Electrochemical Studies of Quinone on Clay-Modified Platinum Electrodes

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ELECTROCHEMICAL STUDIES OF QUINONE
ON CLAY-MODIFIED PLATINUM ELECTRODES

A THESIS SUBMITTED TO
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To myself I am only a child playing on the beach. I was like a boy playing on the sea-shore and diverting myself now and then finding a smoother pebble or a prettier shell than ordinary whilst the vast ocean of truth lay all undiscovered before me.

*Isaac Newton*
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CHAPTER ONE

ELECTROCHEMICAL STUDIES OF QUINONE ON CLAY-MODIFIED ELECTRODES

Purpose

The purpose of this project is to study the electrochemical oxidation-reduction and catalytic effects of a montmorillonite clay modified electrode in a benzoquinone solution.

Our project seeks to better understand if clays might enhance or facilitate the shuttling of electrons from quinone to clay. This project is part of a greater objective in examining the function of clays and clay modified electrodes for potential use in developing efficient and affordable redox catalyst for possible use in bio fuel cells or energy fuel cells, and as redox enhancement in catalytic degradation and bioremediation of environmental contaminants. Investigation of electrochemical systems is also important in understanding of biological assemblies, corrosion, and biological sensors.

Benzoquinone was chosen because of their ubiquitous constituents in several important chemical and biological molecules and serve as a good experimental model of electron transport analysis. Quinones play an active role in electron shuttling in aerobic respiration and are involved as electron carriers in photosystems I and II in photosynthesis. Quinones are also cofactors in blood clotting (K1 phylloquinone and K2 menaquinone) and serve as an excellent study for electron transfer in microorganisms.
Clay Overview

Clays are ubiquitous aluminosilicate minerals that possess several unique chemical and industrial features. Clays have been studied from several branches of science including geology, chemistry, biology, biomedical, organic chemistry, inorganic chemistry and more making them an ideal choice of study in the 21st century [1].

Clays are heterogeneous in composition belonging to the class of phyllosilicates with the general formula \((\text{Al}_{3.15}\text{Mg}_{0.85})(\text{Si}_{8.00})(\text{O}_{20}(\text{OH})_{4}X_{0.85}\text{nH}_{2}\text{O})\). Montmorillonite clay consists of a 2:1 layer with one octahedral layer and two tetrahedral layers. Each tetrahedron consists of a cation coordinated to four oxygen atoms and linked to an adjacent tetrahedra by sharing of the basal oxygen atoms. Common cations within the tetrahedra are \(	ext{Si}^{4+}, \text{Al}^{3+}, \text{and Fe}^{3+}\). The octahedral cations are usually \(\text{Al}^{3+}, \text{Mg}^{2+}, \text{and Fe}^{2+}\) and \(\text{Fe}^{3+}\) but other cations may occur such as \(\text{Li}^{+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{V}^{3+}, \text{Cr}^{3+}, \text{and Ti}^{4+}\) have also been identified (Figures 1 and 2) [2]

One important feature of clays is their capacity to undergo “isomorphic substitution” the ability to exchange various cations within the octahedral or tetrahedral sites of clays. Isomorphic substitution within the clay-framework results in clays with a wide range of unique thermo-mechanical and chemical properties. Figures 1 and 2 show smectite clays with various cations within the octahedral-tetrahedral layer. Replacing these cations with various atoms or molecules within this clay skeletal framework has served to enhance the strength to the clays, has increased the catalytic activities of clays, and has opened up new possibilities for the construction of clay modified electrodes [3, 4].
Some other physical and chemical properties of clays include, intercalation, plasticity, binding and sorptive properties, catalytic enhancement, and more. They come in a variety of sizes, elemental composition, and various ionic charge-layers making them ideal for experimental modifications [5]. One author predicts clays and clay minerals will be recognized as the material of choice in the 21st century because of their abundance, their affordability, they are environmentally friendly, and they have many extraordinary chemical features [6].

Smectite is the name used for a group of phyllosilicate mineral species. The 2:1 silicate layers have a slight negative charge between the two platelets and on the edges of the clay due to vacancies or substitutions in the octahedron or tetrahedron layers. Normally $\text{Al}^{3+}$ is replaced by $\text{Mg}^{2+}$ or $\text{Si}^{4+}$ is replaced by $\text{Al}^{3+}$ leaving an overall net negative charge [7]. Cations such as $\text{Na}^+$, $\text{Mg}^{2+}$, and $\text{Ca}^{2+}$ are attracted to the spaces between the layers due to this overall net negative charge. These cations attracted to the net negative charge in the interlayer of the clay can be exchanged by a procedure called “washing” something that will be discussed in the next section.

Smectites also have the unique ability to swell or contract. This swelling-contraction is due to the slight negative charge in the clay discussed in the preceding paragraph which attracts water molecules or other polar molecules into the interlayer (Figure 3). This swelling feature was another factor that needed to be addressed in our research when constructing our clay-modified electrode. This was done by adjusting
Figure 1. Basic 2:1 octahedral-tetrahedral structure of clay.
Figure 2. Octahedral-tetrahedral basic units of Montmorillonite clay minerals and the silica and alumina sheets (from Mitchell, 1993)

Figure 3. Basic 2:1 structure of clay showing interlayer water
the ionic strength of the solution in order to enhance the diffusion of the quinone through the clay matrix.

The most common clay in the smectite group is Montmorilinite, named after the clay found in the town of Montmorillon, France. The primary source for smectite clay in the United States is in Wyoming and is given the abbreviation of SWy-1.

**Clays as Catalysts**

There is an ever increasing interest in the use of clays and clay-catalysts in several areas of science research. Clays are abundant minerals in nature and possess unique chemical and physical properties including adsorptive properties, high surface area, strong ion-exchange properties, sorptive properties, and reasonably affordable making them ideal candidates for catalytic use [8, 9].

In 1986, Laszlo reported the use of clay-supported catalyst in organic reactions [10]. Chemically modified pillared clays have also been used as catalysts in organic synthesis reactions, rearrangement reactions, and substitution reactions. [11-13].

Clay has been used for decades by the petroleum industry for “cracking” the process whereby organic molecules are broken down into simpler molecules [14].

Clays also show remarkable promise in finding environmentally friendly, useful alternatives in science and in industry. Clay catalysts show promise for the enhanced reduction of nitric oxides [15] and may serve as catalysts for the production of bio-fuels [16].
The various catalytic activities of clay originate from four sources; their Bronstead acidity, their Lewis acidity, the presence of redox species, or from the introduction of a catalytically active transition metals [14]. The catalytic activity can be a natural property of the clay or can be established by acid catalyzing of the clay or by introduction of a metal complex into the clay [14].

One of the goals of our research was to determine if clay modified platinum electrodes would show catalytic enhancement in the oxidation-reduction of quinone.

**Clays as Environmental Assistors**

Acid treated clay minerals kaolinite and montmorillonite have uses in the removal of heavy metal contaminants such as cadmium (II) chromium (VI), and arsenic from the environment [17-19]. Cadmium (II) is an industry by-product and its sources include mining, phosphate fertilizer production, paint manufacturing, and the alloy industry and is an extremely toxic environmental containments [17, 19]. Chromium (VI) is an industrial pollutant and is considered toxic to all life forms.

Some of the health concerns associated with Cadmium II include cancers, lung disease, and hypertension [20]. Research by Bhattacharyyya found that acid activated clay minerals have an enhanced adsorbitivity for both cadmium (II) and chromium (VI) due to their increased surface area, increased pore size and a spontaneous decrease in the Gibbs free energy change \( \Delta G \) [18].

A recent investigation has looked into the use of modified clay-carbon paste electrodes as a portable sensor of the organic herbicide 2, 4-D. The positive results
suggested clay-carbon electrodes can be produced for remote portable analytical sensing and detection of the herbicide [21].

Another area of interest is the use of clays as “greener,” more environmentally friendly alternative in the manufacture and production of plastics. Yadav and Salgoankar’s research showed a significant improvement of yield in the manufacturing of Bisphenol-A (BPA), an important raw material for the synthesis of epoxy resins, polymers, and plastics over conventional methods while at the same time showing a 25% reduction in environmental waste by-products [15].

**Brief Overview of Clay-Modified Electrodes**

Clay-modified electrodes have been of interest for several decades and have been extensively studied [22-30]. One of the earliest papers reporting the use of clay modified electrodes was by Allen J. Bard at the University of Texas at Austin. His research discussed the modification of an electrode surface by attaching a thin layer of treated sodium montmorillonite onto SnO₂ electrodes showing potential electro-catalytic activity [28, 29].

A recent study using modified clay electrodes shows clay’s ability to enhance the electron transfer between the hemoglobin protein and the iron-rich clay for the development of bio-sensors for H₂O₂ determination [30].

One of our research interest was to determine if a clay-modified electrode might enhance oxidation-reduction electron transfer in 1,4-benzoquinone. If it can be shown that clays enhance electron transfer of quinone, perhaps clays could be modified to play a
part in bio-remediation of organic pollutants, bio-fuel application, or as a catalyst for fuel cells.

**Cyclic Voltammetry**

Cyclic voltammetry is a powerful electroanalytical tool used to study thermodynamics, kinetics, mechanistic investigations, qualitative and quantitative information of reactions as well as determining formal redox potentials of half reactions, concepts in diffusion, reversibility of reactions and reaction intermediates [31-34].

Cyclic voltammetry is done by linearly scanning or changing the potential of a stationary working electrode from a potential far positive or negative (depending on if one is starting with oxidation or reduction) where no electron transfer occurs and moving to a potential where electron transfer (oxidation or reduction) takes place between the solution and the electrode. The process is repeated in the reverse direction usually to the original starting potential while at the same time monitoring the current that is flowing.

This changing of potential from beginning to end is called a “waveform” and can be repeated as often as necessary. The plot of the current (y-axis) versus the applied potential (x-axis) is called a voltammogram. Voltammograms can be controlled by varying the scan rate or the speed that electron transfer takes place. This scan rate can vary from a few millivolts per second to several hundred volts per second.

The concept of electron transfer from the electrode to the solution (reduction) is due to a change in potential from the electrode-solution interface and is associated with a difference in energy levels. Electrons in the electrode reside in an electron “cloud band”
called a conduction band. These electrons move about freely in this conduction band and form a continuum known as the Fermi level. The solution however has individual molecules with discrete unfilled molecular orbitals. Before transfer from the electrode to the solution takes place the Fermi level is lower in the electrode than the vacant lowest unoccupied molecular orbital (LUMO) of the reactant species in solution. When scanning begins, the potential is increased (becomes more negative) at the electrode surface causing the Fermi level of the electrons in the electrode to be raised above the energy level of the species in solution (Figure 4).

In the case of a reduction for example, the potential at the electrode is moved from its initial positive-potential to a more negative potential causing the energy level of the electrode to be raised. As the energy level is raised at the electrode surface to a level greater than the energy level of the vacant orbital of the species in solution, electrons will jump from the higher-energy electrode into the vacant LUMO of the species in solution causing a current to flow. The current will reach a maximum value and begin to rapidly fall off due to the depleted concentration of the species near the electrode surface. The potential is then reversed usually back to the initial potential. The applied potentials and the cathodic (reduction) and anodic (oxidation) currents are recorded for the entire process called a voltammogram. The current resulting from this is called a “faradaic current” because it obeys Faraday’s law where 1 mol of substance involves a change of \( n \)-number of electrons x 96,487 Coulombs. A typical voltammogram is shown in Figure 5.
Figure 4. Fermi level electron transfer between the electrode-solution interface.
Figure 5. A typical cyclic voltammogram showing the important peak parameters.
There are several pieces of information that can be obtained from a CV. Some of the important parameters include the following.

