Western Kentucky University
TopSCHOLAR®

Honors College Capstone Experience/Thesis Projects

Honors College at WKU

2010

# Adsorption Efficiency and Partitioning Capabilty of Surfactant Monolayers on Gold

Carrie Jo M. Pruitt
*Western Kentucky University*

Follow this and additional works at: http://digitalcommons.wku.edu/stu_hon_theses

Part of the Chemistry Commons

Recommended Citation
Pruitt, Carrie Jo M., "Adsorption Efficiency and Partitioning Capabilty of Surfactant Monolayers on Gold" (2010). *Honors College Capstone Experience/Thesis Projects.* Paper 239.
http://digitalcommons.wku.edu/stu_hon_theses/239

This Thesis is brought to you for free and open access by TopSCHOLAR®. It has been accepted for inclusion in Honors College Capstone Experience/Thesis Projects by an authorized administrator of TopSCHOLAR®. For more information, please contact connie.foster@wku.edu.

# ADSORPTION EFFICIENCY AND PARTITIONING CAPABILITY OF SURFACTANT MONOLAYERS ON GOLD

A Thesis Project

Presented in Partial Fulfillment of the Requirements for

the Degree Bachelor of Science with

Honors Program Graduate Distinction at Western Kentucky University

By

Carrie Jo M. Pruitt

* * * * *

Western Kentucky University
2010

Thesis Committee:

Dr. Stuart C. Burris, Advisor

Dr. Eric D. Conte

Dr. Andrew Mientaltowski

Approved By

Advisor
Department of Chemistry

Copyright by
Carrie Jo M. Pruitt
2010

ABSTRACT

We are investigating adsorption efficiencies of sodium dodecyl sulfate (SDS) from pH 7 phosphate buffer onto polycrystalline gold substrates using electrostatics as the primary driving force via electrochemical control of the gold surface potential. It is shown through surface capacitance measurements by electrochemical impedance spectroscopy that the adsorption occurs readily. Measurement of the adsorption isotherms of SDS onto the substrate via the change in surface capacitance as a function of the bulk concentration of SDS has allowed us to determine that the minimum concentration of SDS required for efficient adsorption is below 0.011 mM. The investigation of the influence of the gold surface potential will also be presented. Further, we are probing the capability of the SDS monolayers to partition small polycyclic aromatic hydrocarbons (PAHs) from aqueous solutions. The goal of this work is to produce an electrically switchable surface for efficient pre-concentration of PAHs prior to chromatographic determination.

Keywords: Electrochemistry, Surfactants, Self-Assembled Monolayers, Preconcentration, Impedance Spectroscopy, Polycyclic Aromatic Hydrocarbons

Dedicated to 6999 3666222, Mummy, Mr. White, and the rest of my family

ACKNOWLEDGEMENTS

Deepest gratitude is expressed to a number of individuals
who have influenced and shaped me into who I am today…
for better or worse.

$P^3$ – Roll Tide.

CP – The best friend a Nougat could have.

Stewie B – For providing the rope, but not tying the noose

EC – For the trip to Taiwan and the soap

Iceman – Au FTW.

VITA

May 6, 1988……...…..……Born – Bowling Green, Kentucky

2006…….……... Edmonson County High School, Brownsville, Kentucky

2008……...…..South East Regional Meeting of the American Chemical Society

2009…… Pittsburgh Conference for Analytical Chemistry and Applied Spectroscopy

2009…….Western Kentucky University Student Research Conference

2010……Spring National Meeting of the American Chemical Society

FIELDS OF STUDY

Major Field: Chemistry

Minor Field: Mathematics

TABLE OF CONTENTS

Page

Abstract…….……ii

Dedication……iii

Acknowledgments……...……iv

Vita……v

List of Figures……...……..vii

Chapters:

1. Introduction……..1

2. Theory…… ……..…...4

A. Experimental Background…….4
B. Electroanalytical Methods…… ……7

3. Methods…….....11

A. Instrumentation and Materials……...……..11
B. Establishment of Monolayer……...……12

4. Results and Discussion……..……13

A. [0.33]mM SDS……..……...13
B. [0.22]mM SDS……..……...13
C. [0.11]mM SDS……..……...14
D. [0.033]mM SDS……..……14
E. [0.022]mM SDS……..……..……..14
F. [0.011]mM SDS……..…….……14

5. Conclusions……...…….22

6. Future Work……...23

References……...24

LIST OF FIGURES

Figure Page

2.A.1 Sodium Dodecyl Sulfate (SDS) surfactant molecule……...4

2.A.2 Experimental Background Image I……..5

2.A.3 Experimental Background Image II……...……..6

2.A.4 Experimental Background Image III….……..6

2.A.5 Experimental Background Image IV……...7

2.B.1 Current Response to Sinusodial Potential……8

2.B.2 Equivalent Circuit Model for Electrochemical Cell……9

4.A.1 Graph of Change of Capacitance for [0.33]mM SDS……15

4.A.2 Graph of Change of Capacitance versus Potential for [0.33]mM SDS……...……..16

4.B.1 Graph of Change of Capacitance for [0.22]mM SDS……17

4.C.1 Graph of Change of Capacitance for [0.11]mM SDS……18

4.D.1 Graph of Change of Capacitance for [0.033]mM SDS……..……19

4.E.1 Graph of Change of Capacitance for [0.022]mM SDS……..……20

4.F.1 Graph of Change of Capacitance for [0.011]mM SDS……..……21

# CHAPTER 1

# INTRODUCTION

Trends in recent years show a growing demand in environmental concerns. One area of particular concern is limiting the exposure to and removing a group of organic molecules known as polycyclic aromatic hydrocarbons (PAHs). The Environmental Protection Agency has classified PAHs as a significant contributor to pollution, in addition to classifying several as carcinogenic, mutagenic, and tertaogenic in nature. (*1*) PAHs are generated from a variety of processes, both natural and synthetic, such as volcanic activity, forest fires, and the combustion of fossil fuels. (*2*) (*2*) As a part of the effort to limit exposure and remove PAHs from the environment, it is necessary to know at what concentration levels PAHs are present in order to prioritize and triage hazardous waste sites. In order to determine concentration levels of PAHs, raw samples must be collected from a matrix under study and taken through specific steps of sample preparation. Sample preparations often include the task of pre-concentrating an analyte. Pre-concentration is most easily defined as a process that increases the ratio of the analyte (the PAH to be analyzed) to the matrix. (*3*) This is a necessary step due to detection limits of modern instrumentation used in executing these types of analyses. The amount of PAHs present in raw samples can often be high enough to pass human toxicological thresholds, however, those thresholds are below the detection limits for many common techniques such as high performance liquid chromatography (HPLC);therefore, to increase the amount of PAHs to a detectable level

the sample undergoes a pre-concentration process. Some relatively common means of pre-concentration of PAHs include: cloud-point, liquid-liquid extraction, and solid phase extraction.

