high frequencies (>100 KHz). For low frequencies, these have been ascribed to adsorbed intermediates [50] or relaxation of adsorbed anions on a metal surface [51]. However, these inductances appear at frequencies (1 and 0.1 Hz) much lower than what we have observed (10 kHz). At high frequencies, the usual suspects are stray inductances from wire leads. Indeed, at these frequencies (>100 kHz), we do see an inductive phase shift. However, neither of the high or low frequency explanations account for the fact that the inductive phase in our data appears at 10 kHz, a frequency intermediate between low and high frequency situations above. Vanysek and Birss have suggested that this may be partly due to the potentiostat itself (capacitance at the reference input in conjunction with high capacitance and low resistance at the working electrode) at frequencies greater than about 10 kHz [52]. Using various model circuits with the above characteristics, we were unable to recreate the peaked, positive phase shift at 10 kHz by using model circuits; thus, we are continuing to
investigate the matter. One other possibility is the coupling of the capacitance of the electrodes and wires to the Faraday cage where the experiments on the monolayers were carried out [53].

To develop models for categorizing SAMs into those that are defect-free or those having induced defects, the corresponding impedance data were fitted to equivalent circuits by using the algorithms built into the Echem Analyst software package (Gamry, Inc.). Models were constructed by using the built-in Model Editor. The Levenberg-Marquardt method was used to fit the data to the CPE-resistor circuit shown in Figure 9a. The results are shown in Table 1. The 1-Hz frequency was chosen for measurements due to the relaxation times in which diffusion related phenomena occurs for alkane SAMs. This has been consistent with previous studies, which have characterized SAM layers on gold using EIS [30, 38].

![Figure 3.9. Equivalent circuits of the thiol monolayer: (a) CPE in series with a solution resistance, indicative of a “defect-free” SAM and (b), an equivalent Randle circuit of a SAM with potential induced defects.](image)

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For a monolayer that does not exhibit purely capacitive behavior, a Randles circuit was used. Figure 3.9b constitutes a Randles circuit, which includes a solution resistor in series with a RC circuit. The RC circuit includes the double layer capacitance of the surface and the charge transfer resistance, due in part to the ionic transport through the monolayer.

Taken as a whole, the results show that the CPE value decreases, while the $\alpha$ parameter approaches unity as the incubation time increases. The high CPE (although lower than the bare gold CPE value) at 3-h, suggests the presence of defects collapsed sites, implying a thinner dielectric. The presence of pinholes leading to $\alpha=0.944$ means that the electrolyte has access to the metal, further adding to the overall capacitance. A low $\alpha$ could also imply low uniformity of dielectric thickness. Increasing incubation time anneals the alkanethiolate into a sufficiently uniform, very close to defect-free, blocking monolayer as evidenced by the low CPE value and $\alpha$ approaching unity for 120-h. The schematic below (Figure 3.10) shows the evolution of the SAM surface with incubation time. This is consistent with the results of kinetic studies of alkanethiol adsorption as reviewed by Ulman [54] and Schreiber [27], where two distinct steps in the absorption kinetics were observed: a very fast step and a second slow step, which can be described as a surface crystallization process. The kinetics of the second step is related to chain disorder, chain-chain interaction (van der Waals) and mobility of the surface chains. As previously suggested, the pinhole size remains invariant, while the number of pinholes decrease with increasing immersion time in thiol solution [29].
More importantly, however, the present study demonstrates that beyond 24-h, an improvement of the insulating character of the SAM is possible; and EIS is a sensitive tool for monitoring the state of the monolayer. Figure 3.11 shows a Bode plot of each monolayer at different incubation times. At 3-h, it is apparent that the number of defects and pinholes greatly affects the impedance at frequencies in the 1-10 Hz range in terms of both magnitude and phase.

**Figure 3.10.** Schematic of alkanethiolate SAM evolution on a gold surface over a range of incubation times.
Figure 3.11. Bode plot of undecanethiol applied at 0 V (vs. Ag/AgCl) for different incubation times.

Table 2 is a summary of results for incubation times of voltages ranging from -0.4 to 0.5 V (vs. Ag/AgCl). It can be observed that we were able to extend the critical voltage range to -0.3 V for an incubation time of 120 hours. This was not observed in previous work for alkane chains n<15. The results of Table 2 also show that beyond the critical voltage, the charge transfer resistance increases as the incubation time of the monolayer increased. Table 2 demonstrates that the critical voltage is not only dependent on chain length, but also the amount time that the monolayer is grown. For monolayers grown for
120-h, the critical voltage was extended to larger anodic and cathodic potentials, which in this case is -0.3 V to +0.5 V vs. Ag/AgCl. The critical voltage behavior of this shorter chain alkanethiol (n=10) was previously achieved only for longer alkane chain lengths (n=15) [48].

Figure 3.12 is a plot of the CPE and α values from the fit of the EIS data obtained for various thiol incubation times (15-, 24- and 120-h), and recorded at different DC potentials. The voltage ranges vary for each SAM, since SAMs grown for lower incubation times have lower resistances for ion conduction to occur through the SAM. The motivation behind these two plots is to demonstrate the potential in which the SAM behaves as an ideal capacitor. Beyond the critical voltage for each SAM, the CPE model is no longer valid. As incubation time is increased, the critical potentials are extended from -0.1 and +0.2 V (15 h) to -0.3 to +0.5 V at 120-h. This extends the useful range of the Au/SAM electrode for use in biosensor applications where applied potentials are needed to induce signal transduction currents.

**Figure 3.12.** Plot of model data (CPE and α) obtained from fitting the EIS data for various incubation times. The DC potential was varied from -0.3 V (vs. Ag/AgCl) to 0.5 V. For immersion times shorter than 120 h, the CPE model did not hold over the full DC potential range due to ion penetration.
Table 3.2. Fitting parameters for the impedance measurements of SAMs incubated at different times. Calculated using the Levenberg–Marquardt method$^1$.

<table>
<thead>
<tr>
<th>Immersion time</th>
<th>E/V (vs. Ag/AgCl)</th>
<th>CPE in series with Resistor</th>
<th>Randles Equivalent Circuit b</th>
<th>α</th>
<th>Ctot (μF/cm$^2$)</th>
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<td>Equivalent Circuit b CPE (μF*s$^α$ cm$^{-1}$)</td>
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<td>1.69 ± 0.02 0.984 ± 0.004</td>
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$^1$Two equivalent circuit models were used to describe the insulative behavior of the SAMs depending on the potential applied to each SAM.

$^2$A CPE model is (Fig. 4a) used due to the insulative behavior of the SAM.

Figure 3.13 shows the phase shift from EIS measurements performed at a range of voltages. As can be seen, the monolayer grown for 15 h exhibits a small voltage range
before ion transport through the monolayer becomes relevant. The 48-h monolayer exhibits a larger potential range up to -0.2 V (vs. Ag/AgCl). It can be seen that the phase shift is > -80° for cathodic potentials beyond -0.2 V (vs. Ag/AgCl). However, the monolayer that has grown for over five days exhibits a phase shift ≤ -80° for voltages ranging from -0.3 to 0.5 V (vs. Ag/AgCl). The authors of this study consider this to be evidence that the number of pinholes within the monolayer has been reduced, thus increasing the resistance for ions to transport through the monolayer. Even in the absence of a well-grown SAM, ion conduction beyond a cathodic potential of -0.3 V will occur.

Figure 3.13. Plot of phase shift at 1 Hz from EIS measurements performed at voltages ranging from -0.3 V-0.5 V (vs. Ag/AgCl).

Figure 3.14 is a plot of the double layer capacitance ($C_{dl}$) and ion conduction resistance ($R_{ion}$) at an applied potential of -0.4 V. The double layer capacitance and ion conduction were calculated by fitting a Randles circuit to the impedance data. Although ion conduction occurs through for SAMs incubated for different times, the ion conduction resistance is highest and double layer capacitance is lowest for the SAM grown at five days.
Figure 3.14. Plot of Double Layer Capacitance and Ion Conduction Resistance at -0.4 V (vs. Ag/AgCl).