- $E_{pa} =$ anodic peak potential. The potential at which the anodic current is the maximum.
- $E_{pc} =$ cathodic peak potential. The potential at which the cathodic current is the maximum.
- $E_{p/2} =$ half-peak potential. The potential where the current is half of the peak current. $E_{p/2}$ can be obtained by drawing a vertical line from the point at which the current is at its peak, down to the baseline. Then measure half the distance of this vertical line and draw a perpendicular horizontal line bisecting the vertical line. The point at which the vertical line crosses the CV is the half-peak potential. $E_{p/2}$ can be expressed as either a cathodic half peak potential $E_{p/2c}$ or an anodic half peak potential $E_{p/2a}$ and is related to the half-wave potential $E_{1/2}$ by the following equation.

$$E_{p/2} = E_{1/2} \pm \frac{0.028}{n} \text{ V}$$

- $I_{pa} =$ peak anodic current. The highest peak in the anodic branch of the current.
- $I_{pc} =$ peak cathodic current. The highest peak in the cathodic branch of the current.
- $E_{1/2} =$ the half-wave potential. The half-wave potential $E_{1/2}$ is calculated using the following equation.

$$E_{1/2} = \frac{1}{2} (E_{pc} + E_{pa})$$
E$_{1/2}$ can also be calculated using the following equation where E$^0$ is the formal potential, $D_o$ and $D_i$ are the diffusion coefficients for the oxidized and reduced species, $n$ is the number of electrons transferred and \( \frac{RT}{F} \) have their usual corresponding values.

$$E_{1/2} = E^0 + \left( \frac{RT}{nF} \right) \ln \left( \frac{D_r}{D_o} \right)^{1/2}$$

Because the diffusion coefficients of the oxidized and reduced species are normally close in value, E$_{1/2}$ is usually ~ within a few millivolts of E$^0$.

- **E$^0$ = standard electrode potential.** The standard potential is centered midway between the cathodic and anodic peak potential where $E^0 = \frac{E_{pa} + E_{pc}}{2}$

- **$\Delta E_p$ = potential peak-to-peak separation.** The difference in potentials between the anodic peak potential $E_{pa}$ and the cathodic peak potential $E_{pc}$.

This value is expressed mathematically in the following equation known as the Nernst Equation.

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.059}{n} \text{ V}$$

Peak separation can be used as criteria for “reversible” or “nernstian behavior.”

Reversible systems will have fast electron transfer kinetics ($k^0$) which maintains proper surface-electrode equilibrium concentrations and will have theoretical peak separations of 0.059V or 59mV. In order to achieve reversibility, the surface concentrations of reactants and products must be stable and the electron transfer rate must be fast so that concentrations at the surface are in equilibrium throughout the voltammogram. Systems that are termed reversible are independent of the scan rate as well as concentration.
For the reaction of \( A + e^- \stackrel{\leftrightarrow}{\longrightarrow} B \) for reversible systems it is implied that surface concentrations of \( A \) and \( B \) obey nernstian equilibrium throughout the voltammogram.

\[
E = E^0 + \frac{RT}{F} \ln \frac{[B]}{[A]}
\]

\[
\ln \frac{[B]}{[A]} = \frac{1}{[e]} = \frac{1}{[2.7183]} = -1
\]

\[
\ln \frac{[B]}{[A]} = 1 = \ln 1 = 0
\]

\[
\ln \frac{[B]}{[A]} = \frac{[e]}{[1]} = \frac{2.7183}{1} = 1
\]

It is difficult to experimentally achieve nernstian behavior because electron transfer between the electrode and the solution can be slow. It may be possible to approach a “quasi-reversible” process (\( \Delta E_p > \frac{59}{n} \) mV) by decreasing the scan rate. By slowing down the scan rate, the electron transfer has an improved chance of being fast as compared to the diffusion rate. Slowing down the scan rate means there is less current flowing and the electron transfer is faster relative to the diffusion rate and avoids depletion of reactants at the electrode surface. This allows the surface concentration of products and reactants to stay in the necessary nernstian equilibrium allowing mass transport (diffusion) to keep pace with the rate of electron transfer required for reversible reactions.

A faster scan rate causes a thinner diffusion layer which in turn controls the rate of mass transport to the electrode. If the electron transfer rate is greater than the rate of mass transport, systems tend to be reversible. If the electron transfer rate is less than the mass transfer rate, systems tend to be irreversible.
Another important equation in cyclic voltammetry is the Randles-Sevcik equation.

The Randles-Sevcik equation allows one to determine the current for a reversible couple

\[ i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C^* \] at 25°C

Where \( i_p = \) peak current in amps (A/cm²)

\( n = \) number of electrons

\( A = \) area of the electrode in cm²

\( D = \) diffusion coefficient in cm²/s

\( C^* = \) concentration of the bulk species in mol/cm³

\( v = \) scan rate in V/s

From the above equation it can be seen that peak currents will depend on the square root of the scan rate.

Another important analysis in cyclic voltammogram is the peak current ratio.

\[ \frac{i_p}{i_{pc}} = 1 \]

The value of \( i_p \) to \( i_{pc} \) should be close to one for a reversible voltammetric couple.

Deviations from unity point to kinetic complications or other complications in the electrode process [33].

**Kinetic Study of Peak Separation**

One feature of cyclic voltammetry is it can be used as a tool for the measurement of \( k^0_{(f,b)} \) the heterogeneous electron transfer rate constant by evaluating cathodic and anodic peak potential separations where

\[
\begin{align*}
O + ne & \xrightarrow{\text{forward}} ko_{(f)} & \xrightarrow{\text{back}} & ko_{(b)} & R
\end{align*}
\]
and \( k^0_r \) and \( k^0_h \) are the heterogeneous rate constants for electron transfer and \( O \) and \( R \) are the oxidized and reduced species.

The earliest investigation into the quantitative relationship of \( k^0 \) to peak separation was by Nicholson and Shain [35, 36] whereby they related peak separation to a dimensionless parameter psi (\( \Psi \)) and obtained a working curve relating \( \Delta E_p \)-peak separation to the scan rate. Others have since developed similar procedures and tables for working with larger or smaller values of \( \Delta E_p \) [37, 38].

Several factors can influence peak separation in a cyclic voltammogram including the electron transfer rate, the scan rate, the rate of diffusion, migration—the movement of charged particles along an electric field, the electrode surface, and more. For systems that are reversible, it assumes a fast \( k^0 \) and proper surface-electrode equilibrium with a peak separation of \( \frac{59}{n} \) mV. Sometimes reversibility can be achieved by slowing the scan rate. At slow scan rates, solution equilibrium can generally be maintained at the electrode surface resulting in a thicker diffusion layer and greater reversibility. For quasi-reversible systems however or when the scan rate is increased a sufficient amount, a competition exists between the rate of electron transfer rate \( k^0 \) and the increasing scan rate-potential. Faster scan rates result in a thinner diffusion layer and greater irreversibility. This causes a change in the equilibrium of the redox couple as the potential is increased and thereby causes a larger \( \Delta E_p \)-peak separation.

For systems where the electron transfer rate is less than the mass transfer rate (small value \( k^0 \) and diffusion dominated) the system will be irreversible.
As a point of interest, electrochemists commonly talk of electron transfer as being “fast” or “slow.” However, as Scholz points out [39] this is not entirely accurate because electron transfer in itself is quite rapid and on the order of $10^{-16}$s. Furthermore, according to Marcus theory and others, what determines fast or slow electron transfer kinetics is the reorganization energy of the structure of the reactants and products which have solvation sphere or ligand energies on the order of $10^{-11}$ s to $10^{-14}$s which results in slowing the electron transfer process.

The quantitative relationship between peak separation and $k^0$ developed by Nicholson and Shain is shown by the following equation.

$$\Psi = \frac{k^0 \left( \frac{D_o}{D_r} \right)^{\alpha/2}}{\sqrt[5]{D_o \pi \nu \left( \frac{nF}{RT} \right)^2}}$$

Where the symbols have the following definitions.

- $D_o = \text{the diffusion coefficient for the oxidized species}$.
- $D_r = \text{the diffusion coefficient for the reduced species}$.
- $\alpha = \text{the electron transfer coefficient (a value between 0-1)}$.
- $\Psi = \text{the dimensionless parameter based on } \Delta E_p \text{ from the cyclic voltammogram}$.
- $\nu = \text{the scan rate (V/s)}$.

And all other symbols have their usual values. Once $\Psi$ is determined from the tables, $k^0$ is obtained in a fairly straightforward and convenient way shown in the equation below.

$$k^0 = \Psi \left[ D_o \pi \left( \frac{nF}{RT} \right) \right]^{\frac{1}{5}} \left( \frac{D_r}{D_o} \right)^{\alpha/2}$$
The results from the Nicholson paper in determining $k^o$ included the following:

- An electron transfer reaction and no associated chemical steps such as protonation.
- No adsorption or precipitation of the reactant or product onto the electrode surface.
- The iR drop between the reference electrode and working electrode is negligible. Nicholson points out that the effect of iR is similar to the effect of a small value for the rate constant.

The switching potential is at least $141/n$ mV negative of the half wave potential. Best results are obtained when $\Delta E_p$ is between 80mV and 140mV. Nicholson points out the relation of alpha to cathodic and anodic peak shape for $\alpha < 0.5$ the cathodic peak is more rounded than the anodic peak and is responsible for a lowering of peak heights. For $\alpha > 0.5$ the anodic peak is more rounded than the cathodic and shows a broadening in the shape. By obtaining the value of $\Delta E_p$ and correlating this with the values of $\Psi$, a value for $k^o$ can be determined. For large values of $\Psi$ ($\Psi > 7$) $k^o$ is large or the scan rate is small and the cyclic voltammograms behave identical to Nernstian behavior.
Table 1. Relating peak separations $\Delta E_p$ in a cyclic voltammogram to the dimensionless parameter $\Psi$. By determining $\Psi$ and calculating into the equation above, a value for $k^0$, heterogeneous electron transfer rate can be obtained.

From Bioanalytical Systems Inc. West Lafayette, IN.

$$k^0 = \Psi \left[ D_o \pi \left( \frac{nF}{RT} \right) \right]^{1/2} \left( \frac{Dr}{D_o} \right)^{\alpha/2}$$

<table>
<thead>
<tr>
<th>Peak Separation $\Delta E_p$ (mv)</th>
<th>$\Psi$</th>
<th>$\Delta E_p$ Peak Separation (mv)</th>
<th>$\Psi$</th>
</tr>
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<tbody>
<tr>
<td>60</td>
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<td>61</td>
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<td>90</td>
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</table>
For extremely small values of $\Psi$ ($\Psi < 0.1$) $k^o$ is small or the scan rate is very fast and the reaction is termed irreversible. For intermediate values of psi, the reaction is termed quasi-reversible and the reactions are highly dependent on the $\Psi$ and alpha for determining $k^o$. Also for intermediate values of psi there is a small dependence on the electron transfer coefficient alpha whereby alpha somewhat affects the symmetry of the voltammogram causing a shifting of the anodic and cathodic peaks as well as broadening of the peak and lowering of the peak height.

The peak separation tables of Nicholson and Shain were expanded (Table 1) by Bioanalytical Systems Inc. (BASi) [40] to include more $\Delta E_p$ separations.