The cloud-point method takes advantage of the effects of temperature on solubility. In this method, a solution is cooled by various means and added to a 1% surfactant solution. As the solution cools, the solute and surfactant start to precipitate because their solubility decreases with the temperature of the solution. This results in the formation of a cloudy second phase. Decanting the matrix without the analyte leaves a concentrated level of the analyte in the surfactant phase. (*4*) (*5*) The cloud-point method is relatively environmentally friendly, typically not requiring the use of harsh organic solvents and can recover almost 100% of the PAHs. (*6*) However, pre-concentrating using the cloud-point method requires that the temperature of the solution be controlled accurately, making certain that the temperature of the solution does not surpass the cloud-point of the surfactant, which can vary based on the structure of the surfactant in use. (*7*)

Liquid-liquid extractions as a means of pre-concentrating PAHs require the use of organic solvents to achieve separation based on solubility and miscibility. When using liquid-liquid extractions as a means to pre-concentrate, an aliquot of an organic solvent, typically dichloromethane, is added to an aqueous solution of the analyte in a separatory funnel. This particular method requires the use of a large volume of solvent to extract the analyte. Another method involves having a dedicated apparatus that cycles through a given volume of solvent to complete the extraction. The appeal of liquid-liquid extractions is that it is a relatively straight forward means of pre-concentration. However, liquid-liquid extractions have drawbacks that overshadow the simplicity of the method. One drawback of liquid-liquid extractions involves the use of highly dangerous organic solvents in large volumes. Dichloromethane is known to readily absorb into the skin and cause depression in the central nervous system, mutations in blood, as well as being listed as a carcinogenic compound, thusly creating a serious safety concern for those completing the extractions. (*8*) In addition to this, due to the large volume of solvent used, a

decrease in potential sensitivity is lost because only a small volume of the extract will be analyzed. (*9*)

Pre-concentrating using solid-phase extractions employs the use of a mobile phase and a stationary phase. In a solid-phase extraction the sample containing the analyte is known as the mobile phase and is passed through a solid known as the stationary phase. The affinity of the analyte for either the mobile phase or the stationary phase (depending on the parameters of the analysis) separates the sample into desired and undesired components. If the analyte is in the mobile phase after the extraction, the sample is said to be pre-concentrated. However, if the analyte is adhered to the solid phase it must be removed by eluting it. Solid-phase extractions are more effective than liquid-liquid extractions at pre-concentrating analytes, but often involve the same type of hazardous organic solvents as eluting agents. In addition to this, solid-phase extractions are further complicated by the need for specific properties of the stationary phases based on the analytes present.

In summary, current methods for the pre-concentration of PAHs involve hazardous chemicals that are often more dangerous than the analytes being analyzed and can suffer a loss in sensitivity due to the poor quality of pre-concentration associated with large extraction volumes. As a result of the shortcomings of modern methods of pre-concentration of PAHs, there is a growing demand for a more effective method of pre-concentration. A new method of pre-concentration for PAHs needs to be effective, environmentally friendly, simple, and sensitive. With these needs in mind, work has begun on creating a novel method of pre-concentration utilizing an environmentally friendly, anionic surfactant, sodium dodecyl sulfate (SDS) and employs simple electrostatics as the primary driving force to create a monolayer of SDS on a polycrystalline gold substrate. This monolayer of SDS then captures PAHs, which allow for the effective pre-concentration of the PAHs prior to further analysis using HPLC.

CHAPTER 2

THEORY

A. EXPERIMENTAL BACKGROUND: When examining the molecular structure of SDS (Figure 2.A.1), it is clear that there is an electron rich region on the surfactant molecule around the sulfate head.

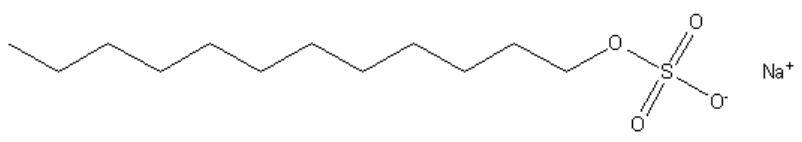


**Figure 2.A.1:** Sodium dodecyl sulfate (SDS) surfactant molecule

In solution, at concentrations below the critical micelle concentration (CMC), individual surfactant molecules are disordered and free to move about in the system. (Figure 2.A.2) By taking advantage of the anionic character of SDS, simple electrostatics is employed as the primary driving force to create the monolayer of SDS on the surface of the substrate.

(Figure 2.A.3) This is accomplished by using a potentiostat to apply a positive bias to the substrate to attract and orientate the surfactant molecules perpendicular to the gold substrate.

Through electrochemical impedance spectroscopy, the amount of positive bias applied to the gold substrate can be manipulated. It is possible to keep the layer adhered to the substrate, by applying a positive bias to the substrate, or remove the monolayer by applying a negative bias to the substrate. Once the SDS monolayer has been established, a sample containing the analyte is introduced into the electrochemical cell by an exchange of solution. The alkyl tails of the surfactant molecules in the SAM promote the entrapment of the PAH into the system. (Figure 2.A.4) By applying a negative bias to the gold substrate, the dynamics of the system change. This allows for the removal of the SDS monolayer and the partitioned PAHs from the surface of the gold substrate, pre-concentrating the PAHs and SDS into a volume equivalent to that of the electrochemical cell.