The bi-modal shape of the CPE curve for 120-h incubation is intriguing, as it suggests two different PZC values. This behavior implies two sites governed by different charge environments. The more negative of the two (-0.1 V) probably corresponds to the alkanethiol PZC; however, this is to be expected at more negative potentials. The PZC of an n=11 alkanethiol was reported to be in the vicinity of -0.37 V vs. SCE [55], to -0.49 vs. Ag/AgCl [31, 56] for UDT SAMs on Au(111). More studies are required to understand the reason a shift in PZC is observed. The minimum at +0.2 V probably corresponds to PZC of pinholes or defects where electrolyte can access small areas of bare gold. The PZC of Au(111) was measured by cyclic voltammetry in the absence of specific adsorption (HClO₄ and NaClO₄, 0.1M) to be about 0.23 V vs. SCE [38] or 0.275 V vs. Ag/AgCl. Due to specific adsorption of phosphate anions, we expect a shift towards more negative PZC in the plot, where a minimum is seen at 0.1 V for 15- and 48-h incubations. It is interesting to note that unlike the rest of the monolayers, the 120-h incubation positive PZC has shifted from 0.1 V to 0.2 V (vs. Ag/AgCl). At this point, further comment is not warranted without
additional data. The measured CPE corresponding to this PZC, however, is not an indication of the surface concentration of pinholes, as its capacitance is expected to be much higher than that of a full monolayer. The high α values and the low CPE, as well as the ion flux, for the 120-h incubated sample is an indication of a crystalline, uniform monolayer that has the lowest number of defects across the various incubation times.

3.7. Conclusion, Recommendations and Further Work

The use of thiol–modified gold as a blocking mechanism to ion conduction under an externally applied electric field to the membrane surface was demonstrated, with the purpose of studying the potential range on a gold-coated glass substrate -solution interface. The range of voltage and quality of the SAM helped in determining the minimization of Faradaic activity and the prevention of adsorption on the electrode surface. Comparisons of CV and EIS measurements for determination of a quality of a SAM were compared, and was determined that EIS could show more subtle effects that are not clearly seen in a cyclic voltammogram. This lays the groundwork for the application of thiol-modified membranes for study of ion-selective transport through charged Au coated membranes. As such, it is important to understand the stability of thiol monolayers used in this application. We also investigated the effect of immersion time on the quality of the monolayer formed, and found that longer immersion time improves the insulating properties of the monolayer, as demonstrated by EIS. The present work has laid the groundwork for finding the limits of applied potentials across the membrane with minimal faradaic currents. In Chapter 5, studies of ionic transport through gold-coated nanoporous PCTE membranes will be addressed.
3.8. References


Chapter 4: Nanoscale Transport Phenomena

4.1. Introduction

Electrokinetics is the study of ionized particles or molecules and their interactions under an applied electric field. The transport phenomena include fields such as fluid mechanics, colloidal phenomena, and the interaction of charged particles in electrolyte solution under an externally applied electric field.

As discussed earlier, ED systems use anion and cation exchange membranes to separate ionic species. Charge separation occurs due to electric double layer interaction from charged surfaces. An electric double layer is an electrostatic force, which creates a non-uniform distribution of ions adjacent to a phase boundary. The electrostatic field of the species at the interface induces a spatially-varying local electric potential, field, and ion population. This force is created as a result of the membrane pore walls carrying either a negative (cation selective) or positive (anion selective) surface charge. The theory of EDL falls into the field of electrokinetics.

There are mainly two different types of flow regimes in electrokinetics: electromigration and electroosmosis. The study of electromigration is the transport of ions or particles under an applied electric field. Sometimes the transport of molecules, such as proteins under an applied electric field, is also called electrophoresis. This differs slightly from ion transport because the particles are large enough such that a relative motion between the solution and particle develops.

Electroosmotic flow occurs due to the interaction of the particles with the electric double layer (EDL) at the surface of the system under an applied electric field. This
interaction creates a body force, which acts on the fluid. The efficacy of electroosmotic flow can be observed by comparing the volumetric flowrates of pressure-driven flow to electroosmotic flow. For thin electric double layers, the volumetric flow ratio (VFR) scales to $1/r^2$, where $r$ is the radius of the capillary. The VFR demonstrates that for small nanochannels/nanopores, electrokinetic flow is advantageous for transport of molecules.

4.2. Electrokinetic Flow

The Boltzmann distribution describes the amount of work that is required to bring an ion from infinity (i.e. the bulk solution, where $\psi=0$) to a given location having a potential $\psi_x$. The expression for the Boltzmann distribution is as follows:

$$n_i = n_{i,\infty} \exp \left( \frac{-z_i e \psi}{k_B T} \right)$$ \hspace{1cm} (4.1),

where $n_{i,\infty}$ is the ionic number concentration when $\Psi=0$ and $n_i$ is the number concentration of the $i^{th}$ species. The relationship between the free charge density and the number concentration can be expressed as:

$$\rho_f = \sum_{i=1}^{N} z_i \ e n_i$$ \hspace{1cm} (4.2).

The total potential within a nanocapillary under an externally applied field is given as:

$$\phi(r, x) = \psi(r) + (\phi_0 - x E_x)$$ \hspace{1cm} (4.3),

where $\psi(r)$ is the potential from the double layer which relates the state of equilibrium where no fluid or externally applied field is present. The second term of Equation 4.3 is the local potential at any axial location within the nanopore. Equation 4 is the Poison equation, which describes the potential distribution within the nanopore:

$$\nabla^2 \phi = \frac{-\rho_f}{\varepsilon}$$ \hspace{1cm} (4.4).
Substituting the free charge density within the Poison equation gives the Poison-Boltzman (PB) equation, shown in equation 5:

\[ \nabla^2 \phi = -\frac{1}{\epsilon_0 \epsilon_r} \sum_i z_i e n_o \exp \left( -\frac{z_i e \psi}{kT} \right) \]  

(4.5),

The PB equation can be simplified by assuming a symmetric (z:z) electrolyte and low surface potential. These two assumptions lead to the Debye-Huckel (DH) approximation. For a cylindrical nanopore, the DB equation is given as

\[ \frac{1}{r} \frac{d}{dx} \left( r \frac{d\psi}{dr} \right) = \kappa^2 \psi \]  

(4.6),

where \( \kappa \) is defined as the inverse of the Debye length. The Debye length is defined as

\[ \kappa^{-1} = \left( \frac{\epsilon_0 \epsilon_r \kappa_B T}{2a^2 z^2 n_\infty} \right) \]  

(4.7).

The DH equation can be analytically solved and expressed as:

\[ \psi = \zeta \frac{I_o(\kappa r)}{I_o(\kappa a)} \]  

(4.8),

where \( I_o \) is the zeroth-order Bessel function.

The Debye length is a measure of the thickness of the electric double layer. The double layer thickness is usually defined as the distance from the charged pore wall to the point where the potential decays to approximately 33% of the surface potential. As can be seen by Figure 4.1, there are three different parts of the EDL. The inner layer contains non-solvated ions, which are specifically adsorbed to the surface by chemisorption. This layer is defined as the Stern layer or compact layer. The locus of centers of specifically
adsorbed ions is called the Inner Helmholtz Plane (IHP). Within this layer, the ions are assumed to be immobile and adhere to the charged walls. The Outer Helmholtz Plane (OHP) is a region in which counterions are electrostatically attracted to the surface. These ions are nonspecifically adsorbed and are solvated molecules. There is a finite distance at which the proximity of ions may approach the wall. Because of thermal agitation, these ions are distributed in a three dimensional region called the diffuse layer. The OHP is the location in which a shear plane is defined for purposes of defining a no-slip boundary condition, which solves the velocity field for electrokinetic flow. The last layer is the bulk solution. In this regime, the solution is considered to be electro-neutral.