In the case of quinone peak separation, the reduction-oxidation is not a simple electron transfer reaction but is a two-electron transfer reaction and depending on the pH of the solution and the type of solution can be coupled with none, one or two proton transfers. Because of this, the shape and the position of the CV will be affected by both the electron transfer rate $k^o$ and the equilibrium rate constants as well as the rate constants of the protonation steps, all which leads to challenges to obtain precise values for the electron transfer $k^o$. Forster points out that when electron transfer and proton transfer are coupled, both the formal potential and peak separations are affected by both the pH of the solution and the buffering capacity of the solution [41].

One final factor needs to precede the discussion of quantitatively determining $k^o$ from peak separation and that is peak separation experiments and analysis are done at scan rates ranging from a few millivolts per second (e.g. 10 mV/s) up to extremely high
scan rates e.g. 1000 V/s (1,000,000 mV/s). At the time of this research our instrument’s scan rate capability was only within a few hundred millivolts per second and we were not able to produce the high scan rates necessary to see divergent peak separations in a system. This would be an area to consider for future research.

**Quinone Chemistry**

There is much interest in the study of the redox properties of quinones in both buffered aqueous solutions as well as non aqueous solutions. Quinones are an important group of lipid-soluble compounds that function in unique and highly specialized ways and play key roles in everyday life. Quinones function as electron carries in ATP synthesis in cellular respiration, function as electron carries in photosystems I and II, and are co-factors in blood clotting (K₁ phylloquinone and K₂ menaquinone) [42, 43].

Recent studies have identified over 60 quinone-type molecules isolated in plant-foods that play a critical role in chemotherapeutic and chemoprevention [44]. It would be hard to imagine life without quinones!

There are many points of view that can be looked at when studying quinones; however our research goals focused on only two specific perspectives. The first was to determine if smectite clay would provide any catalytic enhancement to electron transfer in the redox chemistry of quinone. The second was to seek to better understand the redox chemistry of quinones at a clay modified electrode surface in unbuffered aqueous solutions.
It is important to consider some background information on the redox chemistry of quinones in aqueous and non-aqueous solutions. There is a large body of research of quinones in both non-aqueous solutions as well as buffered aqueous solutions. By comparison there are relatively few studies of quinones in unbuffered aqueous solutions [45]. As Smith points out, the reason for the lack of research of quinones in unbuffered aqueous solutions may be because either the electrochemistry in a buffered solutions is similar to that in unbuffered solutions (depending on the pH of the aqueous solution this may be somewhat true) or the chemistry in unbuffered solutions is difficult and not well understood [45]. Most likely the lack of research of quinones in unbuffered aqueous solutions are due to difficulty in interpretation of the reaction mechanism.

It is generally accepted that in a non-aqueous aprotic solvents, quinone undergoes a simple two-step reduction mechanism (Figure 6). The two-step reduction mechanism involves the electron transfer to quinone to produce the radical anion $Q^-$ followed by a second electron transfer to produce the dianion.

![Figure 6. Quinone two-step electron transfer to produce the dianion.](image)

A typical cyclic voltammogram the reduction of quinone in aprotic solvent shows two distinct cathodic and anodic peaks with a large peak separation between cathodic peaks $E_{1c}$ and $E_{2c}$ and a large peak separation between anodic peaks $E_{1a}$ and $E_{2a}$ (Figure 7).
Figure 7. A typical two-electron cyclic voltammogram of quinone. $E_{1c}$ and $E_{2c}$ denote cathodic waves and $E_{1a}$ and $E_{2a}$ denote anodic waves.
The redox chemistry of quinone in buffered and unbuffered aqueous solutions is more challenging to interpret. In buffered aqueous solutions where the \([\text{H}^+] > [\text{Q}]\), quinone undergoes a \(2e^-, 2\text{H}^+\) reaction to produce hydroquinone as the final product (Figure 8). In an unbuffered aqueous solution two difficulties present themselves. The first is that as the electron transfer proceeds, protons are consumed creating an “effective pH” near the electrode surface. This is not a problem as long as the \([\text{H}^+] > [\text{Q}]\) as in very acidic conditions of pH 1.0 to about 3.0. However if the concentration of \([\text{H}^+] < [\text{Q}]\) protons are consumed and an effective pH at the electrode surface results.

\[ E = E^0 - \frac{0.059}{n} * \text{pH} \]

The second challenge in working with quinone in unbuffered aqueous solution is the “nine-member square scheme” reactions of quinones as shown in Figure 9. In the case of a two electron transfer the possible reaction mechanism (\(e^- \text{H}^+ e^- \text{H}^+\) or \(\text{H}^+ e^- \text{H}^+ e^-\) where \(e\) stands for the electron transfer and \(\text{H}^+\) the protonation) can vary with pH along with other conditions.

**Figure 8. Coupled electron-proton transfer**

This consumption of protons near the electrode surface causes a shift in the pH at the electrode (an effective pH) which in turn causes a shift in the redox potentials as shown in the equation below.
Figure 9. Nine-membered square scheme for quinone
Shim and Park \[46\] show variable CV’s in unbuffered solutions as the pH changes from 1.3 to 2.5, from 2.5 to 4.5, and from 4.5 to 9.5. At pH 1.3 to 2.5 a single oxidation and reduction wave with a large peak separation (270 to 340 mV) is observed. This is interpreted as a two electron-two proton reaction to produce hydroquinone.

Between pH 2.5 and 4.5 two oxidation and two reduction peaks are observed with each anodic-cathodic couple separated by \(\sim 60\) mV. They attributed the two waves to two different reacting species, a radical anion or its protonated form as shown in the reaction below and suggested a pH dependence due to the depleted proton concentration during the reaction.

\[
\begin{align*}
Q + e^- & \rightarrow Q^- \\
Q^- + H^+ \xrightarrow{\text{slow}} & QH^-
\end{align*}
\]

Above pH 4.5 through 9.5 they show once again a single oxidation and reduction peak.

They state that the reduction of quinone in unbuffered or buffered aqueous solutions is not fundamentally different from that in non-aqueous solutions and proceeds by the formation of the fairly stable anion radical (\(Q^-\)) followed by slow protonation. They also state that the reduction of quinone in unbuffered solutions with a pH value above 2.5 is a one-electron transfer producing the radical anion which is then protonated in an \(e^- H^+ e^- H^+\) reaction.

Tang and Wang \[47\] describe a typical cyclic voltammogram of the reduction of quinone as a single pair of waves (one cathodic and one anodic) at pH below 3.0, two
pair of cathodic and anodic waves at pH between 3 and 5, and a single pair of waves from pH 5 to 9. They believe that Q\(^{-}\) is NOT the product of the direct one-electron reduction of Q but is from the comproportionation reaction of Q with Q\(^{2-}\) to produce the dianion radical Q\(^{-}\) as shown in the reaction below.

\[
Q + Q^{2-} \rightarrow 2Q^{-}
\]

Kelley and Forster reached the same conclusions as Tang and Wang [41].

A third interpretation of the data was reached by Smith et al [45]. Like others they suggest the Q/QH\(_2\) reaction where [H\(^+\)] > [Q]. However their interpretation for changes in behavior of the CV’s as the pH increases is quinone in unbuffered neutral water is similar to aprotic solvent. They suggest the mechanism is e e to form Q\(^{2-}\).

\[
\begin{align*}
1^{st} \text{ electron transfer} & : Q + e^- \rightarrow Q^- \\
2^{nd} \text{ electron transfer} & : Q^- + e^- \rightarrow Q^{2-}
\end{align*}
\]

This can occur in aprotic solvents or at higher pH values with little proton concentration. In an aprotic environment two waves are observed because the second electron is harder to insert due to electrostatics causing a shift in the E\(^{o}\). The reason for the lower E value (harder to reduce) in aprotic and unbuffered neutral pH water is the electrostatic argument where it is harder to add electrons to an already negatively charged species.

In unbuffered neutral water there is one wave. The reason for only one wave in water is likely due to some stabilization from hydrogen bonding of the Q\(^{-}\) by the water stabilizing the anion making electron transfer easier.
In aqueous solutions where \([H^+] > [Q]\) in either a buffered or unbuffered pH, one pair of voltammetric waves are observed. Their interpretation of this wave is in agreement with others is due to a \(2e^- 2H^+\) reaction \(e,c,e,c\) (where \(e\) stands for electron-transfer step and \(c\) stands for chemical step) to produce hydroquinone (Figure 8).

When the \([H^+] \leq [Q]\) two sets of voltammetric waves are produced. Once protons are consumed, the reaction mechanism switches and the \(Q\) is now being reduced at a more negative potential. Eventually the first wave disappears entirely and only the second wave appears. Smith suggests that under those conditions, the reaction is best described as shown in Figure 1.8 where the overall \(2e^-\) reaction gives the dianion \(Q^{2-}\).

![Figure 10. A 2e\(^-\) reaction to give the hydrogen-bonded dianion](image)

The \(Q^{2-}\) is strongly hydrogen-bonded to water and is basic therefore it can exist in water as a mixture of \(Q^{2-}\), \(QH^-\) and \(QH_2\) with the exact distribution depending on the \(pK_a\)'s of the hydroquinone and the total concentration of the hydroquinone species.

Smith goes on to suggests that in unbuffered neutral water where protons are not available, protonation of the intermediate \(Q^-\) is not likely but is stabilized by the strong hydrogen bonds occurring from the three lone pairs on each oxygen atoms in the dianion. This stabilization causes a shift in the potentials.

Overall the underlying difference between aprotic solvents and unbuffered neutral water is that in aprotic solvents there is no stabilization of the anion making it more
difficult to add an electron which leads to applying a larger potential which leads to two cathodic and anodic waves. In unbuffered neutral solutions hydrogen bonding occurs stabilizing the anion leading to one single peak. The E values are not “inverted” as they are in protonation but are close enough in E value to merge into one CV.
CHAPTER TWO
MATERIALS AND METHODS

Clay Purification

The bulk clay found in the earth is often mixed with other amorphous minerals and materials such as carbonates, iron oxides, minerals, or organic materials therefore a purification process is required to remove such materials before studying their properties [48].

SWy-1 clay was supplied by the Department of Geology at the University of Missouri at Columbia (Figure 11) and was purified by suspension and sedimentation using the method formulated by Jackson [49]. Approximately 20.0 g sample of SWy-1 clay was suspended in 500mL Erlenmeyer flask with 18-Ω deionized water and stirred for 24 hours (Figure 12). After stirring, the clay suspension was allowed to sit for 24 hrs to allow the debris in the clay to settle. The clay slurry was then decanted into another 500ml beaker and filled with an 18-Ω, 2M NaCl deionized water solution and stirred for another 24 hours (Figure 13). The water-washed clay solution was placed in centrifuge tubes and centrifuged for 45 minutes at 1500 rpm to remove the excess water (Figure 14). The precipitate was removed and again placed into a 500 ml 18-Ω, 2M NaCl solution and stirred for 24hrs. This centrifuge-sodium washing procedure was repeated 3-times and afterwards the clay precipitate was collected. The sodium exchanged clay
suspension was then poured into a 500ml beaker and filled with 18-Ω deionized water and stirred for 1 hour. The clay suspension was poured into a Fisher Scientific Spectrapor standard cellulose dialysis tubing (m.w. cutoff: 12,000-14,000) and the bags were placed into 500 ml beakers containing 18-Ω deionized water and soaked for 24 hours to allow sodium to diffuse out of the clay and into the DI water (figure 15). This process was repeated several times until there was no detection of sodium present in the DI water by testing with 0.1m AgNO₃ until no precipitate forms. On average it took anywhere from 4 to 6 water exchanges to rid the clay of excess sodium.