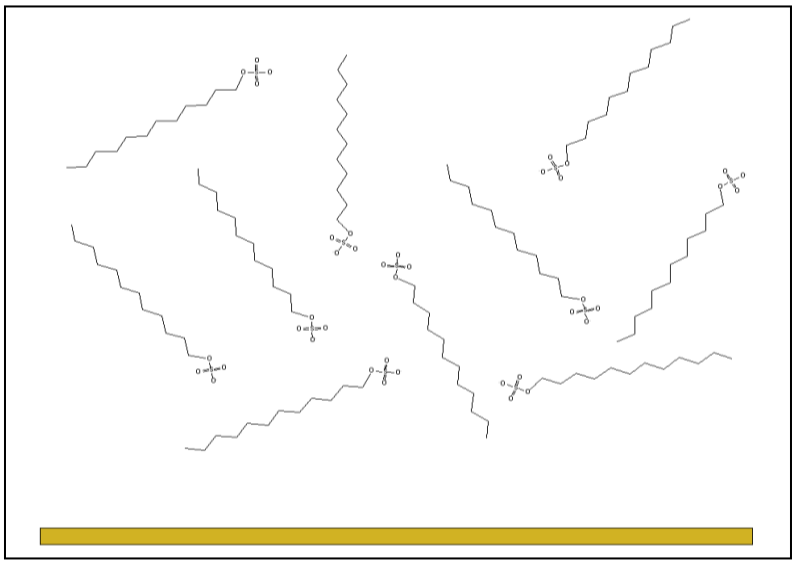

**Figure 2.A.2**: No bias on the gold substrate

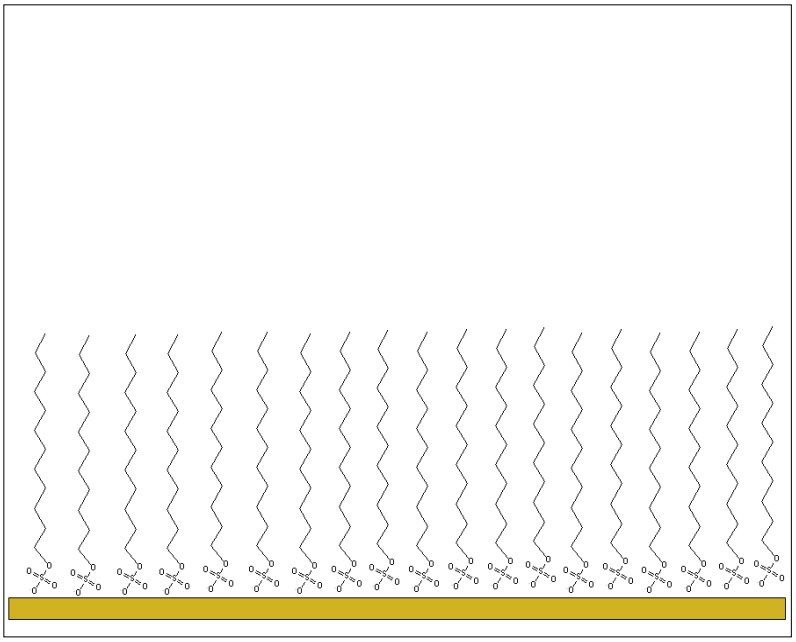

**Figure 2.A.3:** Positive bias applied to gold substrate promotes SDS SAM formation

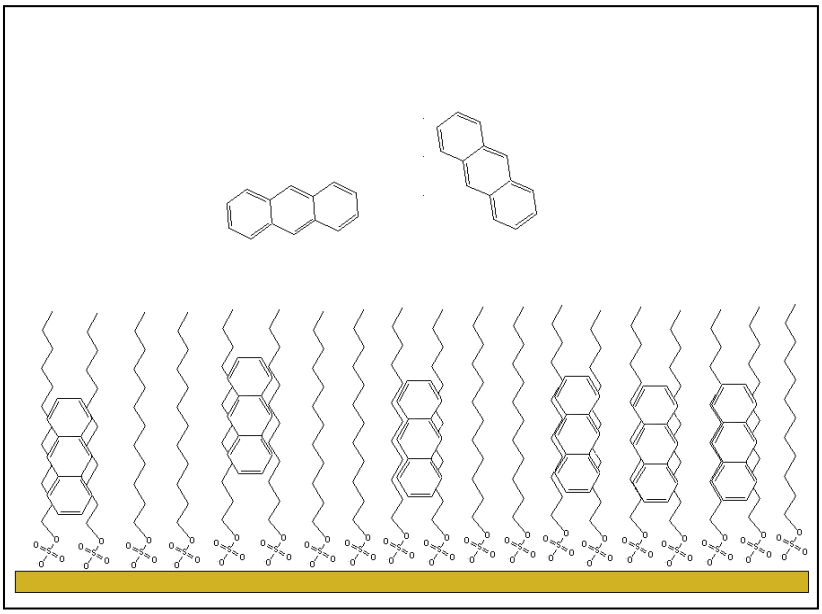

**Figure 2.A.4:** Alkyl tails serve to trap PAHs in the SDS SAM

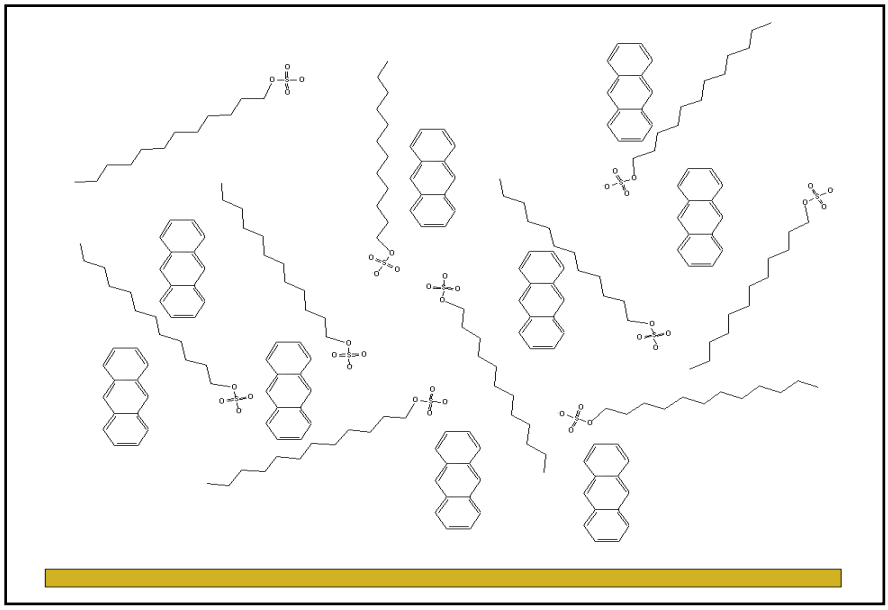

**Figure 2.A.5:** The SDS SAM and PAHs are repelled off the gold surface by applying a negative bias

<u>B. ELECTROANALYTICAL TECHNIQUES:</u> Cyclic voltammetry (CV) is one of two electroanalytical techniques employed in this project. In CV, the potential of the working electrode is ramped at a constant rate, similar to linear sweep voltammetry (LSV), to a specified potential. Unlike LSV though, CV then proceeds to invert the potential of the working electrode, taking the potential of the electrode back to its initial potential. Through the use of CV, the amount of usable surface area of the working electrode, the substrate, is increased. This happens through the oxidation and reduction of the gold coating on the substrate. The oxidation of the substrate strips elemental gold off of the substrate, converting it to gold(III) oxide and tetracholoraurate ion – $[AuCl_4]^-$. Gold(III) is then reduced and deposited back on the surface of the substrate as elemental gold again. In this application, CV cleans and slightly roughens the surface of the gold substrate.  CV can also used to measure the capacitance of the system, though this is not the primary application of the technique in this project.

Activity at the substrate-solution interface in the system is determined by measuring the change in the capacitance of the system using electrochemical impedance spectroscopy (EIS). EIS works on the basis of applying an AC potential to an electrochemical cell and measuring the current through the cell. Normally, this is accomplished by using small excitation signals so that the response of the cell is pseudo-linear. Linearity allows for the current response to a sinsusodial potential to be a sinusoid at the same frequency but shifted in phase. (Figure 2.B.1) (*10*)

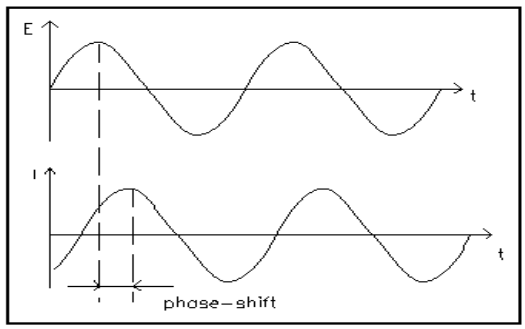


**Figure 2.B.1**: Current response to a sinsusodial potential

As a function of time, the potential can be expressed by equation 1:

$$E(t) = E_0 \sin(\omega t) \quad (1)$$

where $E(t)$ is the potential at a given time, $E_0$ is the amplitude of the excitation signal, and ω represents radial frequency. The radial frequency is related to the frequency of the system by equation 2:

$$\omega = 2\pi f \quad (2)$$

where $\omega$ is the radial frequency measured in radians/second and $f$ is the frequency of the system measured in hertz. The response of the system to the excitation signal is given by equation 3:

$$I_t = I_0 \sin(\omega t + \phi) \quad (3)$$

where $I_t$ is the response signal, $I_0$ is the amplitude of the response signal, $\omega$ is the radial frequency, and $\phi$ is the shift in the phase angle. From the excitation signal and the response of the system to the excitation signal, the impedance of the system can be determined using equation 4:

$$Z = \frac{E_t}{I_t} \quad (4)$$

where $Z$ is the impedance of the system and $E_t$ and $I_t$ are as previously defined. Once impedance data is collected, it is analyzed by equivalent circuit modeling. This uses common elements such as resistors, capacitors, and inductors to model the actual impedance response of the system. The equivalent electrical circuit model applied to the electrochemical cell used in this project consisted of a simple resistor and capacitor. (Figure 2.B.2)

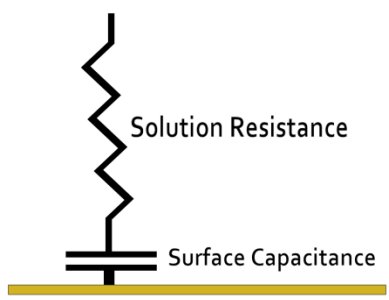


**Figure 2.B.2**: Equivalent electrical circuit model for electrochemical cell

The resistor represents the solution inside of the cell while the capacitor represents the interface between the substrate and the solution, separated by the layer of surfactant, acting as the dielectric. Capacitance can be defined as in equation 5:

$$C = \frac{\varepsilon_o \varepsilon_r A}{d} \qquad 5$$

where $C$ is the capacitance, $\varepsilon_o$ is the permittivity of free space, $\varepsilon_r$ is the relative electrical permittivity (dielectric constant), $A$ is the area of the substrate, and $d$ is the distance between the substrate and the solution interface. Upon examination of equation five, it is evident that the capacitance decreases for two reasons with the addition of the surfactant molecules to the substrate. First is the change in dielectric constant from that of water (~80) to that of the carbon chain in the surfactant (< 5). Second is the increase in the distance between the substrate and the solution. The application of the RC model to the EIS data allows for the extraction of resistance and capacitance data, a crucial step in this project.