![Diagram of Electric Double Layer](image)

**Figure 4.1.** Schematic of Electric Double Layer

The governing equations for the velocity fields, pressure, and distribution of ions is given by the following systems of equations:
\[ \nabla \cdot \mathbf{u} = 0 \]  
(4.9),

\[ \rho \left( \frac{\partial \mathbf{c}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} + \rho_e \mathbf{E} \]  
(4.10),

\[ \nabla \cdot \mathbf{E} = \rho_e \]  
(4.11),

Equations 4.9 and 4.10 are the conservations of mass and momentum for an incompressible (Newtonian) fluid with constant thermodynamic properties where \( \rho \) is the fluid density; \( \mathbf{u} \) is the fluid velocity vector; \( p \) the pressure; \( \mathbf{E} \) the electric field vector; and, \( \mu \) is the fluid dynamic viscosity. The last term in the momentum equation is the contribution to the electrical body force. The transport equation of \( c_i \) (of the \( i^{\text{th}} \) species) within a dilute electrolyte solution within the fluid domain is given as:

\[ \frac{\partial c_i}{\partial t} + \mathbf{u} \cdot \nabla c_i = D_i \nabla^2 c_i - \nabla \cdot (\nu_i z_i c_i F \mathbf{E}) \]  
(4.12),

where \( D_i \) is the diffusion coefficient, \( F \) is Faraday constant, \( \nu_i \) is the mobility, and \( z_i \) is the valency of the \( i^{\text{th}} \) species.

By assuming fully-developed laminar flow conditions, the velocity field can be solved for analytically yielding:

\[ u_x(r) = \frac{a^2 p_x}{4 \mu} \left[ 1 - \left( \frac{r}{a} \right)^2 \right] - \frac{\kappa}{\mu} \left[ 1 - \frac{i_p(kr)}{i_p(ka)} \right] E_x \]  
(4.13).
Electrokinetic phenomena result from an unbalanced-net charge within the diffuse layer. When there is an electric field applied across a nanopore or nanochannel, the first-term Equation 4.13 cancels, resulting in a fluid flow entirely due to electroosmotic flow. If no pressure gradient is present and the thickness of the electric double layer is much smaller than the diameter of the nanopore, then \( \kappa a \ll a \), eqn 13 reduces to:

\[
 u_x = -\frac{\varepsilon \zeta E_x}{\mu} \quad (4.14)
\]

This classical result is known as the Helmoltz-Smoluchowski (HS) equation. The fluid moves as a plug flow within the nanopore. Figure 4.2 is a plot of the electroosmotic equation for different normalized radius values. The HS approximation is valid for \( r/a \gg 1 \). For \( r/a \gg 1 \), the fluid moves as plug flow:

\[ \text{Figure 4.2. Electroosmotic velocity for a zero pressure gradient plotted as a function of dimensionless radius. Reprinted with permission from Journal of Separation Science, 30, 1398-1419, Holtzel, A., Tallerek, U., Review, Ionic conductance of nanopores in microscale analysis systems: Where microfluidics meets nanofluidics, Copyright 2007, John Wiley and Sons.} \]
For overlapping double layers ($\kappa a \gg 1$), with no pressure gradient, the electroosmotic equation simplifies to:

$$u_x = -\frac{\Omega}{4} E_x (\kappa a^2) \left[ 1 - \left( \frac{r}{a} \right)^2 \right]$$ \hspace{1cm} (4.15).

As the radius approaches the size of the Debye length, the effective EMF velocity is reduced to a finite value. As $\kappa a \to 0$, the electroosmotic velocity ($u_x$) reduces to zero. The term $-\frac{\Omega}{4} E_x (\kappa a^2)$ is similar to the term found in Poiseuillie flow for fully developed flow under an applied pressure across the nanopore. The similar flow characteristics are a result of a liquid body force attributed to the net free charge density across the nanopore. The net liquid body force is similar to the body force found from a pressure gradient across a nanopore.

### 4.3. Computational Studies

Several authors have theoretically studied ionic transport through charged nanopores-nanochannels, which address the depletion-enrichment zones formed from concentration polarization (CP) [2-4]. There have also been several studies that address the entrance effect as a result of the surface charges from the entrance of the nanopore-nanochannel [5-9]. If the pore density of a nanoporous membrane is large enough, then ionic transport can be treated as a continuum problem based on the ergodic principle [10]. Several studies have been done for demonstrating the behavior of ionic transport through nanopores for charged nanopore surfaces from chemisorption of charged species. These studies do not address the behavior of molecular transport through nanopores when the surface is conductive and controlled through an applied potential. When the surface charge
of the nanopore is created by chemisorption of ionic species, the surface depends only on the ionic strength of the electrolyte solution. However, computational studies have demonstrated that, for a conductive nanopore in which the surface charge is controlled through an externally applied field, the electrostatic interaction will not only depend on the concentration of the electrolyte, but also on the potential difference between the metal phase and electrolyte solution [11].

The limitations of using the Gouy-Chapman model ions are assumed to be point charges, which allow ions to directly interact the charged surfaces. Assuming that ions may approach the surface at contact can lead to an over-prediction of the potential across the EDL. In addition, the PB equation does not take into account ion-ion interactions, as well as multivalent ions [12]. This can lead to erroneous results at high surface potentials. Studies have been performed to take into account that ions are solvated and can only approach the surface up to a finite distance. Several authors have investigated the deviations of using the GC theory under different electrochemical environments [13-17]. Fawcett and Smagala reviewed ways to improve predictions of EDL interactions [18]. The studies of EDL were based on Monte Carlo simulations, which were then compared with empirical results. The potential distribution was solved for a 1:1 electrolyte by using a modified Poisson-Boltzmann equation to account for finite particle size. Figure 4.3a shows the potential across the diffuse layer. The Gouy-Chapman model’s potential over-predicts as compared with both the empirical and Monte Carlo Simulations. The over-prediction of the potential distribution is a result of the absence of accounting for the finite size of particles. Figure 4.3b. shows the deviation of the Gouy-Chapman and the Monte Carlo simulations as a function of increasing charge density. The deviations increase as
the size of the molecules increase in orders of 200, 300, and 400 pico-meters. The molecules studied in Chapter 5 were methyl-viologen (MV$^{2+}$) and napthalenedisulfonate disodium salt (NDS$^{2-}$). The molecular radii for MV$^{2+}$ and NDS$^{2-}$ are approximately 600 and 700 pico-meters [19,20]. In this size regime, there will be some deviation from the classical GC theory. However, due to the simplicity of the GC theory, its assumptions are still widely accepted for many studies.

Figure 4.3. Plot (a) demonstrates Monte Carlo simulations done by Fawcett and Smagala, which demonstrate the over prediction of the diffuse layer potential when point charges are assumed. Plot (b) are the results of the diffuse layer potential for three different molecular radii. The results show that the deviation from the Guoy Chapman’s solution increases as the molecular size increases. Reprinted with permission from Langmuir, New Developments in the Theory of the Diffuse Layer, Fawcett W.R., Smagala, T.G., Copyright 2006, American Chemical Society.

When the velocity field and distribution of species are solved, the total current density within the nanopore can be found from the Nernst-Plank equation expressed as

$$i = Fu \sum z_i c_i - F \sum D_i z_i \nabla c_i - \frac{F^2}{RT} \nabla \psi \sum z_i^2 D_i c_i \tag{4.16}.$$
The first term is due to the bulk flow of motion of the fluid, the second term is due to the concentration gradient across a nanopore, and the third term is due to electromigration of a particle due to an external applied electric field.

4.4. Ionic Transport Through Nanopores

Many studies have been performed on ion permselectivity across gold-coated charged surfaces and charged nanopores. The electroless gold template method was used to study permselectivity of analytes through electroless gold-coated NCAMs. Martin and coworkers first introduced this method in the mid 1990’s [21]. Many authors have used the electroless gold-coated PCTE membrane to study different mechanisms of ionic transport based on the influence of charge, hydrophobicity, steric effects, and pH [22-32].