A 200 ml portion of the purified clay slurry was removed and placed in 18-Ω deionized water and sealed to be used for future freeze drying while the remainder was placed into a 200mL beaker to be freeze dried.
Figure 11. Raw clay mineral from Dept of Geology University of Missouri.

Figure 12. Water washed bulk clay solution after 24 hrs

Figure 13. SWy-1 sodium exchanged bulk clay solution after sodium exchanging
Figure 14. SWy-1 Sodium exchanged clay after centrifuging

Figure 15. Clay Dialysis Purification of SWy-1 Clay
Electrochemical Cell Set-Up

The cyclic voltammograms were obtained using an Obbligato Objectives, Inc. Faraday MP potentiostat model MP 1.6 with a (GUI) Graphical User Interface running on a host computer.

The electrochemical cell consisted of a Bantam Ware 25mL four-compartment electrochemical cell shown (Figure 16). The compartments within the cell included one compartment for the lab-prepared platinum working electrode (Shown on left side Figure 16) with an electrode surface area of 0.00417 cm², a second compartment for the lab-prepared platinum counter electrode (shown on right side) a compartment for the saturated calomel (Hg₂Cl₂) reference electrode (shown in center), and the fourth compartment for the pH electrode (located front-center).

The pH meter was a Thermo Scientific Orion PerpHecT® 350 Meter with a Thermo Scientific pH electrode.

The cyclic voltammograms were carried out using Sodium Nitrate crystals (Baker & Adamson reagent grade A.C.S.) as the supporting electrolyte. The concentrations were prepared at 0.195M NaNO₃ for buffered solutions and 0.20M NaNO₃ for unbuffered solutions. The supporting electrolyte is required to decrease the cell resistance in the solution as well as to carry the charge through the solution by the movement of ions.

The 1,4-benzoquinone C₆H₄O₂ (Sigma-Aldrich reagent grade-98%) was prepared to a 3mM concentration for each CV.
**Figure 16.** Four-compartment electrochemical cell set-up.

**Figure 17.** Pine Research analytical rotator for spin-coating clay onto the surface of the electrode tip.
All buffered acidic solutions were prepared using citric acid monohydrate C$_6$H$_8$O$_7$ ($p$K$_a$ 3.15, 4.77, and 6.40) from Fisher Scientific. All non-buffered aqueous solutions were pH adjusted using HCl and NaOH.

All solutions were purged with N$_2$ gas for 10 minutes to remove dissolved O$_2$. This is necessary for several reasons. The reduction of oxygen occurs in a two-step process as shown below.

\[
\begin{align*}
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2 \\
H_2O_2 + 2H^+ + 2e^- & \rightarrow 2H_2O
\end{align*}
\]

The large background current from the reduction of dissolved O$_2$ can interfere with the amplitude of the current being measured as well as chemically interfering with the analyte [50].

**Preparation of Platinum Electrode**

The platinum working electrode was polished with a 0.2μ alumina buffing pad (Buehler Ecomet (II) Inc., Lake Bluff, IL) and water for several minutes, then rinsed with deionized water and sonicated for 10 minutes between each set of experiments to assure no impurities or residues were adhered to the electrode surface. Following sonication, the electrode was removed and rinsed with deionized water and wiped with a lint free cloth.

**Clay Application to the Electrode Surface**

The platinum electrodes were prepared for application of clay to the electrode tip by placing the electrode into a Pine Research Instruments analytical rotator with the
platinum surface facing up (Figure 17). A 5g/L clay suspension was prepared from the freeze dried clay and 10μL of the 5g/L clay suspension was placed onto the tip of the platinum electrode. The electrode was then spun by slowing increasing the rpm’s. Any needed adjustments were made to the electrode to assure even-spinning until the rotator speed reached 400 rpm’s. The purpose of spinning the electrode on the analytical rotator is to create more evenly distributed clay particles onto the electrode surface [51]. The electrode was rotated for 45 minutes until dry. A second application of 10μL of clay was applied and the electrode rotated as above. The second application of clay was applied in order to assure complete and even coverage onto the electrode surface. The electrode was again rotated for 30-45 minutes until dry (Figure 20). Confirmation that even coverage of clay was deposited onto the electrode surface was made by removing the clay modified electrode and placing the electrode into a methylene blue solution for 1 minute. Since methylene blue is a dye that is sorbed by clay, it will confirm that an even application and coverage onto the electrode surface was achieved.

An additional methylene blue dye confirmation test was also done on the clay modified electrode after several voltammograms were performed in order to confirm that clay is still present on the surface and is not lost or affected by the quinone solution. The results were positive and showed that after multiple scans were performed and after being immersed in the quinone solution, the presence of a uniform deposition of clay still remains on the platinum electrode tip (Figure 19).
Diffusion of quinone through clay platelets

Figure 18. Representation of clay-modified platinum electrode showing quinone diffusing through laterally oriented clay platelets.
**Figure 19.** Tip of clay-modified platinum working electrode with application of methylene blue dye used for confirmation of clay coverage.

**Figure 20.** Clay-modified electrode showing presence of clay on the tip of the platinum electrode surface.
Scanning Electron Microscopy Image of Clay-Modified Electrode

A film similar to that formed for the clay-modified electrode was prepared for imagining by scanning electron microscopy (S.E.M.). 10uL of the 5g/L clay solution were placed onto 1.0 cm diameter circular glass cover-slip and spun using the analytical rotator according to the procedure described earlier. One clay-coated glass coverslip was placed into a 0.195 M NaNO₃ solution containing a 3mM 1, 4-benzoquinone. A second was placed in deionized water only. The cover-slips were allowed to soak for 10 minutes to allow the clay to reach equilibrium swelling in the solution. The coverslips were removed and allow air-dry overnight.

The clay coated cover-slips were then examined using a JEOL® 804A scanning electron microscope. Our goal in taking the SEM images was to determine if the quinone might cause any morphological changes to the clay as compared to the combination NaNO₃ 1,4-benzoquinone solution.

Clay Isotherm Preparation Procedure

A series of experiments were performed at Purdue University in West Lafayette, IN under the direction of Dr. Cliff Johnston in order to determine if sorption of quinone from aqueous suspension into SWy-1 sodium exchanged clay occurs. Quinone-clay solutions and quinone-clay films were prepared at six different concentrations and three different pH values and analyzed using ultra-violet/visible (UV-Vis) spectroscopy and Fourier transformed infrared (FTIR) spectroscopy.
In order to determine the mg of clay per ml water, 40 ml of the sodium exchanged clay slurry was pipetted into a 500 ml beaker and an additional 360 ml of deionized H$_2$O was added to make a 400 ml total solution. The solution was stirred with a magnetic stirrer for 30 minutes until a homogeneous solution was achieved. 2ml of the clay was drawn out and placed into previously massed glass vials. The clay vials were then dried in an oven at 110º F for 1 hour and removed and massed again. The amount of clay was determined to be 3.162 mg/ml.

The 400ml clay solution was separated into four 100 ml beakers and each beaker was adjusted to the proper pH and ionic strength. pH values were set to 2.0, 3.4, and 7.0 using KCl as the supporting electrolyte. A final 100ml solution was prepared at pH 3.4 using NaNO$_3$ as the supporting electrolyte.

A 1 mg/ml 1000 ppm quinone stock solution was prepared by placing 25 mg of quinone into 25 mls of deionized water. The stock solution was used to prepare six-30mL poly-tetrafluoroethylene (PTFE) lined screw cap centrifuge tubes and set to concentrations of 0, 25, 50, 75, 125, 200, and 350 ppm and all pH adjusted to pH 2.0. Adjusted molarity of KCl and water was added to the PTFE tubes and filled to a final volume of 25mL. The molar concentration of KCl per PTFE tube was 0.195M. The above procedure was repeated for pH of 3.4, and 7.0. A series of solutions were also prepared at pH 3.4 with NaNO$_3$ as the supporting electrolyte.

The samples were placed in an orbital shaker at room temperature for 18 hours to achieve apparent sorption and equilibrium. The samples were then centrifuged at 6000
rpm for 30 minutes. 5ml of the supernatant from each sample was removed and placed into separate small vials. Figure 21 shows a flow chart for the technique used in preparing a 25ppm sample and the process used for determining the final concentration of quinone sorbed into the clay.

Standards of quinone were also prepared for UV-Vis analysis at pH 2.0 at concentrations of 0, 0.5, 1.0, 2.0, 4.0, 5.0, 10.0, and 20.0 parts per million. The absorbance for these UV-Vis spectrums of quinone was obtained from 271-209 nm wavelength. Standards were graphed in order to determine concentrations of quinone in clay (Figure 22-24). All spectrums obtained were normalized and baseline corrected. An additional quinone standard was prepared at 10 ppm at pH 2.0, 3.4, and 7.0 in order to determine if pH would cause a shift in UV-Vis analysis (Figure 25). All UV-Vis spectrums were normalized and baseline corrected and an equation of the line was obtained based on area and peak height for determining the concentration of unknown quinone in solution. A typical UV-Vis quinone-clay sorption is shown in Figure 26.

Some of the samples obtained from the 5ml supernatant required dilution due to some concentrations being outside the range of the standards. Samples were diluted accordingly (Table 2 & 3). Procedure of determination of concentrations of quinone in clay is shown in Table 4.

Self-supporting clay films were prepared by removing 15mls of supernatant from each of the (PTFE) lined screw cap centrifuge tubes. The quinone solutions were passed through a 45mm diameter 0.45μm hydrophilic polyethersulfone membrane filter on a
Millipore holder. Vacuum was attached to the holder for 30 minutes until films were
dried. Clay films were removed and separated from the filter by running the filter and
clay deposit over a knife edge. The clay films were prepared from the solutions of the
original samples including at pH 2.0, 3.4, and 7.0 using KCl as the supporting electrolyte
and at pH 3.4 using NaNO₃ as the supporting electrolyte.

A KBr-quinone blank was prepared for FTIR analysis using 249.5 mg KBr and
0.5mg quinone (Figure 2.17). The KBr pellet was pressed using a hydraulic press and air
was vacuumed from the pellet at 10 psi of pressure for 30 minutes. KBr pellets are used
because it has no known vibrations in the IR region of 4000-400 cm⁻¹.

Clay films were prepared as described in an earlier procedure and analyzed using
a Perkin-Elmer Spectrum-GX2000 FTIR spectrometer. Graphs for FTIR absorbance
were obtained from 1337 to 1330 cm⁻¹, from 1605 to 1705 cm⁻¹, and at 1657 cm⁻¹ (Figure
28-29). The spectrum at 1657 cm⁻¹ was the chosen because it was the strongest peak. All
spectrums were baseline corrected and normalized. A total of 64 scans were done for
each FTIR isotherm sorption clay film.

The clay solutions were UV-Vis analyzed using a Perkin-Elmer UV-Vis Lamdba-
19 Spectrophotometer and FTIR analyzed using a Perkin-Elmer GX2000 FTIR
spectrometer.