# CHAPTER 3

# METHODS

A. INSTRUMENTATION AND MATERIALS: A Princeton Applied Research (PAR) PARSTAT 2263 Advanced Electrochemical Workstation (potentiostat), operating with Electrochemistry PowerSUITE™ was utilized for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments. A Ag/AgCl reference electrode filled with 1.0 M potassium chloride solution was used with a custom built electrochemical cell. All potentials herein are with respect to this Ag/AgCl reference electrode which has a potential of 0.222 V versus the Standard Hydrogen Electrode. Gold substrates were purchased from EMF Corp (Ithaca, NY) as item number TA134, a standard 25.4 × 76.2 mm by 1 mm thick microscope slide coated with 5 nm of Ti and 100 nm of Au. To maximize the usable area these slides are scored and snapped into~19 × ~25 mm pieces. Once the cell has been assembled, it is rinsed thoroughly with Type I water (specific resistivity ≥ 18 MΩ-cm). The working surface of the gold substrate is electrochemically etched using cyclic voltammetry in a solution of 5.0 mM potassium chloride in 0.1 M sulfuric acid. Upon the completion of the etching process the etching solution is removed from the cell, it is rinsed thoroughly with regular deionized water, then with Type I water, and finally with pH 7 phosphate buffer. The cell is then filled to capacity with pH 7 phosphate buffer and the cell, along with the reference electrode, is connected to the potentiostat.

B. ESTABLISHMENT OF MONOLAYER: To establish that a monolayer of SDS molecules is formed on the surface of the gold substrate, background CV and EIS scans were taken. The background scans are taken while the cell contains only the pH 7 phosphate buffer to establish a baseline capacitance. This is accomplished by running a CV scan from +0.7 V to -0.3 V. Next EIS scans are collected from +0.7 V to -0.4 V in 0.05 V steps. After the conclusion of the first series of EIS scans, the electrochemical cell is turned off. The buffer solution inside of the cell is exchanged for a solution of SDS at a concentration of interest somewhere below the CMC in pH 7 phosphate buffer. With the introduction of SDS into the cell complete, the electrochemical cell is reconnected. Next, EIS scans with a bias of +0.7 V on the gold substrate are run in a twenty iteration loop. The bias of +0.7 V induces the positive surface charge that is responsible for driving the construction of the SDS monolayer. This happens as a result of electrostatic interactions between the electron rich region of the sulfate group in the surfactant and the net positive charge on the gold substrate. After the completion of this scan, the electrochemical cell is left on, meaning that the positive bias is still on the gold substrate. The SDS solution is exchanged for a solution of pH 7 phosphate buffer while the bias remains applied. Another twenty EIS scans are then taken , still with a bias of +0.7 V. These data establish the existence of the SDS monolayer by confirming a significantly lower capacitance on the gold substrate with the surfactant molecules adhered. To remove the surfactant monolayer from the gold substrate, a final series of EIS scans are ran from +0.7 V to -0.4 V in 0.05 steps. This ultimately applies a negative bias to the gold causing the electrostatic attraction between the substrate and the surfactant to be disrupted. The data collected from the EIS scans was compiled and modeled using ZSimpWin.

# CHAPTER 4

# RESULTS AND DISCUSSION

## A. [0.33]mM SDS

Several experiments were run with the concentration level of the surfactant at [0.33]mM. The average drop in capacitance for this concentration was 1.35 x $10^{-5}$ Farads. From the change in the capacitance of the system, it can be concluded that the electrostatic forces attracting the surfactant molecules to the gold substrate were sufficiently strong to support the formation of the surfactant monolayer. (Figure 4.A.1) Further more, this study showed that the surfactant layer was exceptionally stable, only being removed from the gold substrate at a bias of approximately -0.3V. (Figure 4.A.2)

## B. [0.22]mM SDS

At a concentration level of [0.22]mM, the average drop in capacitance was determined to be 9.43 x $10^{-6}$ Farads. The overall drop of the capacitance is smaller for the [0.22]mM concentration of SDS compared to the capacitance drop for the [0.33]mM concentration. From the graph of the change in capacitance of the system at the [0.22]mM concentration, it can be determined that the fluctuation of the capacitance was smaller than that of the more concentrated solution. (Figure 4.B.1)

C. [0.11]mM SDS

The [0.11]mM concentration of SDS had an average capacitance drop of 7.40 x $10^{-6}$ Farads. This continues the trend of a decrease in the capacitance of the system with a decrease in the surfactant concentration. However, the change in the capacitance of the system for the [0.11]mM concentration of surfactants does appear to obey the same general curve as the other samples. (Figure 4.C.1)

D. [0.033]mM SDS

An average capacitance drop of 6.70 x $10^{-6}$ Farads was observed for the [0.033]mM SDS concentration level.(Figure 4.D.1) Compared to the [0.33]mM concentration, this capacitance drop is half as severe. This is a result of the monolayer not being as densely packed onto the surface of the substrate.

E. [0.022]mM SDS

. In comparison to the [0.22]mM concentration of SDS, the change in capacitance for the [0.022]mM SDS is roughly seventy-seven percent of the reported value for the [0.22]mM concentration. The average capacitance drop was determined to be 7.31 x $10^{-6}$ Farads. This is a slight increase to the capacitance drop of the [0.033]mM SDS solution. The change in the capacitance for this concentration of SDS observes the same hemi-parabolic shape as the previous concentrations. (Figure 4.E.1)

F. [0.011]mM SDS

The average capacitance drop for the [0.011]mM concentration of SDS was determined to be 5.84 x $10^{-6}$ Farads. (Figure 4.F.1) This capacitance drop is roughly seventy-one percent of

the drop associated with the [0.11]mM solution. Based on the capacitance drop associated with this concentration, it can be said that the concentration required to construct the monolayer of SDS on the substrate is below the concentration levels tested here.