Nguyen, et. al. fabricated ion-tracked polyethylene terephthalate (PET) membranes, which had a surface and pore-wall carboxylate terminal group [33]. The membranes selectively transported cations and prevented diffusion of anions. They were able to reverse the selective properties of the membrane by making an amino terminal group on the surface and pore wall of the membrane. Other studies have included the study of mass transport of molecules based on the hydrophobicity of the pore, which was made conductive through the electroless gold deposition process. The gold-coated nanotubules were modified with a fluorinated thiol [34]. Zenglian et al. used an electroless gold-deposited PCTE membrane with a modified thiol surface that was hydrophobic to study mass transport experiments of two molecules and the effects of adding alkyl surfactants to change the hydrophobic properties of the membrane surface [35]. Hou and coworkers used an electroless gold-
deposited PCTE membrane that was modified with carboxylic-acid functionalized thiols onto gold to study the pH dependency of mass transport of molecules through the membrane [36]. In addition to separation based on hydrophobicity and electrostatic interactions, it has been demonstrated that analytes can be excluded based on size. Martin and coworkers were able to use electroless gold-coated NCAMs to exclude ions by molecular sieving [31, 36, 37]. Diffusion experiments were initially performed in an electrochemical system with no confined walls to investigate the ratio of diffusion coefficients of two molecules with different molecular sizes. When diffusion experiments were performed for NCAMs with pore diameters of 5-nm or less, the diffusion coefficient ratio increased by over a magnitude. These studies proved that when the diameter of the nanopore approaches the molecular dimensions of a molecule, there is an increase of interaction with the molecular walls of the nanopore. The diffusion coefficient can be expressed as:

\[ D_i = \frac{k_B T}{6\pi \mu a} \]  

(4.17),

where \( a \) is the diameter of the molecule and \( \mu \) is the dynamic viscosity. The expression in the denominator is known as the Stokes-Einstein friction factor. The observation can be made that there is an increase in molecular friction as the particle size increases, which in turn increases the frictional drag on the molecule, decreasing the diffusion coefficient of the molecule. Due to the requirements that the distance from the center of the molecule to the pore wall be at least greater than its radius, there are certain regions in which the molecule cannot reside. This can be attributed to steric effects from the confined walls of the nanopore [38, 39]. Steric effects arise from the atoms within the molecule that occupy a finite volume of space. Thus, when one atom is brought too close to another, there is an
energy barrier—from overlapping of electron clouds—in order for the molecule to migrate through the nanopore. The degree to which the diffusion coefficient is reduced within a nanopore compared to within a non-confined aqueous solution can be defined as:

\[ \lambda = \frac{r_p}{r_a} \]  

(4.18),

where \( r_p \) and \( r_a \) are the radii of the particle and nanopore, respectively. Many theoretical studies have examined a relationship between the diffusion coefficients within a confined pore and free aqueous solution [38, 40-43]. One of the common equations used for the relationship of the diffusion coefficients is the Renkin equation, which is given as:

\[ \frac{D_a}{D_p} = 1 - 2.10\lambda + 2.09\lambda^3 - 0.95\lambda^5 \]  

(4.19).

Equation 19 demonstrates that as the particle size of a molecule increases, the ratio of diffusivities between the bulk solution and nanopore increases. This is secondary to steric effects between the walls of the nanopore and the molecule.

4.5. Fabrication of Conductive NCAMs by the Electroless Gold Deposition Process

Our first task was to study the permselectivity of electrossly gold-coated NCAMs. In order to perform transport studies, the fabrication technique of electroless gold deposition was examined. There are four main processes for Au coating the membrane. The first process consists of sensitization by immersing the membrane in a tin solution. The second is activation of the membrane surface by immersing the membrane in a solution of silver. The third step involves the process of Au particles galvонically
replacing silver particles due to gold being more noble than silver. The fourth and final step is electroless deposition of gold on the surface and pore wall of the NCAM. The gold nucleation sites, which initially form on the surface, act as catalytic sites for the oxidation of formaldehyde and the reduction of Au$^+$ ions. The reaction is as follows:

$$2\text{Au}^+ + \text{CH}_2\text{O} + 3\text{OH}^- \rightarrow \text{HCOO}^- + 2\text{H}_2\text{O} + 2\text{Au}$$

(4.20).

To ensure “wetting” of the nanopores, the PCTE coated with Polyvinylpyrrolidone (PVP) membrane was immersed in a 50:50 methanol:water solvent, which was sonicated for 48 hours. In order to determine the amount of time necessary to remove air bubbles trapped within the nanotubes, chronoamperometry experiments were done using a 30 nm PCTE PVP coated membrane. A 4-electrode system was used to apply a potential range of -0.5 to 0.5 V across the NCAMs, using a Reference 600 potentiostat. Four leads from the potentiostat were connected to a working, working sense, and two counter electrodes. Figure 4.4 demonstrates the current response to NCAMs pretreated for different immersion times. The electrolyte used for the experiments was a 10 mM potassium phosphate buffer solution (PBS) of pH=7. The plot demonstrates that at least 48 hours is necessary to remove air bubbles inside the nanotubes. The measured current for a 48-hour immersion time was approximately 40 times higher than that of a 24-hour case. Any immersion time less than 48 hours appeared to have no effect on the current response of the system. It can be concluded that the air bubbles are not removed below immersion times of 48 hours.
Figure 4.4. Chronoamperometry experiments for a 30 nm PCTE PVP coated membrane. A 10 mM PBS of pH=7 was used for experiments. The current for the PCTE membrane soaked for several was approximately 40 times higher for smaller pretreatments times.

Figure 4.5 demonstrates the fabrication of the first Au coated membrane attempted with a pore size of 50 nm and a deposition time for 24 hours with a pH=10. The temperature of the gold solution was monitored and maintained at 4° C. The SEM image illustrates that Au nanowires were fabricated. The sample was prepared by peeling off the gold surface of the membrane and plasma etched with oxygen and argon gas for several minutes. To obtain Au-nanotubule membranes, this required a study of the amount of deposition time required to attain the necessary inner diameter nanotubule.
Figure 4.5. Gold nanowires fabricated by electroless deposition of a 30 nm Polycarbonate Track Etched Membrane (PCTE).

The membrane used was a 90-mm, 0.22-µm track etched, polyvinylpyrrolidone (PVP) coated polycarbonate membrane. The pore density and thickness of membrane was $3 \times 10^8$ pores/cm$^2$ with a thickness of 10-µm. Figure 4.6 shows the surface of the polycarbonate membrane coated with gold for a deposition time of 240 minutes. A membrane holder was used to prevent “wrinkles” on the surface of the membrane. Reducing the amount of wrinkles on the surface led to a smoother gold-coated surface.
Figures 4.6. Image (a) of the electroless coated membrane placed in a membrane holder to prevent “wrinkles” on the membrane surface, which results in a smoother gold-coated surface. Image (b) is an image of an electroless membrane surface that was not placed in a membrane holder. Image (c) is a SEM image displaying the nanopores and gold-coated membrane surface.

Figure 4.7 displays the deposition time study for the electroless gold deposition process. As can be seen, the rate of kinetic reaction decreases over time due to the consumption of gold ions in solution.
Figure 4.7. Plot of deposition time and inner diameter of the Au coated membrane. The deposition time ranged from 0 to 480 minutes. The plot shows how the rate of gold deposition decreases as a function of time. Some of the factors may be the result of the consumption of gold particles during, which leads to a lower concentration of gold ions available for the reaction to occur.

Figure 4.8 shows SEM images of gold nanotubules after 4 hours of deposition time. As can be observed, the walls of the Au nanotubules are uniform. SEM image studies were only done for nanotubules with a radius greater than 50-nm due to the challenges of imaging at characteristic dimensions below those dimensions.

Figure 4.8. SEM images of gold nanotubule membranes for a deposition time of 4 hours. All images are seen are from the same sample of the membrane but with different magnifications. The gold nanotubules were imaged by removing the gold surface of the PCTE membrane and subsequently O₂ etched.
4.6. **Ionic Selective Transport Studies Using Potentiometric Measurements**

The goal of the selective transport experiments was to demonstrate that ion selective transport through gold-coated NCAMs could be achieved by chemisorption of chloride ions. When diffusion occurs through a nonselective membrane, there is no unbalance of charge across the membrane, and the electrochemical potential across the membrane is zero. When diffusion occurs through a membrane that is permselective, a Donnan equilibrium potential is established assuming the electrochemical potentials across the interfaces are equal at equilibrium. The current experiment explored the permselectivity of gold-coated NCAMs for different ionic strengths. Electroless gold deposition was performed for five hours on a 30 nm PCTE membrane, with nanotubule pore sizes being reduced to approximately 1-2 nm [25]. The membranes were pretreated in potassium chloride solution to allow chloride ions to adsorb on the surface and pore wall of the membrane. Chemisorption of chloride ions on the gold-coated NCAM ensured a negative surface charge on the surfaces of the membrane. The membrane was therefore made permselective for potassium ions. The concentration on the feedside varied from 0.1-100 mM, while the permeate side of the membrane was kept constant at 0.1 mM. The experiments were performed using a concentrated cell, and the potential of the membrane was measured between two Ag/AgCl reference electrodes shown in figure 4.9.
Figure 4.9. Schematic of the concentrated membrane cell used to measure the membrane potential. Magnetic stirrers were used to reduce the unstirred diffusion boundary layer.