Qualitative and quantitative methods using UV-Vis and FTIR were used to
determine if a linear adsorption isotherm relationship exists between known amounts of
quinone in solution to the amount of quinone adsorbed in the clay.
Table 2. Quinone-Clay initial suspension preparation table. Quantities of the above were required for preparing clay-quinone solutions for UV-VIS and FTIR analysis. Stock solution of 1mg/ml (1000ppm) quinone used. Procedure repeated for pH 3.4 and 7.0, in KCl and pH 3.4 in NaNO₃.

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<th>Amount Quinone Conc. (s) mg Q in 25ml required</th>
<th>Amount Quinone stock solution (1mg/ml) required</th>
<th>Amount mL of deionized H₂O required</th>
<th>Amount Clay Suspension (3.1mg/ml) required</th>
<th>Total volume (ml) needed</th>
<th>pH</th>
<th>KCl Ionic salt [conc] in 25ml</th>
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<td>25</td>
<td>2.0</td>
<td>0.195M</td>
</tr>
<tr>
<td>10pr8n</td>
<td>200</td>
<td>5.0</td>
<td>5.0</td>
<td>9.8</td>
<td>10.2</td>
<td>25</td>
<td>2.0</td>
<td>0.195M</td>
</tr>
<tr>
<td>10pr8o</td>
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<td>8.75</td>
<td>8.75</td>
<td>6.05</td>
<td>10.2</td>
<td>25</td>
<td>2.0</td>
<td>0.195M</td>
</tr>
</tbody>
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Table 3. Quantities used in preparation for UV-Vis analysis of supernatant prepared at pH 2.0. Procedure repeated for pH 3.4, and 7.0 in KCl and pH 3.4 using NaNO₃ as supporting electrolyte.

<table>
<thead>
<tr>
<th>Supernatant Sample id#</th>
<th>Sample #</th>
<th>Original Conc. ppm.</th>
<th>Supernatant volume used (mls)</th>
<th>Volume H₂O used (mls)</th>
<th>Total Volume (mls)</th>
<th>Dilution Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>10pr8i</td>
<td>1</td>
<td>0</td>
<td>3.0</td>
<td>0ml</td>
<td>3.0</td>
<td>0X</td>
</tr>
<tr>
<td>10pr8j</td>
<td>2</td>
<td>25</td>
<td>0.5</td>
<td>2.5</td>
<td>3.0</td>
<td>6X</td>
</tr>
<tr>
<td>10pr8k</td>
<td>3</td>
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<td>0.3</td>
<td>2.70</td>
<td>3.0</td>
<td>10X</td>
</tr>
<tr>
<td>10pr8l</td>
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<td>75</td>
<td>0.150</td>
<td>2.85</td>
<td>3.0</td>
<td>20X</td>
</tr>
<tr>
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<td>125</td>
<td>0.150</td>
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<td>20X</td>
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<tr>
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<td>200</td>
<td>0.150</td>
<td>2.85</td>
<td>3.0</td>
<td>20X</td>
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<td>0.150</td>
<td>2.85</td>
<td>3.0</td>
<td>20X</td>
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</tbody>
</table>
Figure 21. Flow chart showing method for determining amount of quinone sorbed in 31.62mg of clay.
### pH 2.0

<table>
<thead>
<tr>
<th>Quinone Sample #</th>
<th>Initial Conc. Quinone ppm</th>
<th>Area</th>
<th>Height</th>
<th>Calculated Conc. ppm from graph of standards x area (y=14.32x + 0.6371)</th>
<th>Dilution Factor</th>
<th>Column G final equilibrium conc. ppm (calculated x dilution)</th>
<th>final mg Quinone in 25 ml (Column G /1000 *25ml)</th>
<th>Initial mg Q in 25 ml</th>
<th>Quinone sorbed by clay</th>
<th>Quinone Sorption mg/g</th>
</tr>
</thead>
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<tr>
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<td>0</td>
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<td>0</td>
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<tr>
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<td>0.003</td>
<td>1.450476</td>
<td>3</td>
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<td>0.0049</td>
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<td>6</td>
<td>12.139656</td>
<td>0.303491</td>
<td>1.25</td>
<td>0.9465086</td>
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</tr>
<tr>
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<td>0.0952</td>
<td>0.0048</td>
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<td>5</td>
<td>3.594562</td>
<td>113.68001</td>
</tr>
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<td>0.0147</td>
<td>4.799924</td>
<td>20</td>
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<td>2.399962</td>
<td>8.75</td>
<td>6.350038</td>
<td>200.82346</td>
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</tbody>
</table>

**Table 4.** Table for calculating quinone sorption in clay UV-Vis analysis. Procedure was repeated for pH 3.4 and 7.0
Figure 22. Quinone standards concentration vs. area reverse-order from UV-Vis analysis.

Figure 23. Quinone standards concentration vs. peak height from UV-Vis analysis.

Figure 24. Quinone standards concentration vs. area from UV-Vis analysis.
Figure 25. UV-Vis absorbance for a 10 ppm quinone standard at pH 2.0, 3.4, and 7.0 showing near identical max peak height and wavelength absorbance at 246 nm.

Figure 26. UV-Vis absorbance for quinone/clay solution at various concentrations. Absorbance at 246nm concentrations of 0, 25, 50, 75, 125, 200, and 350 ppm.
Figure 27. FTIR spectrum of quinone-KBr pellet. Spectrum of quinone (blue) baseline corrected and normalized Na SWy-1 self supporting clay film (red) at 350 ppm of sorbed quinone pH 2.0. Absorbance at 1000 cm\(^{-1}\) shows large presence of clay interference along with quinone.
Figure 28. FTIR spectra of Na SWy-1 self supporting clay films with quinone at 0, 25, 50, 75, 125, 200, and 350 ppm concentrations pH 2.0 baseline corrected and normalized absorbance in cm\(^{-1}\).

**Figure 29.** Magnified FTIR spectrum of Na SWy-1 clay films with quinone at 0, 25, 50, 75, 125, 200, and 350 ppm concentrations baseline corrected and normalized absorbance in cm\(^{-1}\).
CHAPTER THREE
RESULTS AND DISCUSSION

Scanning Electron Microscopy Images

Figure 30 shows the SEM of the clay only, magnification was at 335X and the primary beam set at 10KV. The slide shows the characteristic three-dimensional criss-cross stacking of the colloidal clay onto the surface. Figure 31 shows the SEM of clay that was soaked in a solution containing 3mM 1, 4-benzoquinone and 0.195M NaNO₃. The image is magnified to 339X and the primary beam set at 10KV. By comparing Figure 30 with Figure 31, there seems to be no apparent morphological differences to the clay caused by the presence of the quinone with only a slight difference caused by the NaNO₃ attached to the clay. Figure 32 shows the SEM of the clay the clay only magnified to 995X. The characteristic criss-cross stacked clay on the surface is clearly seen at higher magnification. Figure 34 shows the SEM of the clay soaked in a 3mM quinone and 0.195M NaNO₃ solution magnified to 2100X. The presence of the NaNO₃ crystals appears but again, there is little change to the clay due to the presence of the quinone.
**Figure 30.** SEM of clay coated glass coverslip magnification 335X.

**Figure 31.** SEM of clay coated glass coverslip soaked in 1, 4-benzoquinone and 0.195M NaNO$_3$. Magnification 335X.
Figure 32. SEM of clay coated glass coverslip magnification 995X.

Figure 33. SEM of clay coated glass coverslip soaked in 0.195M NaNO₃ and 3mM 1, 4-benzoquinone. Magnification 2100X
Analysis Quinone Sorption for UV-Vis /FTIR

Figure 34 shows the graph of the sorption for quinone pH 2.0 for all concentrations. The x-axis represents the equilibrium concentration of quinone present in the supernatant after the samples were shaken overnight and centrifuged. The y-axis represents the amount of quinone sorbed in the clay in mg/g determined from

\[ Q \text{ initial} - Q \text{ final} = Q \text{ sorbed in clay} \]

Table 4 shows an initial concentration of quinone of 25 ppm or 0.625 mg initial of quinone (0.625mg of quinone in 25ml = 25 ppm) along with 31.62 mg of clay (10ml of 3.162 mg/ml clay added to each PTFE tube). The final concentration of quinone in solution after sorption equilibrium was 0.108 mg which yields a quinone sorption into clay of 0.516 mg for sample #1. This represents an 82.5% sorbance of quinone into the clay from the original starting concentration. Similar sorption results for pH 2.0 for values of 50-350 ppm shows a strong linear relationship of quinone sorption to SWy-1 sodium exchanged clay with an \( R^2 \) value of 0.992 for all data points. Figure 35 is a bar-graph representation showing the initial and final concentration of quinone (in mg) in solution and the concentration of quinone sorbed in the clay.

Figure 36 is a graph showing the percentage of quinone sorbed by the clay for pH 2.0 from UV-Vis analysis. The percentage of quinone sorbed by the clay was fairly consistent and ranged from 72% to 82% with slight variances at initial concentrations and most likely due to small differences in quinone solution concentrations or differences in clay concentrations present in each sample.
What can be seen from this is that a dynamic equilibrium exists between the quinone in solution and the quinone within the clay layers where a nearly constant percentage of quinone-in-solution to quinone-in-clay is present at all concentrations.

Figure 37 shows the quinone absorbance obtained from FTIR clay film at pH 2.0. The graph shows a similar linear relationship of quinone sorption by clay to that of UV-Vis. Figure 38 is a side-by-side plot comparing UV-Vis to FTIR sorption isotherms. The results give further support that quinone is sorbed by SWy-1 clay.

Figure 39 shows UV-Vis isotherm sorption of quinone at pH 3.4. For initial values of 25 and 50 ppm the UV-Vis sorption isotherm shows a linear relationship similar to pH 2.0, but at concentrations beyond 50 ppm, sorption of quinone increases noticeably. This may have been due to an initial error in quinone concentration calculations or may possibly be attributed to other factors. Since much of the variance in our cyclic voltammograms also occurred within this pH range, possibly other factors may be occurring between the clay and quinone. Repeated trials at pH 3.4 would be necessary to see if this trend is repeated. Figure 40 is a bar graph representation showing quinone sorption at pH 3.4. Figure 41 is the FTIR clay film sorption isotherm at pH 3.4. Figure 42 is a comparison of UV-Vis to FTIR at pH 3.4. Although the trend is not linear, sorption of quinone by clay still occurs in a noticeable way.

For pH 7.0, Figure 43 for UV-Vis isotherm sorption of quinone also shows a strong linear relationship similar to pH 2.0 however where pH 7.0 differs from pH 2.0 is in the noticeable overall drop-off in the amount of quinone sorbed into the clay. At pH
2.0 for the 25ppm concentration, the amount of quinone sorbed into 31.62mg of clay was
0.516 mg which results in an 82.56% sorbance. However for pH 7.0 at 25 ppm the
amount of quinone sorbed by 31.62 mg of clay was 0.471 mg for a 75.3% sorption. The
concentration of quinone initial was the same for both pH values but the final amount of
quinone was noticeably less between the two.

Figure 47 shows the comparison of quinone sorption at all pH values showing a
decreasing trend of quinone sorption as pH increases. Comparing the slope for pH 2.0
the equation for the line is 2.02-X contrasted with pH 7.0 which has a slope of 0.92-X.
Also, the sorption quinone by clay at pH 2.0 for 350 ppm sample was 6.35 mg for a
72.5% sorption but at pH 7.0 the amount of quinone sorbed was 4.82 mg for a 55.0%
sorption. This represents nearly a 25% loss of sorption of quinone into the clay when
changing from pH 2.0 to 7.0. It is likely this decreasing sorption is due to the lack of
protonation of the quinone at higher pH values or how the protons are impacting the clay.
At a lower pH, much of the quinone would be present initially as the protonated species
QH$^+$ or QH$_2$$^{2+}$ and would create favorable sorption sites within the negatively charged
clay. Another possibility is at low pH the protonated quinone may help orient the clay
particles creating more favorable sorption sites with less competition from water
molecules surrounding the exchangeable cations and creating less competition from water
molecules [52].