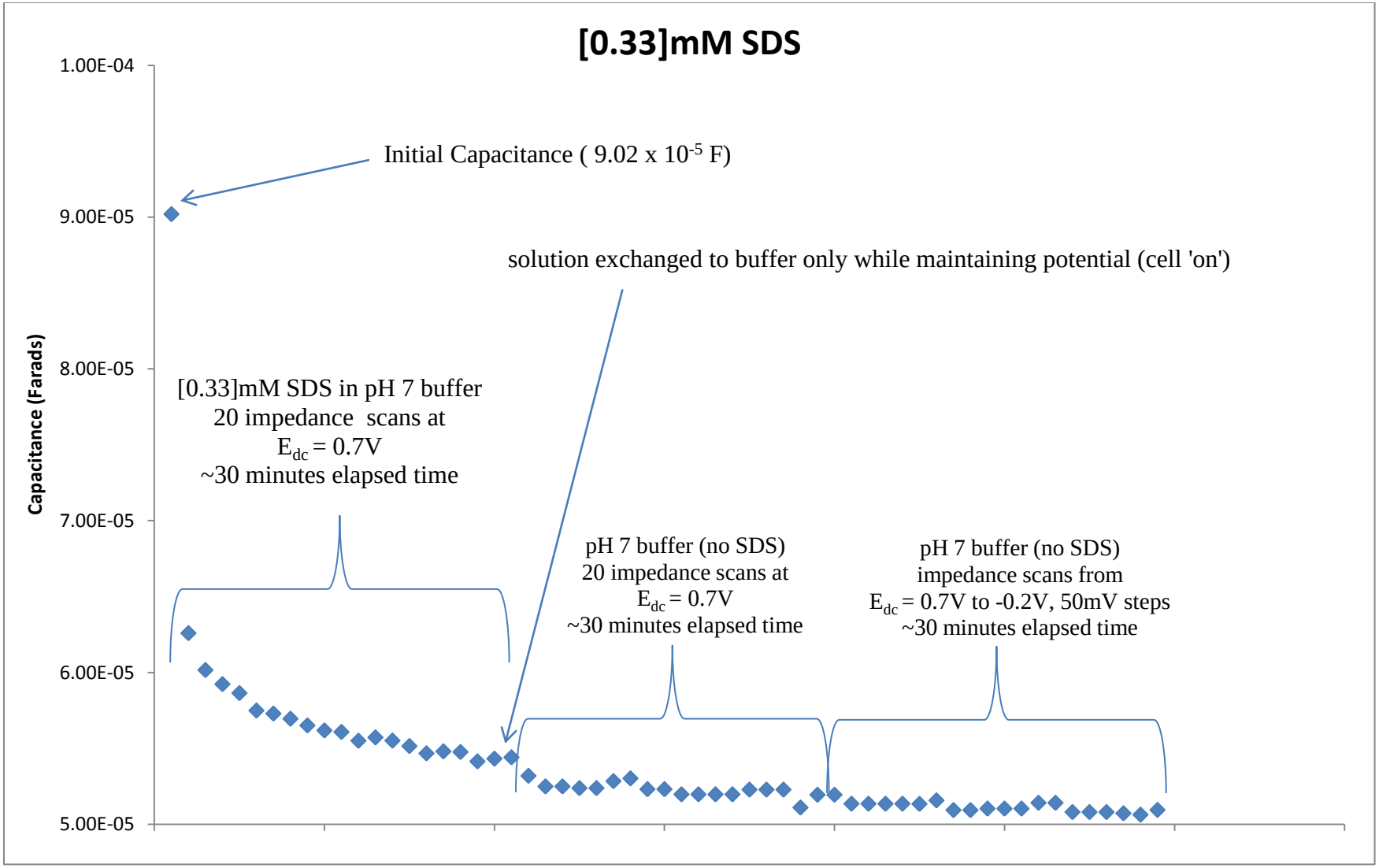


**Figure 4.A.1**: Change in capacitance for [0.33]mM SDS solution

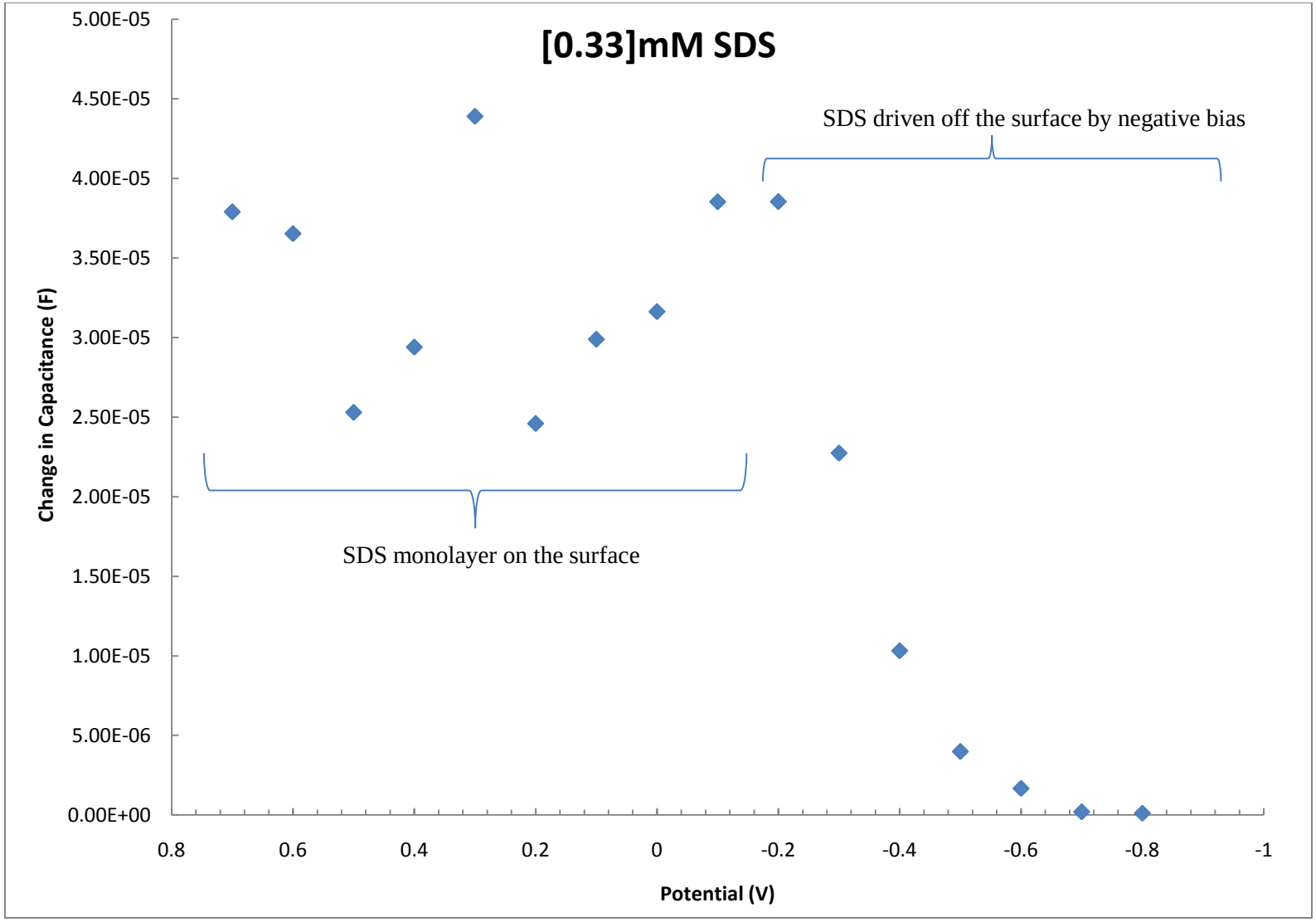


Figure 4.A.2: Change in capacitance versus potential for [0.33]mM SDS solution

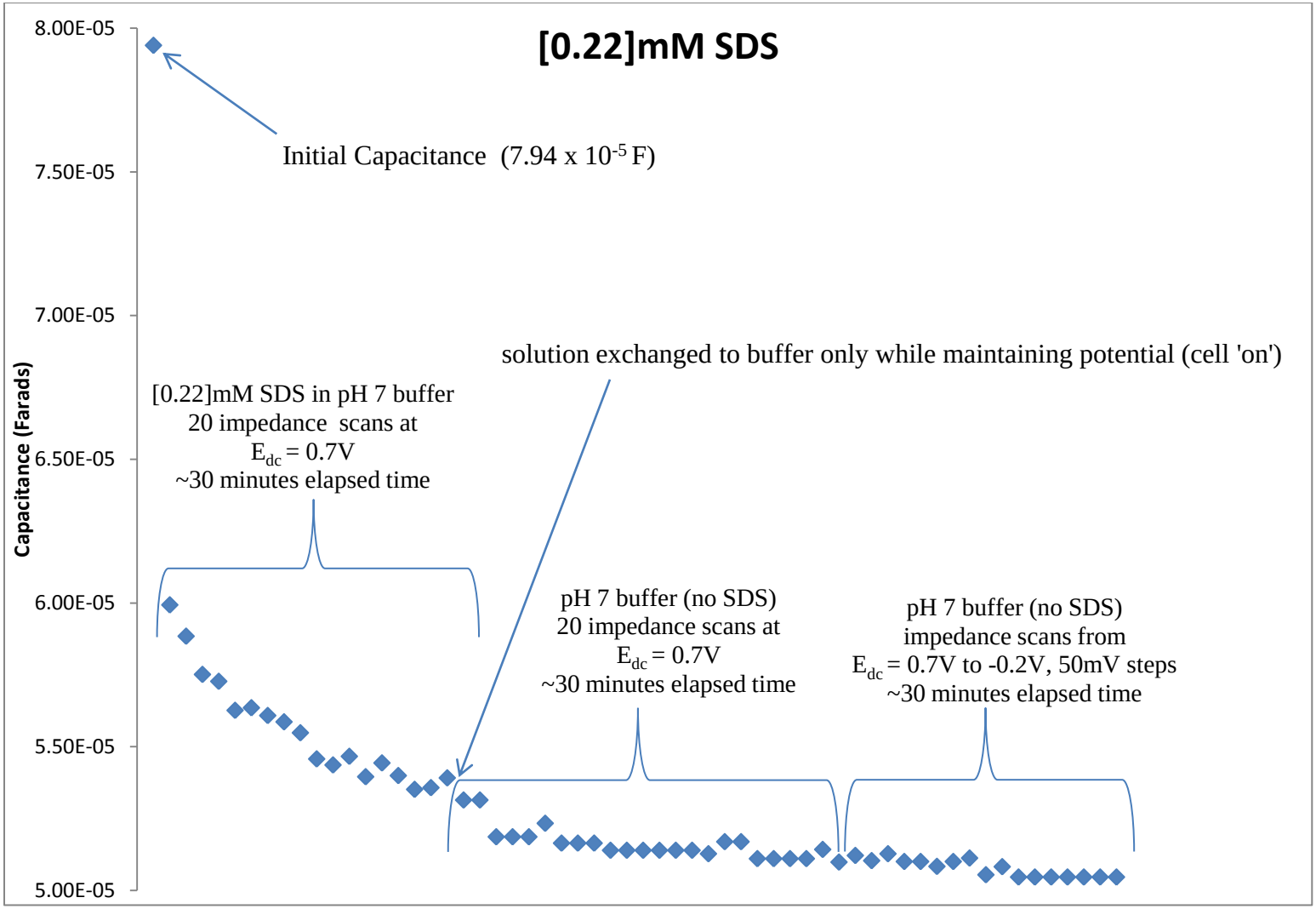


Figure 4.B.1: Change in capacitance for [0.22]mM SDS solution

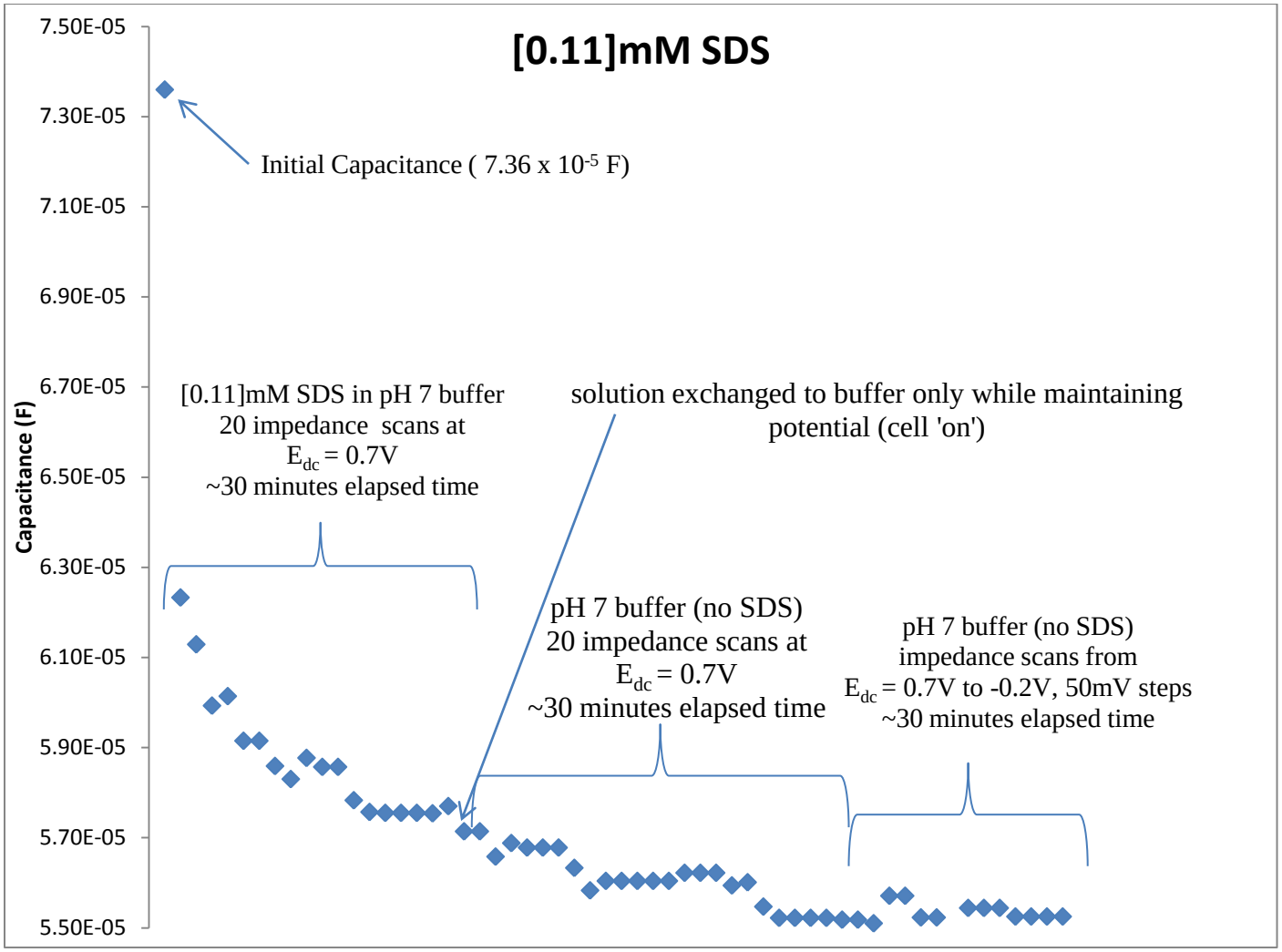


**Figure 4.C.1**: Change in capacitance for [0.11]mM SDS solution

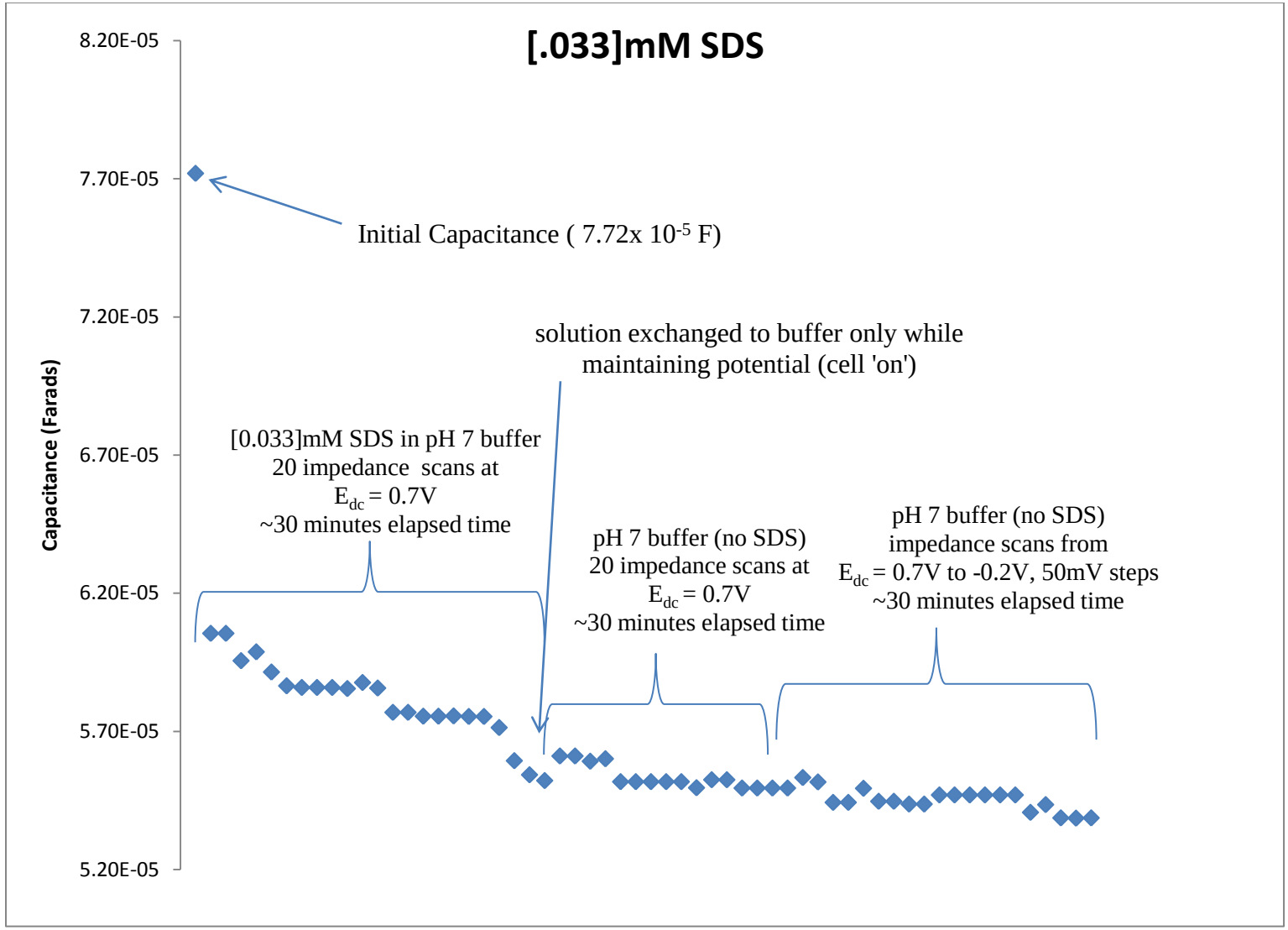


**Figure 4.D.1:** Change in capacitance for [0.033]mM SDS solution

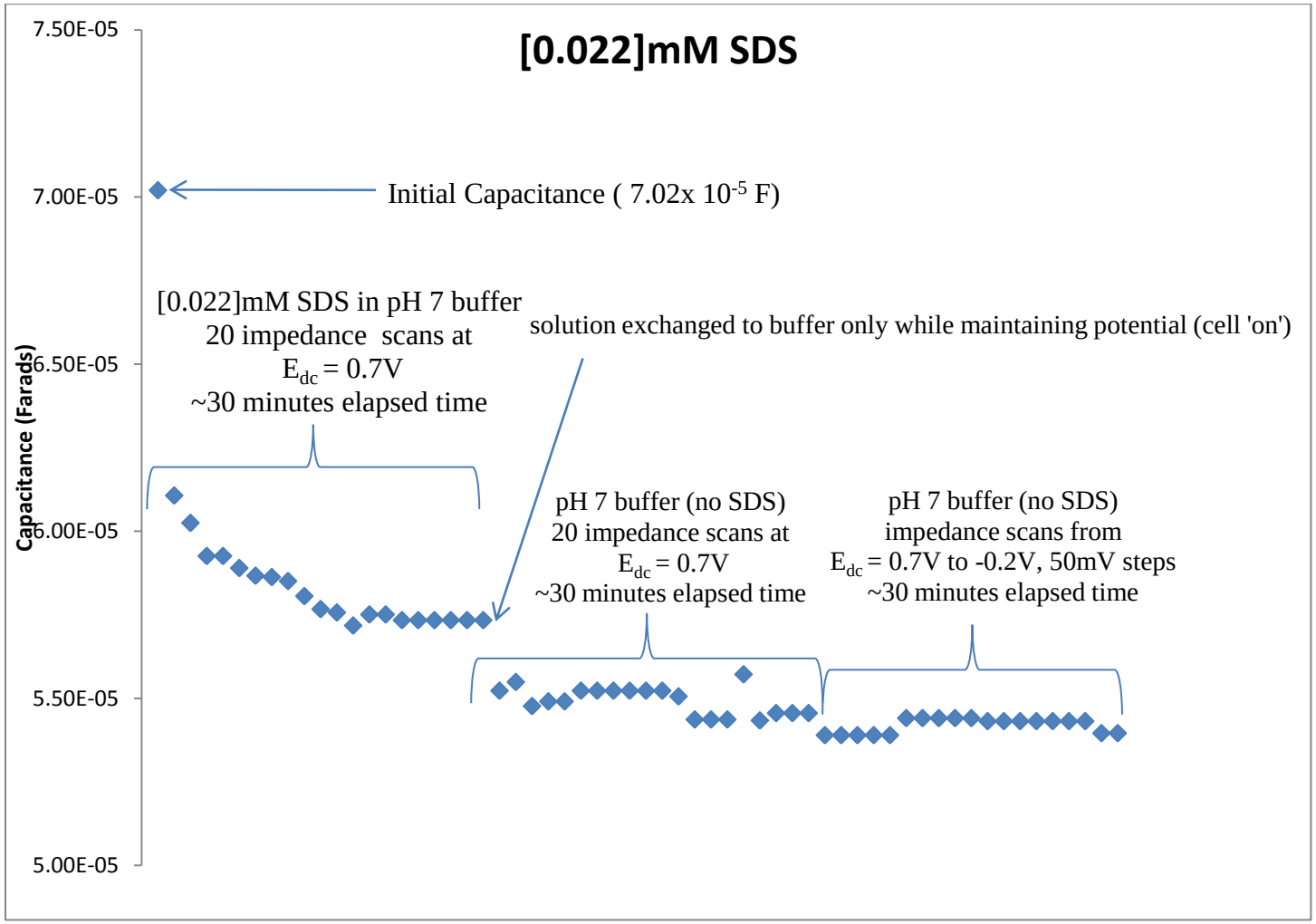


**Figure 4.E.1**: Change in capacitance for [0.022]mM SDS solution

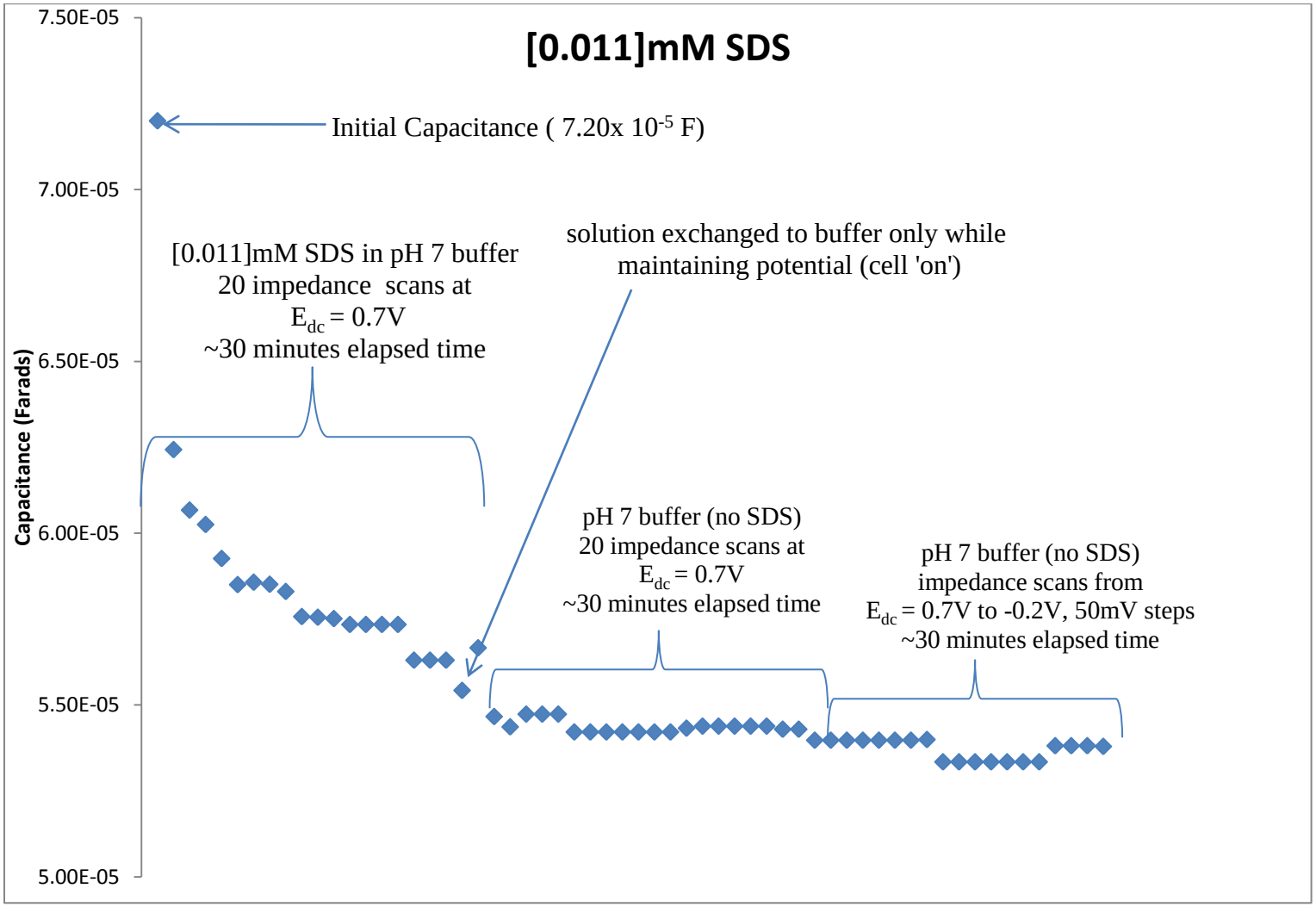


**Figure 4.F.1:** Change in capacitance for [0.011]mM SDS solution

# CHAPTER 5

# CONCLUSIONS

From the results collected during this portion of the project, it can be determined that the electrostatic forces between the applied positive bias on the substrate and the electron rich region of the surfactant molecule is strong enough to support the development of a monolayer atop the gold substrate. This is a fundamental step toward the ultimate goal of creating an electrically switchable surface for pre-concentration. With this evidence, further work can be continued with the goal of partitioning target PAHs into the surfactant monolayer on the substrate.