The membrane potential was also calculated by using the Donnan equilibrium equation expressed as:

$$E_m = \frac{2.303}{nF} \left( t_+ - t_- \right) \log \left( \frac{a_h}{a_l} \right)$$

(4.21),

where $t_+$ and $t_-$ are the transference numbers of potassium chloride, and $a_h$ and $a_l$ are the activity coefficients of the feed and permeate concentrated cells. For an ideal cation selective membrane, $E_m$ would vary with $\log(a_h/a_l)$, with an intercept of zero and a slope of 59.1 mV. Figure 4.10 shows the membrane potential as a function of $\log(a_h/a_l)$. The plots show that the permselectivity of the membrane is in good agreement with the theoretical value up to $\log(a_h/a_l) \approx 2$. Above a ratio of 2 or a 10 mM feed concentration, both ionic species are able to diffuse across the membrane. As the ionic strength is increased, the selectivity of the membrane decreases due to a decrease in the electrostatic interaction with the ions and pore walls of the NCAM. The deviation from cation selective membranes
was demonstrated to be slightly lower than previous studies which demonstrated selectivity up to \(\log(a_h/a_l) \approx 3\) for similar deposition times [21]. The higher selectivity which was shown in previous work can be attributed to a pH=11, which was used for the gold bath solution [25]. A higher pH level increases the kinetic reaction of the electroless deposition process with an increase of hydroxide ions, as demonstrated in Equation 4.20. Therefore, for the same deposition time, the gold nanotubule membranes radius will be smaller for a pH=11 compared to a gold bath solution with a pH=10. The electric double layer varies from 30-nm (lowest concentration) to 0.3 nm (highest concentration) during these experiments. This confirms that the permselectivity of a membrane is a strong function of the Debye length, which is in turn a function of the ionic strength of the solution.

\[ \begin{align*}
E_m (mV) & \quad \text{log}(a_h/a_l) \\
0 & \quad 0 \\
50 & \quad 1 \\
100 & \quad 2 \\
150 & \quad 3 \\
200 & \\
\end{align*} \]

**Figure 4.10.** Membrane cell potential measured as the concentration on the feedside varied from 0.1 mM to 100 mM of potassium chloride.
4.7. References


Chapter 5: Ionic Transport Through Sputter Gold-Coated NCAMs by UV Absorption Spectroscopy

5.1. Introduction

In this work, the fabrication of a membrane permeate flow cell is described with the aim of subsequently studying the transport of methyl viologen (paraquat, MV2+) and napathalenedisulfonate disodium salt (NDS2-), using a conductive polycarbonate track etched membrane (PCTE). The membrane was made conductive by sputter coating gold on the PCTE membrane surface. In particular, transport studies were done in a voltage range in which the faradaic current was minimized at the surface of the Au coated nano-capillary-array-membranes (NCAMs). The procedure for the Preparation of Au-Coated Membranes will be carefully outlined. This includes the procedure for sputter coating the membrane, preparation of the monolayer on the membrane surface, and pretreatment of the membrane to eliminate air bubbles inside the nanopores. In addition, the fabrication of Kapton Electrodes is described, for the purpose of applying a potential across the NCAM. The goal of this work is to demonstrate how ion selectivity can be accomplished based on creating high field strengths across the NCAM.

There are mainly three interactions that govern ionic transport through nanopores and nanochannels: steric effects, hydrophobicity, and electrostatic interactions. Because both NDS2- and MV2+ both have nearly the same molecular volume and hydrophobic properties (each contain two benzyl rings), electrostatic interactions is the main contribution of transport of these two analytes across the nanopore. The fluxes of NDS2-
for differently applied potentials are compared for the conductive NCAM with and without the presence of undecanethiol.

5.2. Motivation

Electrodialysis (ED) uses a DC bias as a driving mechanism to selectively transport ions across a series of membranes. This process has been used for the production of drinking water from brackish and seawater. The current efficiency (CE) is a parameter, which can determine the optimum range for ED systems to operate under. Some of the losses in ED systems can be attributed to nonperfect permselectivity and physical leakage of the membrane. Our group has used NCAMs coated with gold to study how permselective the membranes can be under an applied electric field. In the absence of functionalizing the Au-coated membrane surface, it was found that the system is limited to small voltage ranges, which can be applied with limited selectivity. Irreversible changes in charge selectivity can occur by the adsorption of ions on the surface of the Au coated membrane. Functionalizing the membrane with self-assembled monolayers (SAMs) can help reduce irreversibilities at the membrane surface. In our lab, we have electrochemically studied the quality of SAMs under various electrochemical environments. Improving the SAM structure on the membrane surface can lead to improved charge selectivity across the membrane.

Membranes have been used for various applications such as chemical sensing. Authors have shown that detection of analytes can be achieved by interaction with the membrane surface/pore wall. If specific adsorption of a molecule occurs on the membrane
surface, then the detection limit will be inhibited by the loss of interaction between the membrane surface and analyte as seen in Figure 5.1a. If the selectivity can be improved,

![Diagram](image.png)

**Figure 5.1.** Schematics (a) and (b) of a gold coated NCAM, which illustrates the improvement when a well-grown SAM is attached to the monolayer.

then detection can be improved for a specific molecule of interest. SAMs can be used to improve selectivity by minimizing the adsorption of ions on the surface of the membrane (Figure 5.1b). Achieving selectivity at lower voltages results in minimizing faradaic currents. This can play an important role for improving noise-to-signal (S/N) ratios. It is also critical to understand the amount of time needed to have a well-grown monolayer on the membrane surface. Past studies have shown that a minimum of 48 hours is needed to minimize adsorption of ions on the membrane surface [1]. Redox currents typically
increase the background noise. If detection can be accomplished with low voltages, then faradaic currents can be minimized, thus improving S/N ratio.

5.3. Experimental Details

5.3.1. Preparation of Gold-Coated Membranes

PVP coated polycarbonate membranes (PCTE) (Osmonic Inc., MN) membranes were sputter-coated with gold on both sides of the membrane surface, with a 6-nm thick titanium adhesion layer. The membranes are 6-μm thick, with 30-nm pore size and have highly monodisperse distributions of pores with pore densities of $6 \times 10^8$ cm$^{-2}$. The sputtering power was 300 W with a 23 nm/min deposition rate. The chamber pressure during sputtering was 5 mTorr, and the distance between the gold target and the sample was approximately 30-cm. To avoid electrical shortage between each side of the membrane, the edge of the permeation area was not coated. After 2 min of gold sputtering, the diameters of nanopores on the membrane did not change. 11-undecanethiol, purchased from Sigma Aldrich, was dissolved in absolute ethanol (Pharmaco-Aaper, Shelbyville, KY) at a concentration of 1 mM. The NCAM was immersed in undecanethiol solution for 48 hours.
Figure 5.2 shows a summary of the steps involved for preparing a gold-coated NCAM functionalized with an SAM. The monolayer-coated gold was then rinsed with absolute ethanol and DI water and blow-dried with N₂. Prior to experiments, the NCAM was subjected to the channel outgas technique in order to fill the membrane pores with electrolyte. While the membrane was immersed in DI water, the membrane was placed in
vacuum conditions for 24 hours in order to release any trapped bubbles in the pores. Prior to experiments, the NCAM was pretreated with a 1 mM phosphate buffer solution, in order to establish equilibrium conditions for the transport experiments. The gold-coated membranes were SEM-imaged using a Hitachi S4700, with 10 kV electron voltage and 10 μA current as shown in figure 5.3.