The UV-Vis sorption isotherm for pH 7.0 is shown in Figure 43. A bar graph
representation is shown in Figure 44. Figure 45 is a comparison of UV-Vis to FTIR
analysis for pH 7.0. Similar to pH 2.0 and 3.4, patterns of quinone sorption occur in a noticeable linear relationship.

Lastly, quinone FTIR sorption isotherms for pH 3.4 using NaNO₃ as the supporting electrolyte were carried out. There were no UV-Vis isotherms due to interference by NaNO₃ in the analyzed spectral regions. Clay-film FTIR isotherms were collected between 1690-1590 cm⁻¹ specifically at 1657 cm⁻¹ where no interference by NaNO₃ occurred. Figure 46 shows again the typical linear sorption of quinone by SWy-1 sodium exchanged clay similar to other pH values.

This demonstrates that at pH 2.0, 3.4, and pH 7.0 with KCl as the supporting electrolyte there is a linear increasing trend for sorbance of quinone by the SWy-1 clay as pH decreases and a greater favorability for the SWy-1 clay as pH decreases.

Furthermore this demonstrates that quinone is strongly sorbed in SWy-1 clay at pH 3.4 with NaNO₃ as the supporting electrolyte.
<table>
<thead>
<tr>
<th>Final Equilibrium concentration (mg/L)</th>
<th>Quinone Sorption in Clay (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4.351428</td>
<td>16.32556293</td>
</tr>
<tr>
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<td>56.21752</td>
<td>113.6800127</td>
</tr>
<tr>
<td>95.99848</td>
<td>200.8234662</td>
</tr>
</tbody>
</table>

Table 5. Quinone UV-Vis analysis pH 2.0 taken from Table 4 and graphed below.

Figure 34. UV-Vis analysis showing the amount of quinone sorbed (in mg) per g of clay pH 2.0.
**Figure 35.** Bar graph showing initial, final, quinone concentrations in clay for pH 2.0

**Figure 36.** Percentage of quinone sorbed into clay from samples at pH 2.0 based on initial concentration of quinone vs. final concentration of quinone is solution.
Figure 37. FTIR analysis of clay film at 1657 cm$^{-1}$ showing amount of quinone sorbed pH 2.0.

Figure 38. FTIR vs. UV-Vis analysis of clay film vs. supernatant concentration of quinone pH 2.0.
**Figure 39.** UV-Vis analysis of quinone sorbed (in mg) per gram of clay pH 3.4

**Figure 40.** Bar graph showing initial, final, and quinone concentration in clay at pH 3.4
Figure 41. FTIR analysis of clay film sorption at 1657 cm$^{-1}$ showing amount of quinone sorbed at pH 3.4.

Figure 42. FTIR vs. UV-Vis analysis of clay film pH 3.4.
Figure 43. Graph showing the amount of quinone sorbed (in mg) per gram of clay pH 7.0

Figure 44. Bar graph showing initial, final, and quinone concentration in clay at pH 7.0
Figure 45. FTIR vs. UV-Vis analysis of quinone sorbed pH 7.0.

Figure 46. FTIR quinone sorption pH 3.4 in NaNO₃ supporting electrolyte
Figure 47. UV-Vis isotherm sorption comparisons of quinone in clay at pH 2.0, 3.4, and 7.0.
CHAPTER FOUR

ELECTROCHEMICAL RESULTS

Initial Investigation of Possible Catalytic Effect of Clay Modified Electrodes

Our initial investigation of quinone chemistry oxidation-reduction on clay modified electrodes (CME) began with the method of cyclic voltammetry investigating the oxidation-reduction currents and peak potentials for sodium ferricyanide Fe(CN)$_6^{3-}$ ferricyanide/ferrocyanide couple ($Fe^{3+}$/ $Fe^{2+}$) and comparing a CME to that of a bare platinum electrode (Figure 48). When comparing ferricyanide/ferrocyanide couple using cyclic voltammograms of anodic peak potentials ($E_{pa}$) and cathodic peak potentials ($E_{pc}$) of a bare platinum electrode to a CME shows some interesting features and served as a spring-board to our study of quinone chemistry using a CME.

The cyclic voltammogram in Figure 48 has a ($Fe^{3+}$/ $Fe^{2+}$) couple that shows a value of $\sim$0.183V vs. SCE or 0.427V vs. NHE ($0.183V + 0.244V = 0.427V$) for the formal potential. Both the anodic and cathodic peak currents for the ($Fe^{3+}$/ $Fe^{2+}$) couple are less in the clay than in the bare and is probably due to the reduced movement of the solution and through the clay platelets. The clay sets up a brick-type stacking that consists of charged particles the solution must channel through as it diffuses toward the platinum electrode. The anodic peak potential for the bare electrode was 0.226V and was 0.228V for the CME. This is only a 0.002V (2.0 mV) separation for the anodic peak potentials between bare and clay. The cathodic peak potential for the bare electrode
was 0.120V compared with 0.112V for CME. This was a small difference of 0.008V (8mV) cathodic peak potential separation between bare and clay.

From the data it is apparent that the oxidation and reduction peak potentials for the (Fe$^{3+}$/Fe$^{2+}$) couple for CME and bare electrodes occur at relatively the same voltage. This in turn means the peak separation between the two electrodes are relatively equal suggesting the rate of electron transfer $k^0$ for the heterogeneous electron transfer couple at a bare electrode vs. a clay-modified electrode are also relatively the same.

The cathodic peak potential for quinone (Figure 49) at the bare electrode was +0.10V compared with +0.14V at the CME. This is an enhancement in reduction of 40mV for the CME over the bare platinum electrode. The anodic peak potential at the bare platinum electrode was +0.529V compared with +0.478V for the CME. This is an enhancement in oxidation of 51mV for the CME over the bare platinum electrode. The total enhancement can be measured by the peak separation. Peak separation for the bare platinum electrode was 429mV and was 338mV for the clay-modified electrode, a difference of 91mV.

These results suggest that both reduction and oxidation were thermodynamically easier in the presence of the clay and that $k^0$ electron transfer may be faster in the presence of clay. This trend was further investigated under several different parameters including buffered and unbuffered solutions, several different pH values and several different scan rates to see if this trend continues.
Figure 48. Cyclic voltammogram of sodium ferricyanide $\text{Fe(CN)}_6^{3+}$ showing anodic and cathodic peak potentials nearly the same for the clay modified electrode (CME) and bare platinum electrode.

Figure 49. Cyclic voltammogram initial investigation of quinone showing larger peak separation for anodic and cathodic peak potentials for the clay modified electrode (CME) and bare platinum electrode.
The Influence of pH on Quinone Reduction

Plots of anodic and cathodic peak potentials vs. pH are useful for determining stability in regions and are useful analysis in cyclic voltammetry. The formal electron transfer process for an A/B couple in a given reversible reaction is shown below.

\[ A \pm e^- \leftrightarrow B \]

For a process involving both electron transfer and proton transfer there is a direct relationship between the pH and the where the peak potential occurs. For a chemically reversible electron transfer process, this can be shown below for the transfer of \( m \)-protons and \( n \)-electrons

\[ A \pm mH^+ + ne^- \leftrightarrow B \]

For a chemically reversible process, the above reaction behaves according the Nernst equation

\[
E = E^{0}_{(A/B)} - \frac{RT}{nF} \ln \frac{[B]}{[A][H^+]^m}
\]

\[
E = E^{0}_{(A/B)} - \left( \frac{RT}{nF} \ln \frac{[B]}{[A]} - \frac{RT}{nF} \ln [H^+]^m \right)
\]

\[
E = E^{0}_{(A/B)} + \frac{RT}{nF} \ln [H^+]^m - \frac{RT}{nF} \ln \frac{[B]}{[A]}
\]

\[
E = E^{0}_{(A/B)} + 2.303 \frac{RT}{nF} \log [H^+]^m - \frac{RT}{nF} \ln \frac{[B]}{[A]}
\]

\[
E = E^{0}_{(A/B)} + 2.303 \frac{mRT}{nF} \log [H^+] - \frac{RT}{nF} \ln \frac{[B]}{[A]}
\]

\[
E = E^{0}_{(A/B)} + (-2.303 \frac{mRT}{nF} \ast \log [H^+]) - \frac{RT}{nF} \ln \frac{[B]}{[A]}
\]

\[
E = E^{0}_{(A/B)} + (-2.303 \frac{mRT}{nF} \ast pH) - \frac{RT}{nF} \ln \frac{[B]}{[A]}
\]
\[ E = E^0_{(A/B)} - 2.303 \frac{mRT}{nF} \times \text{pH} - \frac{RT}{nF} \ln \frac{[B]}{[A]} \]

In the case where the concentration of \([A] = [B]\) the pH dependent Nernst equation becomes

\[ E = E^0_{(A/B)} - 2.303 \frac{mRT}{nF} \times \text{pH} \]

\[ E = E^0_{(A/B)} - 0.059 \frac{m}{\text{pH}} \]

This corresponds to a 59 mV shift per pH unit at 25°C assuming a one electron one proton ratio in the transfer.

In the case of the reduction of quinone in an acidic solution where \([H^+] \geq [Q]\), there is an abundance of protons so we can assume a 2 electron \((n)\) and 2 proton \((m)\) transfer as shown in the following reaction.

\[
\text{Quinone} + 2\text{H}^+ + 2\text{e} \rightarrow \text{Hydroquinone}
\]

The theoretical plot of pH vs. peak potential should move by -59 millivolts per pH unit negative of the formal potential up to where the pH = pKa for the QH2.

The pH at the electrode may be different from that of the solution due to a coupled reaction where protons are consumed. Therefore it is critical when performing
cyclic voltammograms to consider not only the pH of the solution, but whether the solution is buffered or unbuffered.

**The Effect of Buffered pH on Formal Potential $E^\circ$**

In looking at graph Figure 50 the pH dependence for quinone in a buffered aqueous solution changes by a slope of -37mV when moving from pH 2.5 to 3.5. This corresponds to a one proton-two electron exchange, and based on the square-scheme would yield QH\textsuperscript{-} as the product. Because at pH 2.5 to 3.5 the [Q] is relatively equal to the [H\textsuperscript{+}] it would be reasonable to conclude that QH\textsuperscript{-} is one of the more abundant products of quinone reduction within this pH value for both platinum and clay modified electrode.

From pH 3.5 to pH 4.5 however the interpretation of the mechanism in a buffered solution is more challenging. This is no doubt due to the change in pathway and mechanism discussed earlier (Chapter 1) that is occurring within this pH value.

Within the pH values 3.5 to 4.5, the mechanism begins to change from a simple two-electron two-proton process yielding the hydroquinone (QH\textsubscript{2}) and begins to move toward other pathways to yield other products of the nine-member scheme. The square-scheme of quinone with possible multiple pathways does not lend itself to simple one or two electron transfers or simple one or two protonations because several pathways may be involved and all occurring at the same time. From buffered pH 5.5 to 7.2, the slope of $E^\circ$ vs. pH yields a value of -80mV per pH unit. This is somewhat close to a -59mV per pH unit and very close to normal experimental results and is likely a two-proton, two-
electron reaction. Again, because of the complexity of the square scheme and the resultant various products that can be obtained depending on [Q] and the [H\(^+\)], it is difficult to simply use this one set of experiments and analysis to draw precise conclusions. By comparison to literature however, the likely reaction is Q/QH\(_2\).

