THE EFFECT OF ADSORPTION OF BENZO-(f)-QUINOLINE ON THE ELECTROCHEMICAL KINETICS OF THE QUINONE-HYDROQUINONE AND THE IRON(III)/IRON(II) SYSTEMS

BY

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1980
ACKNOWLEDGEMENTS

I wish to express my sincere thanks and appreciation to my supervisory committee for their assistance with this dissertation: Dr. G. M. Schmid, for his patience and guidance throughout my graduate studies, and for serving as my committee chairman; Dr. E. Verink, for his interest and concern shown during my graduate career; and to Dr. J. D. Winefordner for his support throughout my career. My appreciation is also expressed to Dr. R. G. Bates and Dr. R. C. Stoufer for reviewing this work and attending its defense. Furthermore, I acknowledge Dr. G. Born and Dr. R. Ferrante for adding a degree of color to my life as a graduate student. Lastly, I would like to thank my parents for their constant encouragement to my education and to my wife, Whitney, for providing the necessary incentive and tolerance to complete my graduate commitments.
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Abstract of Dissertation Presented to the
Graduate Council of the University of Florida
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

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June 1980

Chairman: Gerhard M. Schmid
Major Department: Chemistry

The adsorption of benzo-(f)-quinoline has been investigated on smooth gold in 1.0 M perchloric acid and 1.0 M sulfuric acid using alternating current impedance methods. In 1.0 M perchloric acid, the adsorption between 0.20 V and 0.90 V versus the saturated calomel reference electrode (SCE) could be described using the Langmuir isotherm. The adsorption equilibrium constant was found to decrease with increasing potential from $6.83 \times 10^5$ L mole$^{-1}$ at 0.20 V to $1.36 \times 10^5$ L mole$^{-1}$ at 0.90 V. This decrease was explained as being due to the increased electrostatic interaction between the positively charged benzo-(f)-quinoline cation and the electrode making the adsorption process less favorable with increasing potential. In 1.0 M sulfuric acid the fractional coverage versus concentration relationship was found to fit
the Frumkin isotherm and the isotherm with virial coefficients equally well between -0.20 and 0.50 V versus SCE. For the Frumkin isotherm the adsorption equilibrium constant was essentially constant over the range of potentials studied with an average value of $(5.89 \pm 2.19) \times 10^5$ L mole$^{-1}$. The constant $a$ which represents the two-dimensional interaction between the adsorbed particles decreased in value from -3.51 at -0.20 V to a minimum of -4.58 at 0.10 V before increasing to -2.36 at 0.50 V. The average value of $a$ was found to be $-3.70 \pm 0.71$. Using the isotherm with virial coefficients the adsorption equilibrium constant was essentially constant with an average value of $(1.35 \pm 0.37) \times 10^6$ L mole$^{-1}$. The interaction parameter, $a$, reached a minimum value at 0.10 V as before and was more negative. The average value was $-5.34 \pm 0.45$. The negative value of $a$ found for both isotherms indicates the interaction between the adsorbed molecules is repulsive in nature.

The 1.0 M sulfuric acid electrolyte system was used to study the electrochemical kinetics of the quinone-hydroquinone and the Fe(III)/Fe(II) reactions at various benzo-(f)-quinoline concentrations. The quinone-hydroquinone system was studied using direct current measurements at low overpotentials. In 1.0 M sulfuric acid the standard rate constant was found to be $1.98 \times 10^{-3}$ cm s$^{-1}$ with the charge transfer coefficient equal to 0.57 for the variation of the concentration of quinone and equal to 0.38 for the variation of the concentration of hydroquinone. These results indicate that the quinone-hydroquinone reaction is composed of two one-electron steps.
This result is supported by the literature. In the presence of benzo-(f)-quinoline, the standard rate constant decreased with increasing concentration from $1.98 \times 10^{-3} \text{ cm s}^{-1}$ in 1.0 M sulfuric acid to $3.16 \times 10^{-4} \text{ cm s}^{-1}$ in 1.0 $\times 10^{-3}$ M benzo-(f)-quinoline. The decrease in the standard rate constant with fractional coverage was logarithmic. The charge transfer coefficient was constant with increasing concentration of benzo-(f)-quinoline and equal to $0.54 \pm 0.09$ for the variation of quinone concentration and equal to $0.44 \pm 0.05$ for the variation of hydroquinone concentration.