Figure 5.3. SEM image of the surface of a gold-sputtered PCTE 30 nm, PVP coated membrane.

Figure 5.4 is an image of NCAM samples placed within a membrane holder, which was sputter-coated with gold. The membranes were placed in a holder to ensure that the samples were completely immersed in solution.
Figure 5.4. Image of gold sputtered on the surface of a NCAM. The NCAM samples were placed in a holder when functionalizing the surface with undecanethiol and removing the trapped air bubbles inside the nanopores by the outgas technique.

5.3.2. Preparation of Kapton Electrodes

To establish an electrical connection to the gold layer on the membrane, two pieces of Kapton (Du Pont 500 HN, 127 μm), gold-coated on one side, were used as working electrodes to apply a potential across the membrane, as shown in Figure 5.5. Kapton films were scored in a long rectangular shape and with a 5-mm diameter hole to allow the transport of ions. The Kapton film was cleaned with solvents followed by 1 min of oxygen plasma treatment at 100 W, which smoothened out the surface and improved the bonding between the adhesion and gold layers. 12-nm of titanium layer was deposited as an adhesion layer, followed by 200-nm of gold layer. A wire was added to the electrodes for electrical connection to the bipotentiostat.
5.3.3. Transport Experiments

Figures 5.6a and 5.6b are schematics and images of the membrane permeate flow cell (MPFC). The membrane was sandwiched between two gold-coated Kapton electrodes. The Kapton electrodes were then clamped between the feed and membrane permeate flow cell (MPFC). An Ag/AgCl reference electrode and gold counter electrode were placed in the feed cell. A CBP Pine Instruments bipotentiostat was used to apply a potential across the conductive NCAM. 1-mM of phosphate buffer solutions was prepared as a ratio of mono- and dihydrogen potassium phosphate salts (Sigma-Aldrich, St. Louis, MO) in DI water, serving as an electrolyte. The permeate cell initially had 1-mM potassium phosphate buffer solution PBS) with pH of 7. The total dead volume of the circulating solution was 1 mL. A peristaltic pump (Masterflex L/S 7520-47) was used to circulate the PBS solution from the MPFC through a Z-cell (FIA Lab) for UV detection of molecules.
Figure 5.6. Schematic (a) and image (b) of the membrane permeate flow cell connected to the UV spectrometer system and the bipotentiostat.
The two molecules being investigated for permeability experiments were methyl viologen dichloride (MV$^{2+}$) and naphthalene 1,5 naphthalenedisulfonic acid disodium salt (NDS$^{2-}$), each purchased from Sigma Aldrich.

Figure 5.7. UV absorption spectra for NDS$^{2-}$ and MV$^{2+}$.

Initial concentrations of each molecule in the feed cell were 1 mM in a 1 mM PBS solution of pH 7. The flowrate used for all experiments was 2.16 ml/min. The effective membrane permeation area was 0.5 cm$^2$. Ionic transport through the NCAM was monitored by UV absorption spectroscopy using a DH-2000 Deuterium Tungsten Halogen Light Source and Jaz spectrometer, Ocean Optics. The concentrations of ions were determined according to wavelengths: MV$^{2+}$ at 257 nm and NDS$^{2-}$ at 228 nm, as shown in figure 5.7.
5.4. Results and Discussion

5.4.1. Effects of transport of NDS\textsuperscript{2−} and MV\textsuperscript{2+} when NCAM is functionalized with a SAM

Figures 5.8 and 5.9 are permeation experiments of NDS\textsuperscript{2−} with and without a SAM present on the surface of the NCAM. The fluxes for NDS\textsuperscript{2−} are higher for applied potentials of +0.4 V, -0.4 V and 0 V (vs. Ag/AgCl) when the NCAM is functionalized with undecanethiol. The increase of flux of NDS\textsuperscript{2−} when a SAM layer is grown on the membrane surface is believed to be a result of a reduction of adsorption of anions (e.g. phosphate, NDS\textsuperscript{2−}).

Figure 5.8. Permeability measurements of NDS\textsuperscript{2−} through a conductive NCAM when the gold surface of the NCAM is not functionalized with a SAM.
Several studies have confirmed that adsorption of anions on a bare gold surface, which functions as a working electrode, occur when electrochemical potentials are applied [2-6]. As demonstrated in previous work, the porosity of the NCAMs is only 10%, which means that the surface interaction with NDS$_2^-$ and the gold-coated NCAM can be significant [7]. The large surface area can lead to insight into how the entrance effect at the NCAM surface may play an important role on the flux of ions across the membrane. As the pore radius of a membrane approaches the nanoscale regime, a resistance develops along the convergent path as ions approach the nanopore. The convergent path has been expressed as an access resistance (AR), which is inversely proportional to the local conductance at the interface between the electrolyte solution and surface of the NCAM.

![Figure 5.9](image.png)

**Figure 5.9.** Permeability measurements of NDS$_2^-$ through a conductive NCAM when the gold surface of the NCAM is functionalized with undecanethiol.
Although analytical and numerical expressions were proposed [2], the AR is usually accounted by using a classic and simple expression derived by Hall from electrostatics [3]. The challenge of some of the previous studies mentioned were that none of the solutions accounted for a charge density at the surface of the membrane. Neumcke (1970) solved the Nernst–Planck equation to find the ion flux across membranes with charged surfaces and specified that the charged membrane surfaces could induce a local enrichment of counterions [4]. Arzo et al. studied how the contributions from the membrane surface and nanopore wall influenced the local resistivity at the membrane-electrolyte interface [5]. It was numerically demonstrated that when the membrane surface contains a charged density (negative or positive), the AR was considerably reduced as a result of an accumulation of counterions near the pore entrance. For the case of a neutral surface charge, their numerical results were in agreement with Hall’s analytical solution. However, when a membrane surface charge was considered, the numerical results proved that Hall’s solution overestimated the contributions of AR. Many additional studies were done to account for the surface charge density at the membrane entrance [6-11]. Cheng et al. investigated how the surface charge at the nanochannel entrance can affect the ion conductance both experimentally and theoretically [12]. The experiment was setup in which there existed high and low concentration potassium chloride solutions on each side of a 20-nm wide channel. When the membrane surface contained a neutral surface charge with a positive nanochannel wall charge density, ionic current rectification was achieved for positively-applied fields applied across the nanochannel. However, it was demonstrated rectification was enhanced (but with opposite polarity) when a negative surface charge density existed on the surfaces of the membrane. The improvement of ion
current rectification was the result of the membrane entrance at the low concentration side of the nanochannel, acting as a diode. These experimental results provide direct evidence that the surface properties at the membrane-electrolyte interface can affect ionic transport across a nanopore/nanochannel. Moreover, it was determined that if the charged surface at the nanochannel entrance had the same polarity with the pore channel (homogeneous entrance and equal concentrations on each side of the nanochannel), the counterion transference number is near unity. This phenomenon is explained as counterions accumulate at the pore entrance and causes a decrease in access resistance at low ion strengths.

The effects of the AR resistance at the membrane-electrolyte interface can also be observed in the present study. As mentioned earlier, anions adsorb on the gold-coated surface of the NCAM when a monolayer is not present. The adsorption of ions creates a negative surface charge density, which acts to reduce the access resistance, or form a diffuse layer potential at the membrane-electrolyte interface. This in turn distorts the local concentration of ions at the surface. Although the bulk concentration of NDS\(^2^\) is believed to not change over the time of the experiment, the local concentration of ionic species at the entrance of the membrane pore can decrease, leading to a smaller local concentration gradient across the nanopore. This in turn can reduce the driving mechanism for diffusion of NDS\(^2^\) and electromigration across the nanopore. As a result, when no monolayer is added, the NDS\(^2^\) molecules are screened due to the diffuse layer potential at the membrane surface. When a monolayer is added, the negative surface charge density is reduced, thus lowering the driving mechanism for counterions to be enriched and anions to be screened, in order preserve electroneutrality. This enables the NDS\(^2^\) molecules to migrate across the
NCAM with less electrostatic resistance ascribed from the surface charge at the membrane surface; which in turn enables NDS$^{2-}$ to permeate with a higher flux across the NCAM.