In addition to proof of concept, it has been determined that a concentration below the [0.011]mM level is sufficient for constructing the monolayer. This concentration is well below the CMC level for SDS. This provides support for the idea that the majority of the surfactant molecules are taking part in the monolayer instead of forming micelles in solution. In summary, the work completed during this portion of the project supports the notion of creating a novel method of pre-concentration for PAHs.

# CHAPTER 6

# FUTURE WORK

The primary purpose of this portion of the project was to prove that a monolayer of surfactant molecules could be formed on a substrate using electrostatics as the primary driving force. With this goal met, further work can continue toward the idea of creating a novel method of pre-concentrating PAHs in aqueous systems.

The next step of this project calls for the study of the partitioning in of PAHs into the surfactant monolayer. EIS and CV will continued to be used to monitor the change in capacitance of the system. Once the partitioning of the PAHs has been complete, the efficiency rate of this method will be determined using HPLC. In addition to this, future work will include studying methods of increasing the usable surface area where the construction of the monolayer takes place. The most likely direction for this study will include the incorporation of gold nanoparticles into the system.

References


1. Agency for Toxic Substances and Disease Registry. *Toxicological Profile for Polycyclic Aromatic Hydrocarbons;* Government; U.S. Department of Health and Human Services: Atlanta, **1995**(3).

2. Agency for Toxic Substances and Disease Registry. *Toxicological Profile for Polycyclic Aromatic Hydrocarbons;* Government; U.S. Department of Health and Human Services: Atlanta, **1995**(15).

3. International Union of Pure and Applied Chemistry. *Compendium of Chemical Terminology,* 2nd ed.; **1997**.

4. Ferrer, R.; Beltrán, J. L.; Guiteras, J. Use of Cloud Point Extraction Methodology for the Determination of PAHs Priority Pollutants in Water Samples by High-Performance Liquid Chromatography with Fluorescence Detection and Wavelength Programming. *Analytica Chimica Acta* **1996,** *330* (2), 199-206.

5. Pinto, C. G.; Pavón, J. L. P.; Cordero, B. M. Cloud Point Preconcentration and High-Performance Liquid Chromatographic Determination of Polycyclic Aromatic Hydrocarbons with Fluorescence Detection. *Analytical Chemistry* **1994,** *66* (6), 874-881.

6. Yao, B.; Yang, L.; Hu, Q.; Shigendo, A. Cloud Point Extraction of Polycyclic Aromatic Hydrocarbons in Aqueous Solution with Silicone Surfactants. *Chinese Journal of Chemical Engineering* **2007,** *15* (4), 468-473.

7. Dow Chemical Company. Surfactant Basics. http://dow-answer.custhelp.com/cgi-bin/dow_answer.cfg/php/enduser/std_adp.php?p_faqid=3281&p_created=1112809668&p_topview=1 (accessed April 26, 2010).