The Fe(III)/Fe(II) electrochemical system was studied using the Faradaic impedance method. In 1.0 M sulfuric acid the standard rate constant was found to be $1.30 \times 10^{-2} \text{ cm s}^{-1}$ with the charge transfer coefficient equal to 0.58 for the variation of the Fe(III) concentration at constant Fe(II) concentration and equal to 0.51 for the variation of the Fe(II) concentration at constant Fe(III) concentration. In 1.0 $\times 10^{-5}$ M and 1.0 $\times 10^{-4}$ M benzo-(f)-quinoline the standard rate constant was $1.01 \times 10^{-2} \text{ cm s}^{-1}$ and $4.21 \times 10^{-3} \text{ cm s}^{-1}$, respectively. In 1.0 $\times 10^{-5}$ M benzo-(f)-quinoline, the charge transfer coefficient was 0.48 and 0.51 in 1.0 $\times 10^{-4}$ M benzo-(f)-quinoline.

For both electrochemical systems studied, the decrease in the standard rate constant with fractional coverage is logarithmic. The most likely explanation for this behavior is that the adsorption of benzo-(f)-quinoline causes an increase in...
in the free energy of activation for the transfer of the electroactive species to and from the electrode surface.
CHAPTER I
INTRODUCTION

The ability of organic and inorganic molecules and ions to control corrosion of metals has long been of interest due to the tremendous annual cost of corrosion, estimated to be between 1 and 3.5% of the Gross National Product (1). For corrosion to take place at a metal surface, several processes must occur (2). First there must be transfer of charge from the metal to the solution with consequent oxidation of the metal to a higher valence state, the anodic process. There must also be the transfer of charge from the solution to the metal with consequent reduction of a species in solution to a lower valency state, the cathodic process. Between the location of the cathodic and anodic reactions there must be an electronic current path in the metal and an ionic current path in the solution to form a complete circuit. In order to control corrosion, it is necessary to control at least one of the preceding processes. This is frequently done by the use of inhibitors which adsorb on the metal surface and act to retard the cathodic and/or anodic processes.

An inhibitor may affect the corrosion reactions of metals in four ways (3):

1
1. The inhibitor may form a surface film which acts as a physical barrier to restrict the diffusion of ions or molecules to or from the metal surface and so retard the corrosion process. This occurs particularly when the inhibitor molecule is large, as in the case of proteins, polysaccharides, or compounds containing long hydrocarbon chains.

2. The interaction of the inhibitor molecules with the surface metal atoms may prevent these metal atoms from participating in either the anodic or cathodic reactions of corrosion. This simple blocking effect decreases the number of surface metal atoms at which these reactions can occur, in proportion to the coverage at the electrode surface. This has been observed on iron in sulfuric acid solutions containing 2,6-dimethyl quinoline (4), benzo-(f)-quinoline (5), or aliphatic sulfides (6).

3. If the electrode reactions of corrosion involve the formation of adsorbed intermediate species, the presence of adsorbed inhibitors may interfere with the formation of these adsorbed intermediates. Corrosion may then proceed by alternate paths through intermediates containing the inhibitors, thus affecting the activation energy of the reaction. Studies of the anodic dissolution of iron in the presence of inhibitors such as halide ions (7-9), aniline and its derivatives (10,11), and benzoate ion (12), have indicated that the adsorbed inhibitor participates in the anodic reaction.
4. Finally, the adsorption of ions on metal surfaces may change the structure of the electrical double layer at the metal-solution interface, which will affect the rates of the electrochemical processes (13).