Figures 5.10 and 5.11 show that fluxes for MV$^{2+}$ are higher for applied potentials of +0.4V, -0.4V and 0 V (vs. Ag/AgCl) when a SAM is not grown on the surface of the NCAM. The results are in contrast with transport of NDS$^{2-}$ through the NCAM. When a monolayer is not present on the gold surface, the negative surface charge present on the NCAM attracts the counterions (MV$^{2+}$) to accumulate near the surface of the membrane. This in turn, increases the local concentration of MV$^{2+}$ at the entrance of the membrane, resulting in an increase of conductance of MV$^{2+}$ across the nanopore. As mentioned earlier, the net negative surface charge on the membrane surface is significantly reduced when undecanethiol is added to the NCAM surface. This leads to a reduction of a negative surface charge, which acts to reduce the accumulation of MV$^{2+}$ at the membrane surface. The decrease in accumulation of MV$^{2+}$ leads to a smaller flux across the NCAM compared to the case when the gold surface of the NCAM was not functionalized with an alkane SAM.
Figure 5.10. Permeability measurements of MV$^{2+}$ through a conductive NCAM when the gold surface of the NCAM is not functionalized with a SAM.

Figure 5.11. Permeability measurements of MV$^{2+}$ through a conductive NCAM when the gold surface of the NCAM is functionalized with undecanethiol.
5.5. Effects of ion selectivity when monolayer formation is present

Table 1 summarizes the fluxes and selectivity coefficients for transport experiments for NDS\(^2^−\) and MV\(^2^+\). For NDS\(^2^−\), the percentage of increase in flux when a SAM is added were approximately 12\%, 73\%, and 20\% for potentials of 0 V, 0.4 V, and -0.4 V. The percent decrease of flux of MV\(^2^+\) when a monolayer is added is 26\%, 52\%, and 0.50\% for applied potentials of 0 V, 0.4 V, and -0.4 V respectively. The selectivity coefficient for anions is defined as:

\[
\alpha_{+0.4/-0.4} = \frac{\text{flux of anion at 0.4 V}}{\text{flux of anion at -0.4 V}}
\]  \hspace{1cm} (5.1).

<table>
<thead>
<tr>
<th>Applied Voltage (V)</th>
<th>Unmodified</th>
<th>Modified</th>
<th>Unmodified</th>
<th>Modified</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.44<em>10(^2^)±5.71</em>10(^{-4})</td>
<td>1.61<em>10(^2^)±1.30</em>10(^{-3})</td>
<td>1.70<em>10(^1^)±4.42</em>10(^{-3})</td>
<td>1.26<em>10(^1^)±7.61</em>10(^{-3})</td>
</tr>
<tr>
<td>+0.4</td>
<td>4.75<em>10(^2^)±3.23</em>10(^{-3})</td>
<td>8.24<em>10(^2^)±2.18</em>10(^{-3})</td>
<td>1.62<em>10(^1^)±5.71</em>10(^{-3})</td>
<td>7.81<em>10(^2^)±3.73</em>10(^{-3})</td>
</tr>
<tr>
<td>-0.4</td>
<td>1.11<em>10(^1^)±5.71</em>10(^{-3})</td>
<td>1.33<em>10(^1^)±8.33</em>10(^{-4})</td>
<td>2.03<em>10(^1^)±3.65</em>10(^{-3})</td>
<td>2.02<em>10(^1^)±6.34</em>10(^{-3})</td>
</tr>
</tbody>
</table>

\[\alpha_{0.4/-0.4} = 4.3\]

\[\alpha_{-0.4/0.4} = 6.2\]

\[\alpha_{-0.4/0.4} = 1.25\]

\[\alpha_{0.4/-0.4} = 2.6\]

The selectivity coefficient for cations is defined as:

\[
\alpha_{-0.4/+0.4} = \frac{\text{flux of cation at 0.4 V}}{\text{flux of cation at -0.4 V}}
\]  \hspace{1cm} (5.2).

The selectivity coefficient increases from 4.3 to 6.2 when undecanethiol is attached to the gold-coated NCAM. This supports the argument that the irreversibilities on the surface of a gold-coated NCAM can be reduced when a monolayer is grown on the surface. However,
it should also be noted that the absolute flux of NDS$^{2-}$ when applying potentials of 0.4 V, 0 V, and -0.4 V actually increase. This can be attributed to the surface charge density formed on the bare gold surface, which aid in screening the NDS$^{2-}$ molecules from transporting across the NCAM. When the monolayer was added, the electrostatic repulsion towards anions is weakened, leading to a higher flux of NDS$^{2-}$. This in effect meant that the contributions of ionic transport were mainly from the applied electric field and the surface charge density at the PVP coated walls, which will be discussed in the next section. Similarly, MV$^{2+}$ displays a distinct improvement for selectivity when the monolayer is added to the surface. As mentioned earlier, the selectivity of methyl viologen is improved with an added monolayer, due to an increased ability of the membrane to selectively screen MV$^{2+}$ at positively applied potentials. In addition, the challenge of this work is to try and improve the selectivity when applying anodic potentials. This can be achieved by making the selectivity coefficient ratios closer to unity. The ratios of the cathodic and anodic selectivity coefficient with and without a monolayer are approximately 3.4 and 2. What we have demonstrated is that selectivity can be achieved when applying anodic and cathodic potentials.

5.6. Effects of Nanopore Charge and EDL Thickness on the Fluxes of NDS$^{2-}$ and MV$^{2+}$

The three mechanisms for ionic transport across a PCTE membrane are diffusion, electromigration, and electroosmosis. The dominant effect of the three mechanisms of transport depends on the pH of the solution, the ionic strength, and the pore size of the membrane. Although there is no electric double layer overlap, it has been postulated that
EDL overlap is not necessary to distort the equilibrium concentration within a nanopore [13, 14]. It has been demonstrated that electroosmotic effects are especially critical at low ionic strengths (≤ 10 mM). Past work has shown that selectivity of MV\(^{2+}\) could be achieved by functionalizing the membrane with an amine terminal group [13]. The membrane pore size was 20 nm and the ionic strength was 10 mM of potassium phosphate buffer.

At ionic strength of 7mM, the electric double layer covers about 27\% of the pore area for a 30-nm NCAM. That means that the electroosmotic effects cannot be ignored. The index for determining how much the electric double layer covers the pore wall is given as $\kappa a$, where $\kappa$ is defined as the inverse Debye length and $a$ is the diameter of the nanopore. For $\kappa a=1$, the dominant mechanism for transport is electroosmosis. For $\kappa a=15$-150, the electroosmotic effects are still pertinent to the transport of analyte as observed in previous studies [14]. However, the contributions of electromigration are also important within this regime. For $\kappa a<1$, electroosmotic effects are negligible, while electromigration and diffusion components are central. For the present studies, $\kappa a$ is approximately eight. It means that within this regime, electroosmotic and electromigration effects within the pore wall are relevant. The surface charge of PVP coated PCTE membranes contain a negative surface charge density at a pH level of 7 [15]. As mentioned earlier, the ionic mobilities of NDS\(^{-}\) and MV\(^{2+}\) are similar due to similar molecular volumes (0.637 nm\(^3\) for NDS\(^{-}\) and 0.680 nm\(^3\) for MV\(^{2+}\)), similar hydrophobic properties (each contain two benzyl rings), and same valencies ($z=2$) with opposite charge [14]. However, as demonstrated in Table 1, the flux of MV\(^{2+}\) at a potential of 0 V (vs. Ag/AgCl) is 8 and 12 times larger for NCAMs with and without a SAM layer. It should
also be pointed out that the ratio of flux between NDS2- and MV2+ decreases as the irreversibilities from the negative surface charge density at the membrane surface is reduced. The higher flux can be attributed to the electroosmotic effect within the nanopore. Although the double layer only covers approximately 27% of the pore, screening effects of coions still occur. Figure 5.12 shows a schematic of the different mechanisms of charge transport through an NCAM under an external electric field.