What is noticeable is the change in slope for both clay and platinum is fairly similar. This suggests that the clay-modified electrode behaves similarly to the platinum-only electrode and the reaction follows a similar pathway at a very low pH or at a neutral pH. It is in the pH range of approximately 3.5 to 3.9 however where the differences between the platinum and the clay modified electrode exists, as next shown.
Figure 50. $E^0$ vs. pH for quinone in buffered solution for bare and clay-modified electrodes showing slope at various pH values.
**The Effect of Unbuffered pH on Formal Potential E⁰**

The previous section compared the effect of a buffered pH solution on quinone reduction-oxidation formal potentials at a clay-modified platinum electrode (CME) vs. a platinum only electrode. This section will look at the how an unbuffered pH solution effects E⁰ in quinone redox chemistry at a CME vs. a platinum electrode. As previously discussed, when the proton transfer and electron transfer are coupled the formal potential may depend on both the buffering capacity and the solution pH [41].

Cyclic voltammograms were carried out at pH values ranging from 1.5 to 7.2. The pH was adjusted using NaOH and HCl both before the scans as well as several times between scans. Because the solutions were unbuffered, it was more difficult to maintain a constant pH throughout the scans than it was for a buffered pH. This is why the solutions were adjusted for pH throughout the scans in order to insure more consistent results. Slight changes in pH for quinone reduction can have a great impact on the results. A supporting electrolyte NaNO₃ was added to each solution at a concentration of 0.20M.

Looking at the Figure 51 relating the slope of E⁰ vs. pH from pH 1.5 to 3.45 the slope for the CME is -25 mV per pH unit. From the equation relating slope to the change in pH, this would suggest the quinone reduction reaction is a one-proton two-electron mechanism to yield the QH⁻. This value is fairly close to the -37mV/pH unit that occurred in the buffered pH as reported in the previous section.
The slope for the bare platinum electrode was -16mV/pH unit and somewhat different than the results of the clay. This may have been due to normal experimental variances and may also have been due to the changing E° values at pH 3.25 to 3.35. Simply looking at the two graphs of the bare electrode vs. CME from pH 1.5 to 3.0 look to be nearly identical in shape.

The graph of E° vs. buffered pH (Figure 50) differs noticeably from that of unbuffered pH (Figure 51). For quinone unbuffered pH between 3.4 and 3.5 the value of E° drops from approximately +275mV to -150mV, a drop of nearly 400mV. This large shift is likely due to the depletion of protons at the electrode surface producing an “effective pH,” a pH that is higher near the electrode surface than in the bulk solution. This is also an indication of the switch from a proton coupled reaction to a proton independent reaction [41, 45-47].

This change in reaction is also reflected in the cyclic voltammogram where a noticeable second wave occurs at a far more negative peak potential (Figure 51). This second wave occurs for both the CME and platinum-only electrode.

From unbuffered pH 3.5 to pH 7.2 there is little change in slope and formal potential for either bare or clay. This reflects the lack of protons at the electrode surface. The data suggests that the proton transfer is independent of the electron transfer and that suggests the deprotenated hydroquinone is the major product [47].
Figure 51. $E^0$ vs pH for quinone in unbuffered solution for bare and clay-modified electrode showing slope at various pH values.
Figure 52. Cyclic voltammogram of quinone unbuffered pH 3.35 showing appearance of second reduction and oxidation peak.
The Effect of Buffered pH on Peak Potential

We next considered how buffered pH affects anodic and cathodic peak potentials for quinone oxidation-reduction at a bare platinum electrode compared with a clay modified electrode (CME). Shifts in peak potentials to more negative values (in the case of oxidation) or more positive values (in the case of reduction) indicate that the oxidation or reduction is thermodynamically easier and requires less energy at the electrode surface in order to overcome the energy of activation.

Table 6 shows a graph containing cathodic and anodic peak potentials obtained from cyclic voltammetry for platinum and CME electrodes in buffered pH. Figure 53 is a graph of the data which shows that for all values of pH in a quinone buffered solution there is an enhanced thermodynamic favorability for anodic and cathodic potential with the CME over the bare platinum electrode. For example, the anodic potentials from pH 2.5 to 3.5 there is approximately a 33mV advantage for the CME over platinum and is nearly the same mV advantage for the peak cathodic potential at the same pH values.

From pH 3.8 to 6.5 there is an overall favorability of both anodic and cathodic enhancement with the anodic enhancement somewhat greater than the cathodic. Overall this indicates that the clay is somehow acting to lower the energy barrier for electron transfer between the electrode and the quinone in solution.
<table>
<thead>
<tr>
<th>Buffered pH</th>
<th>Q-Clay BUF cathodic potential</th>
<th>Q-Bare BUF cathodic potential</th>
<th>Q-Clay BUF anodic potential</th>
<th>Q Bare BUF anodic potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
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<td>97.1</td>
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<td>3.7</td>
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<td>418</td>
<td>454</td>
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<td>3.8</td>
<td>109.8</td>
<td>41.8</td>
<td>405</td>
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<td>3.9</td>
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<td>4.0</td>
<td>38.6</td>
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<td>412</td>
<td>496</td>
</tr>
<tr>
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<td>64.3</td>
<td>383</td>
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</tr>
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<td>4.5</td>
<td>4.76</td>
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<td>312</td>
<td>384</td>
</tr>
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<td>6.5</td>
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</tr>
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<td>7.2</td>
<td>-165</td>
<td>-133</td>
<td>228</td>
<td>233</td>
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</table>

Table 6. Anodic and cathodic peak potentials in buffered solutions for quinone oxidation reduction obtained from cyclic voltammetry at CME and bare platinum electrodes at 50mV/s scan rate.
Figure 53. Anodic and cathodic peak potentials in buffered pH obtained from cyclic voltammograms of quinone at a clay-modified electrode and bare platinum electrode.
The Effect of Unbuffered pH on Peak Potential

From pH 1.5 to 3.0 oxidation is easier by 50 to 90 mV than at the bare electrode. From pH 3.1 to pH 3.5 however several changes occurred. This can be seen in the cyclic voltammogram for quinone pH 3.1 (Figure 55) for an unbuffered aqueous solution. We observed the peak potentials for bare and clay starting to merge while at the same time a second peak more negative of the first beginning to develop. This second peak that forms is most likely due to the loss of protons at the electrode surface creating an “effective pH” near the electrode surface.

Secondly, after pH of 3.5, both the cathodic and anodic peak potentials are nearly identical for both the CME and the bare platinum electrode. This is evidence that the clay is somehow impacting the reduced-protonated species of quinone to a greater extent than it does simply the reduced-only quinone.

Looking at the nine-member square scheme of quinone (Figure 54) for an aqueous solution where \([H^+] \geq [Q]\), the starting reactant is Q in solution. Once quinone is in solution and before reduction occurs, the possible reactants initially present besides Q are QH\(^+\) and QH\(_2\)^{2+}. Once the first electron is added, the possible reactants in solution are QH\(^-\) and QH\(_2\)^{+} all being protonated species. However when \([H^+] < [Q]\) one can assume that some of the quinone initially may be in the protonated state, but as reduction proceeds the protons that would have been present are quickly depleted leaving Q as present initially, then Q\(^-\) after the first electron transfer, and finally yielding the product Q\(^{2-}\) with none of the reactants being the protonated species.
Comparing buffered pH (Figure 53) to unbuffered pH (Figure 56) we can draw the following four conclusions:

1. *Unbuffered* cathodic and anodic peak potentials *are* enhanced at the CME over bare platinum at low pH values (pH 1.5 to 3.5) and abundant protons *are* present.

2. *Unbuffered* cathodic and anodic peak potentials are *not* enhanced significantly at the CME over bare platinum at pH values 3.9 to 7.2 where abundant protons are *not* present.

3. *Buffered* cathodic peak potentials *are* enhanced at the CME over bare platinum at all pH values from 2.5 to 6.5 where protons *are* present due to buffering.

4. *Buffered* anodic peak potentials *are* enhanced at the CME over bare platinum at all pH values from 2.5 to 6.5 where protons *are* present due to buffering.

It is apparent that when hydrogen-bonded quinone occurs in solution with the clay, there is a lowering of the activation barrier of the quinone-species which leads to easier reduction and oxidation of quinone. The hydrogen-bonded quinone is possibly reacting...
with the negatively-charged clay pulling away electron density from the quinone to the
clay allowing another electron to go in. This is an area that we wish to further in our
research and investigation.
<table>
<thead>
<tr>
<th>pH UB</th>
<th>Q Clay UB cathodic peak potential</th>
<th>Q Clay UB anodic peak potential</th>
<th>Q Bare UB cathodic peak potential</th>
<th>Q Bare UB anodic peak potential</th>
</tr>
</thead>
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<tr>
<td>1.5</td>
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<tr>
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<td>150</td>
<td>440</td>
<td>100</td>
<td>519</td>
</tr>
<tr>
<td>2.5</td>
<td>147</td>
<td>450</td>
<td>61.2</td>
<td>535</td>
</tr>
<tr>
<td>3.0</td>
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<td>437</td>
<td>28.5</td>
<td>530</td>
</tr>
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<td>82</td>
<td>449</td>
<td>104</td>
<td>461</td>
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<td>486</td>
</tr>
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<td>-74.1</td>
<td>-201</td>
<td>-106</td>
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<td>4.5</td>
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<td>-106</td>
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<tr>
<td>7.2</td>
<td>-205</td>
<td>-96.3</td>
<td>-208</td>
<td>-113</td>
</tr>
</tbody>
</table>

**Table 7.** Anodic and cathodic peak potentials in unbuffered solutions for quinone oxidation-reduction obtained from cyclic voltammetry at CME and bare platinum electrodes at 50mV/s scan rate.
Figure 55. Cyclic voltammogram of quinone in unbuffered aqueous solution pH 3.1 showing formation of a second anodic and cathodic peak occurring at more negative potentials.
Figure 56. Anodic and cathodic peak potentials in unbuffered pH obtained from cyclic voltammograms of quinone at a clay-modified electrode and bare platinum electrode.
Experimental Peak Separation in Unbuffered pH

Our results for peak separation $\Delta E_p$ for quinone reduction-oxidation at a clay modified electrode (CME) vs. a bare platinum electrode in an unbuffered pH (Table 8, Figure 57) show that from pH 1.5 to 3.45 the peak separation is noticeably smaller for the CME than for the bare platinum electrode. For pH 1.5 the peak separation for the CME is smaller by 91 mV. For pH 2.0 the peak separation for the CME is smaller by 129 mV. For pH 2.5 the peak separation for the CME is smaller by 170 mV. For pH 3.0 the peak separation for the CME is smaller by 191 mV. The difference in peak separations obtained for the cyclic voltammograms can also be seen (Figure 59-64). At pH 3.1 the peak separations for the CME vs. the bare are similar in value with only a 10 mV difference between the CME and the bare.