A variety of inhibitors is available for the prevention of corrosion (1,14-16). These inhibitors can interact with the metals and affect the corrosion reaction in a number of ways, some of which may occur simultaneously. It is often not possible to assign a simple general mechanism of action to an inhibitor because the mechanism may change with experimental conditions such as inhibitor concentration, the pH of the solution, the nature of the anions in the solution, the nature of the metal, and the extent of reaction to form secondary inhibitors. One approach to a better understanding of the mechanism by which corrosion inhibitors operate is to simplify the electrochemical system. Thus, much work has been done in determining the effect of the adsorption on mercury and solid metals of organic inhibitors on the metal solution interface and on the kinetics of simple charge transfer reactions (17-20). It is the aim of such work to develop a theory which can describe the change in the electrochemical reaction rate that occurs when an organic substance, capable of being adsorbed on the electrode surface, is added to the solution. It will be seen that many of the same mechanisms that control corrosion are applicable to the inhibition of simple electrochemical reactions.
Theory Describing Inhibition of Electrochemical Reactions

Weber et al. (21) and Kuta and Smoler (22) as well as Muller and Lorenz (23) were among the first to suggest the equation:

\[ k_\theta = (1 - \theta) k_{\theta=0} + k_{\theta=1} \]  (1)

for the standard rate constant of an electrochemical reaction at a given value of \( \theta \) (the fractional coverage). Here \( k_{\theta=0} \) and \( k_{\theta=1} \) are the value of the standard rate constant for \( \theta = 0 \) and \( \theta = 1 \), respectively. For \( k_{\theta=0} \gg k_{\theta=1} \) and \( \theta < 1 \), equation (1) becomes the "blocking equation":

\[ k_\theta \approx (1 - \theta) k_{\theta=0} \]  (2)

which predicts a linear relationship between \( k_\theta \) and \( \theta \).

It has been shown in the work of Heyrovsky and Kuta (18) that the electroreduction of \( \text{Co(NH}_3\text{)}_6^{3+} \) and \( \text{VO}^{2+} \) on mercury in 0.1 M sulfuric acid in the presence of polyvinyl alcohol is inhibited according to equation (2). Similar results were obtained by Laitinen et al. (24) for the reduction of titanium(IV) in the presence of camphor.

Data for the reduction of Cd(II) in the presence of the surface active alcohols are contradictory. Biegler and Laitinen (25) studied the reduction of Cd(II) in 0.1 M HClO\(_4\) plus 0.9 M NaClO\(_4\) in aqueous solutions of n-butanol and found that for the reduction of Zn(II) in the presence of n-valeric acid, diethyl ketone, and amyl alcohol, and for the reduction of Cd(II) in the presence of amyl alcohol in
5.0 \times 10^{-2} \text{ M} \ Na_2\text{SO}_4 \text{ equation (2) is obeyed but the rate decreased much more slowly than that determined by Biegler and Laitinen (25). The rate of reduction of Cd(II) determined by Biegler and Laitinen was found to be 100 times greater than that found by Venkatesan et al. (26). This was explained by assuming that perchlorate ions form a bridge which facilitates the electron transfer (26). Sathyanarayama (27) suggested the following empirical relation for the reduction of Zn(II), Cd(II), and Cu(II) in 0.5 \text{ M} \ Na_2\text{SO}_4 \text{ in the presence of } n\text{-butanol to describe his experimental results,}

\[ k_0 = (1 - \Theta)^b k_{\Theta=0} \] (3)

where \( b \) is a constant (\( b > 1 \)) which accounts for the lateral repulsive interaction between the adsorbate molecules. This relation was used by Lipkowski and Galus (28) to describe their experimental results for the electroreduction of vanadium(III), cadmium(II), plumbite ion, manganese(II), and nitrobenzene free radical in propanol, isopropanol, and t-butanol-water mixtures.

Niki and Hackerman (29) have suggested that the electrochemical reaction will proceed only at those sites where at the same time \( b \) water molecules are present on the electrode surface, and that the surface area occupied by such an aggregate will correspond to the cross section of the activated complex. According to this, the probability of finding one water molecule on the electrode surface is proportional to \( (1 - \Theta) \), while that of \( b \) water molecules existing simultaneously
in neighboring positions is \((1 - \theta)^b\), so that the \(\theta\) dependence of \(k_0\) ought to be described by a relationship of the type of equation (3).