When a negatively applied field is applied across (with respect to the feedside), the vector for migrational flux of NDS2- points in the opposite direction to that of the electroosmotic and diffusional flux, as shown in Figure 12a. For MV2+, the migrational flux vector always points in the same direction as the electroosmotic flux, as displayed in Figure 12b. This is a result of the accumulation of mobile cations at the surface of the NCAM secondary to the negative charge density present a pH=7. The mobile cations at the surface migrate towards the cathodic potential.
5.7. Conclusions

In this chapter, it has been demonstrated that functionalizing the NCAM surface with a SAM can enhance charge selectivity. It was demonstrated that entrance effects at low ionic strengths cannot be ignored and can dictate the transport of analytes across a nanopore. This work opens up the possibility of using SAMs with differently charged headgroups to manipulate ions based on the diffuse layer potential at the surface of the

Figure 5.12. Mechanisms of Ionic Transport a conductive NCAM for MV$^{2+}$ and NDS$^{2-}$ under an applied electric field.
membrane. It is also relevant to investigate transport mechanisms at lower and higher ionic strengths to find the critical concentration in which entrance effects become negligible. Future work should also include growing monolayers on the membrane surface for incubation times longer than 48 hours. EIS experiments in previous work have already demonstrated that monolayers grown for five days can significantly enhance the quality of a SAM [1].

5.8. References


Chapter 6: Conclusion

6.1. Summary

In Chapters 2 and 3, it was demonstrated that EIS is a sensitive probe of monolayer condition. Defects in the monolayer are readily detected as deviations from capacitive behavior with the appearance of charge transfer resistance and critical voltage behavior, and are evident even at the usual incubation times reported in the literature. These results have ramifications for investigation and application of electrochemical sensors based on immobilized enzymes on SAMs. EIS is a facile method of screening SAM electrodes for defects, especially since the same equipment (potentiostat in CV or CA mode) used in the enzyme electrode studies is also utilized to check the monolayer (potentiostat in EIS mode). Short-chain thiols (n<7) generally do not form well-ordered monolayers, and sensors built on these thiols are expected to have high double-layer charging from pinholes and background currents from redox species in solution, competing with enzyme catalytic current; and thus, reducing the sensitivity of the method [1, 2]. Sensors made with longer-chain thiols that were not allowed sufficient time to anneal, will likewise suffer from background currents from pinhole conduction [3]. Although the tunneling barrier at long-chain thiols (n≥14) limits the transduction current, the reduction in electron transport rate is not as severe at medium chains, and the ability to form highly-ordered layers resulting in decreased background current is advantageous [4]. The larger range of working potentials afforded by well-ordered monolayer resulting from lengthy incubation times allows a
larger repertoire of enzymes with a wider range of \( E_0 \). For transport studies, utilizing a SAM on a gold-coated nanoporous membrane, EIS can be used similarly as a probe of the insulating property. Insulation is especially crucial for short-length scales found in microchannels and nanopores. A wider range of electrode potentials can be applied when the monolayer is highly ordered, allowing a greater range of available diffuse layer potentials. Permeation of ions into a well-ordered monolayer is reduced, extending the usable life of the device. This laid the groundwork for finding the limits of applied potentials on a blocking monolayer with minimal faradaic current.

In chapter 4, the transport of ions across a conductive permselective membrane was studied. Studies included the fabrication of gold-coated NCAMs by the electroless gold deposition process, which coats the pore wall and surface of the membrane. The challenge for this process was to ensure that the gold deposition process could be controlled in order to prevent fabrication of nanoelectrodes, as opposed to nanotubes. This was accomplished by studying the pH, temperature, and concentration of the gold solution. It was found that a lower pH and temperature led to more uniform gold nanotube structures. The goal of the selective transport experiments was to demonstrate that ion selective transport through electroless gold-coated NCAMs could be achieved by electrostatically screening ions. This process was achieved by creating a negative surface charge on the membrane surface by chemisorption of chloride ions. The membrane was, therefore, made permselective for potassium ions. A u-tube permeate cell was fabricated in order to measure the membrane potential across the electrochemical cell. The driving mechanism of ionic transport was accomplished by providing a concentration gradient between the feed and permeate side of the membrane. The concentration on the feedside varied from 0.1-100 mM, while the
permeate side of the membrane was kept constant at 0.1 mM. Two Ag/AgCl reference electrodes placed on each side of the electrochemical cell measured the membrane potential. At low ionic strength, counterions built up at the surfaces of the membrane were used to maintain electroneutrality. For an ideal cation selective membrane, $E_m$ varies with $\log(a_h/a_l)$, with an intercept of zero and a slope of 59.1 mV. It was demonstrated that cation selectivity could be achieved up to $\log (a_h/a_l) \approx 2$. Results showed that selectivity of the NCAM decreased as ionic strength increased, as a result of a decrease in electrostatic interaction between the analytes and pore wall.

In Chapter 5, the ionic transport through conductive NCAMs was extended by studying how ions could be selectively transported by creating a high field strength (~50 kV/m) across the membrane. The membrane was made conductive by sputter coating gold on the surface of a 30-nm polycarbonate track etched membrane (PVP coated) membrane. These studies differed from Chapter 2, in which the surface and pore wall of the membrane were coated with gold, which did not allow an electric field to be applied across the membrane. Transport experiments were carried out by UV absorption spectroscopy. A membrane permeate flow cell was fabricated to study the transport of NDS$^{2-}$ and MV$^{2+}$ through the conductive NCAM. By varying the potential across the membrane, it was verified that enrichment or screening of ions could be attained based on electrostatic interactions at the surface and pore wall of the membrane. It was demonstrated that at a low ionic strength, the diffuse layer potential could distort the local concentration of ions by attraction of counterions and exclusion of coions at the NCAM surface. Functionalizing the membrane surface with undecanethiol reduced the adsorption of anions.
This in turn diminished the role of the entrance effects by reducing the charge at the surface of the membrane.

### 6.2. Future work

In Chapter 2, the insulative properties of hydroxyl terminated and methyl-terminated groups were investigated. In future work, we would like to investigate how the hydrophobic interaction at the surface of the membrane can affect ionic transport through an NCAM functionalized with a SAM. For example, the number of sulfonates per aromatic ring for NDS$^2$- is one [5]. A ratio of unity signifies that NDS$^2$- can exhibit both hydrophobic and hydrophilic behavior. It would be of interest to study how molecules, which contain both hydrophobic and hydrophilic properties, transport across membranes functionalized with hydroxyl and methyl terminated SAMs.

In addition, an interesting study would be to characterize the quantification of pinhole density (or number of defects) of a SAM and how this may affect the interfacial thermal conductance. In Chapters 2 and 3, it was demonstrated that EIS could be used to study the quality of a monolayer by studying the impedance of SAMs over a wide range of frequencies. However, the pinhole density could not be determined using EIS. Future work can be performed using STM measurements to understand the structure of SAMs for longer incubation times under different applied potentials. Several factors including some of the parameters for growing the SAM (annealing of substrate, temperature of thiol solution, immersion time of substrate in monolayer solution) on a substrate may lead to an overall improved monolayer structure. By quantifying the pinhole density for different electrochemical conditions, an empirical relationship can be derived, which can establish a
relationship between the impedance of the SAM and the number of defects present. Past studies have shown the defect density for alkane SAMs, but not for SAMs where potentials were applied at the monolayer surface. Finding the pinhole density at different applied potentials is critical because it has been shown that conformational changes take place on the SAM structure, especially at potentials negative of the potential of zero charge. As discussed in Chapters 1 and 2, some of the challenges for electrodialysis are energy losses due to the large voltages required to drive ions across the membrane stacks. The large voltages are a result of the highly-uncompensated solution resistance across the ED cell. By applying small potentials across the membrane, high field strengths can be achieved, which can lower the amount of required voltage necessary to drive ions across the membrane. In the future, we would like to fabricate an ED cell, and integrate an AC electrokinetic approach for controlling the surface charge across the membrane. With the introduction of an AC field, the frequency of the AC potential can be the driving force for controlling the rate of separation of ions.

6.3. References