8. Fisher Scientific. *Material Safety Data Sheet for Dichloromethane;* MSDS; Environmental Health and Safety, **1998**.

9. Baltussen, E.; Janssen, H.-G.; Sandra, P.; Cramers, C. A. A Novel Type of Liquid/Liquid Extraction for the Preconcentration of Organic Micropollutants from Aqueous Samples: Application to the Analysis of PAH's and OCP's in Water. *Journal of High Resolution Chromatography* **1997,** *20,* 395-399.

10. Gamry Instruments. Fundamentals of Electrochemical Impedance Spectroscopy, 1997. Electrochemical Impedance Spectroscopy: A Primer. http://www.gamry.com/App_Notes/EIS_Primer/EIS_Primer.htm#About_The_EIS_Primer (accessed May 6, 2010).

11. Macdonald, J. R. Impedance Spectroscopy. *Annals of Biomedical Engineering* **1992,** *20,* 289-305.

12. Zoski, C. *Handbook of Electrochemistry;* Elsevier Science, **2007**.

13. Heinze, J. Cyclic Voltammetry - "Electrochemical Spectroscopy". New Analytical Methods. *Angewandte Chemie International Edition in English* **1984,** *23* (11), 831-847.

14. Bard, A.; Franklin, L. R. *Electrochemical Methods- Fundamentals and Applications,* 1st ed.; John Wiley & Sons: New York, **1980**.

15. Holler; Skoog; Crouch. *Principles of Instrumental Analysis,* 6th ed.; Thomson: Belmont, **2007**.

16. James D. Ingle, J.; Crouch, S. R. *Spectrochemical Analysis;* Prentice Hall: Englewood Cliffs, New Jersey, **1988**.

17. Orazem, M. *Electrochemical Impedance Spectroscopy;* John Wiley, **2008**.