The region from pH 3.25 to 3.35 is what we have termed our “chaotic region,” the region of much change. From pH 3.25 to pH 3.35 two processes are occurring simultaneously. First the peak potentials are changing rapidly due to the “effective pH” at the electrode (proton consumption at the electrode surface) while at the same time the pH change is likely causing a change in the reactant species in solution and thereby a change in the pathway through the nine-member square scheme. Within this region the lack of protons in the coupled reaction affect the shift in $E^\circ$ to more negative values by several hundred millivolts and we know this large shift in peak separation involves the lack of protons, so it seems reasonable that this change to a larger peak separation for the clay is also due to the lack of protons involved with the clay. Where protons are
<table>
<thead>
<tr>
<th>Unbuffered pH</th>
<th>Clay Peak Separation Epa-Epc (mV)</th>
<th>Bare Peak Separation Epa-Epc (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>338.00</td>
<td>429</td>
</tr>
<tr>
<td>2.0</td>
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</tr>
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<td>473.8</td>
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</tr>
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<td>309</td>
</tr>
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<td>3.35</td>
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</tr>
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<td>3.45</td>
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<td>378</td>
</tr>
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<td>95</td>
</tr>
<tr>
<td>7.2</td>
<td>108.70</td>
<td>95</td>
</tr>
</tbody>
</table>

**Table 8.** Anodic and cathodic peak separation ($\Delta$Ep) in unbuffered solution for a clay-modified electrode vs. bare platinum electrode in unbuffered solutions at 50mV/s scan rate.
Figure 57. Peak separation values of quinone in unbuffered pH (in millivolts) for the CME vs. bare platinum electrode. Scan rate 50mV.
Figure 58. Comparison of anodic and cathodic peak separation in unbuffered pH for the bare platinum vs. CME in unbuffered pH. Scan rate 50mv/s.
abundant, the clay shows catalytic enhancement but where protons are lacking, there is no enhancement in peak separation for the CME and an apparently slower electron transfer.

Looking at pH 3.45 an unusual change in peak separation begins to occur. Whereas before the clay had a smaller peak separation than the bare electrode, now above pH 3.5 the clay peak separation becomes larger for the clay and remains so from pH 3.5 to 7.2. Our results show that there appears to be a catalytic enhancement of $k^0$ for the clay at a low unbuffered pH (pH < 3.0) but as the pH is increased above pH 3.5 there is no longer an enhancement of $k^0$ as evidenced by the peak separation values.

This can also be seen by looking at the graph for peak separation vs. pH (Figures 57 and 58). Before pH 3.0 there is a noticeable enhancement of clay over bare but after pH 3.5 peak separations are nearly identical and linear for both the clay and the platinum electrode with a slight favorability of platinum over the clay.

Further support that protons are involved in the catalytic enhancement with clay comes when considering the peak separation in unbuffered pH at values above and below pH 3.5. When we begin with a 3mM solution of quinone at pH 3.0 the concentration of quinone is 0.003M whereas the $[H^+]$ at pH 3.0 is 0.001M so the concentrations are fairly similar. However at pH 3.5 the $[H^+]$ is 0.00032 M compared to 0.003M for quinone or nearly a 10-fold increase in concentration of Q over $[H^+]$. This lack of protons at pH 3.5 and above coincides with our results of peak separation enhancement with clay over bare.
Below pH 3.5 in unbuffered favors the clay, but above pH 3.5 there is little difference between the clay and bare platinum with bare having a slightly smaller peak separation.
Figure 59. Cyclic voltammogram for quinone in unbuffered pH 1.5 at bare platinum and clay modified electrode (CME) showing peak separation comparison for bare and CME.
Figure 60. Cyclic voltammogram for quinone in unbuffered pH 2.0 at bare platinum and clay modified electrode (CME) showing peak separation comparison for bare and CME.
Figure 61. Cyclic voltammogram for quinone in unbuffered pH 2.5 at bare platinum and clay modified electrode (CME) showing peak separation comparison for bare and CME.
Figure 62. Cyclic voltammogram for quinone in unbuffered pH 3.0 at bare platinum and clay modified electrode (CME) showing peak separation comparison for bare and CME.
Figure 63. Cyclic voltammogram for quinone in unbuffered pH 3.5 at bare platinum and clay modified electrode (CME) showing peak separation with noticeable larger peak separation for CME vs. bare.
Figure 64. Cyclic voltammogram for quinone in unbuffered pH 7.2 at bare platinum and clay modified electrode with peak separation still larger for clay over bare platinum electrode at a high pH.
Experimental Peak Separation in Buffered pH

In comparing our results for $\Delta E_p$-peak separation for quinone reduction-oxidation at a clay modified electrode (CME) vs. a bare platinum electrode in a buffered pH (Table 9, Figure 63) the peak-separation $\Delta E_p$ results are interesting. Throughout the entire pH range from 2.5 to 7.2 the peak separation is smaller for the CME than at the bare electrode. Recall that systems that show Nernstian behavior have smaller peak separation and faster kinetics for electron transfer. Looking at the peak separation for buffered pH comparing clay to bare we show the following results.

- For pH 2.5 there is a 57 mV enhancement in peak separation in the clay system.
- For pH 3.5 there is a 51 mV enhancement for clay.
- For pH 3.7 there is a 65 mV enhancement for clay.
- For pH 3.8 there is a 148 mV enhancement for clay.
- At pH 3.9 there is a 192 mV enhancement for clay.
- At pH 4.0 there is a 133 mV enhancement for clay.
- At pH 4.1 there is a 134 mV enhancement for clay.
- At pH 4.5 there is a 112 mV enhancement for clay.
- At pH 5.5 there is an 87 mV enhancement for clay.
- At pH 6.5 there is an 83 mV enhancement for clay.

But a most interesting result is that at pH 7.2 the clay is actually larger in peak separation than the bare platinum electrode showing a +27 mV enhancement for the bare electrode!
<table>
<thead>
<tr>
<th>Buffered pH</th>
<th>Clay Peak Separation Epa-Epc (mV)</th>
<th>Bare Peak Separation Epa-Epc (mV)</th>
<th>Enhancement for CME over Bare Electrode (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>330</td>
<td>387.9</td>
<td>57</td>
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</tr>
<tr>
<td>7.2</td>
<td>393</td>
<td>366</td>
<td>-27</td>
</tr>
</tbody>
</table>

*Table 9.* Anodic and cathodic peak separation (ΔEp) for a clay modified electrode vs a bare platinum electrode in buffered pH at 50mV/s scan rate.
Figure 65. Comparison of peak separation (Epa – Epc) for quinone in buffered pH for the CME and bare platinum electrode, scan rate 50mV. Lower line shows enhancement of clay over bare in mV.
This seems to further support the idea that when proton concentration is abundant as we saw in our very low unbuffered pH or in our buffered systems where pH < 7.0 and protons are still fairly available, when these conditions exist there is always a smaller peak separation suggesting a faster \( k^0 \) electron transfer favorability in the clay system. This enhancement can be anywhere from 50 mV to almost 200 mV favorability for the CME over the bare platinum electrode.

**Conclusion for Peak Separation at CME vs. Bare Electrode in Buffered pH**

Our results seem to suggest that the heterogeneous electron transfer rate \( (k^0) \) increases (heterogeneous electron transfer becomes faster) for the CME over bare in a buffered solution where an abundance of protons are available and \( k^0 \) decrease (heterogeneous electron transfer becomes slower) either as the proton concentration decreases (still acidic pH but \([Q] \sim [H^+]\)) or when the pH is near neutral to basic. As previously suggested this may be due to the stabilization of the protonated quinone species acting on the clay in some manner to facilitate faster electron transfer. Another suggestion of enhancement of \( k^0 \) was that put forth by Forster who had similar results working with anthraquinone at various pH values [41]. He proposed that in a pH dependent electron transfer there is perhaps higher reorganization energy of the quinone species acting on the surface affecting \( k^0 \) or possibly a poor electronic coupling to the electrode surface slowing \( k^0 \). Forster also found that under highly acidic conditions (pH of 1.4) the rate of electron transfer \( k^0 \) quantitatively determined was faster by 10-fold as compared to the rate of \( k^0 \) at pH 4.2.
With our results we can see that our peak separations are smaller for one type of electrode at a low pH (the CME) over the bare platinum. Although we have not yet directly quantified \( k^o \) at a clay vs. a bare electrode for our quinone system, it’s clear that excess protons greater than the concentration of quinone at all pH values are playing a factor in our apparent \( k^o \) enhancement (faster electron transfer) at a clay electrode vs. bare. This seems evident by the differences in our smaller peak separation for the CME compared to bare platinum electrode at a very low unbuffered pH where protons are abundant. We then saw the shift in peak separation for unbuffered solutions for the remaining pH values (pH 3.5-7.2) where the peak separation was actually greater in the clay suggesting protons are a somehow facilitating a faster \( k^o \) electron transfer rate. Lastly, by comparing the above unbuffered pH with what we saw in buffered pH where there is an abundance of protons throughout the entire pH range; peak separation was enhanced in clay throughout the entire pH range as well. When the buffered pH was above 7.0 and no protons are available there was no enhancement for the clay modified electrode.

**Future Work**

Future work would be to determine how the hydrogen bonding is impacting the clay-modified electrodes. One way this could be done would be to cap the edges of the clay with a pyrophosphate solution. This would minimize the charged clay edge sites and still allow protonation of the quinone.
Another area would be to look into how pH is impacting the oxidation of quinone at pH 3.1. We saw that when using high scan rates at pH 3.3 we obtained a reduction current but little return oxidation current. This was an unusual phenomenon and is a further area of interest.

Further research interest is to determine if clay is impacting the $K_a$ of quinone in the nine-member square scheme as shown in a Pourbaix diagram. Our preliminary research seems to suggest a shifting of $K_a$ in the nine-member square scheme but more analysis is required.

Lastly, two other areas to investigate are to consider using different types of clays, perhaps an iron rich nontronite to see if the iron in the clay functions catalytically perhaps more so than smectite.

The final area to further investigate is using x-ray diffraction analysis (XRD) of quinone-clay films. This would quantify the quinone sorption in clay at various pH values.
REFERENCES


**VITA**

Thomas Nelson was born in Hammond, Indiana and grew up in Dyer, Indiana. After graduating high school he began a business career as a self-employed retail businessman in July of 1979.

Thomas began attending college at Indiana University Northwest in August 1995 where he earned a Bachelor of Science in chemistry, (American Chemical Society (ACS) certified) with a minor in mathematics in December 2003. While attending Indiana University Northwest, he completed one semester of undergraduate research at the University of Notre Dame Radiation Laboratory where he worked on deposition of nanoparticles as metal-catalyst for fuel cell applications. He presented his research project at a poster session for the Electrochemical Society meeting in San Antonio, Texas in May of 2004. He also co-authored a paper on the topic entitled *One Step Metal Particle Deposition and Solubilization of Single Wall Carbon Nanotubes for fuel cell applications* which was published in the Annual meeting of the Electrochemical Society in 2004.

After graduating college, Thomas began a teaching career by enrolling in a one year state-certified educational program entitled “Transition to Teaching” at Indiana University Northwest in January 2004 and obtained his Indiana secondary education-chemistry teaching license in January of 2005. He presently continues to teach chemistry at Indiana University Northwest.
Thomas entered Loyola University Chicago’s graduate program in the August 2006. He began his master’s degree research project with Dr. Alanah Fitch involving electrochemical studies of quinone using clay-modified platinum electrodes.

Currently Thomas continues his self-employed business which he started in 1979 as well as teaching chemistry at Indiana University Northwest. Thomas currently lives in Crown Point, Indiana with his wife Sharon and is the father of five children and has four grandchildren.