Lipkowski and Galus (28) obtained equation (3) by using the Flory-Huggins (30,31) isotherm in describing the adsorption of the activated complex. In such a derivation the parameter \(b\) is the number of solvent molecules which are displaced from the surface by the activated complex of the depolarizer. In addition, it is necessary to assume that effects associated with changes in the surface layer structure and the potential (at the center of the activated complex) during surfactant adsorption are always small, or mutually compensating.

Even when it is assumed that adsorbate molecules are uniformly distributed over the entire electrode surface, implying the applicability of equations (1) through (3), substantial deviations from these relations are observed (28,32-35). To account for these deviations several theories have been proposed.

Parsons (36) first proposed that the change in the potential at the outer Helmholtz plane (OHP), due to surfactant adsorption, be taken into account when interpreting kinetic data. An examination of the electroreduction kinetics of Cr(III) (37) and Zn(II) (38) cations in the presence of n-butyl alcohol and different MgSO\(_4\) concentrations showed that at constant fractional coverage, the potential at the OHP calculated by Parsons' method (36) influence the
electrochemical reaction rate in accordance with Frumkin's (39) slow discharge theory.

Damaskin et al. (25) have suggested that the potential at the plane corresponding to the center of the activated complex of the depolarizer particle may be useful in describing the electrochemical reaction rate as a function of fractional coverage. This potential can differ from that calculated by Parsons' (36) method. If the adsorbate molecule is oriented, for instance, with its negative end toward the solution, this would produce an acceleration of the electroreduction of cations, and a deceleration of the electroreduction of anions.

Sathyanarayama (40) discusses an elementary electrostatic model where the dipole and its mirror image give rise to a potential at the site where the activated complex is located. This model has been successful in explaining experimental data concerning the influence of the length of hydrocarbon chains on the electroreduction kinetics of cations (41) and anions (42).

During surfactant adsorption on the electrode surface, one can, in principle, expect a change in the interaction between the electroactive species and the surface layer as the solvent molecules are replaced by adsorbate molecules. A change in the free energy of activation of the electrochemical reaction following the change in the surface layer structure during adsorption can be taken into account in
terms of the electroactive species' activity coefficient in the transition state of the reaction.

This idea has been formalized in terms of models by Parsons (43), Danilov and Loshkarev (44), Avilova et al. (45), and Afanas'ev and Ternovskoi (46) to various degrees of complexity and usefulness. For an unambiguous solution to this problem, one needs a detailed comparison of the inhibition effects by the same organic compound in the discharge of cations and anions, under the same conditions, at the same fractional coverages. This will lead to a better understanding of the individual factors presented and their contribution to the electrochemical reaction rate.

**Inhibition by Benzo-(f)-quinoline**

Hoar (47) has shown that for cold-rolled mild steel strip (C-0.26, Mn-0.36, S-0.031, P-0.038, Si-0.21%), benzo-(f)-quinoline in 10% weight/volume H₂SO₄ can provide corrosion protection. Using the weight loss method for the determination of the corrosion rate (mg/hr), a 1 x 10⁻² M solution provided a 98% reduction in corrosion rate, as compared to a solution not containing benzo-(f)-quinoline, whereas a 1 x 10⁻⁴ M solution provided only an 8% reduction. The fractional coverage, θ, presented as a function of inhibitor efficiency, was basically S-shaped and did not fit the Langmuir isotherm. Meissner and Haberfellner (48) found that in 1 M HCl, AlMg₃ was not protected by benzo-(f)-quinoline but good protection was provided by dibutylamine.
Using benzo-(f)-quinoline as an inhibitor for kinetic studies on mercury, Fischer and Seiler (49) found that the cathodic reduction of V(III), the anodic dissolution of Cu in CuSO₄ and H₂SO₄ solutions, the anodic dissolution of Ni in NiSO₄, and the cathodic deposition of Cu from CuSO₄ and H₂SO₄ solutions were all inhibited by the adsorption of benzo-(f)-quinoline. They found that the inhibition was independent of the physical characteristics of the surface and the nature of the metal of the electrode. The mechanism of the electrode reaction was found not to change in the presence of the inhibitor. In later works, Seiler et al. (50) found that in 1 x 10⁻³ M benzo-(f)-quinoline, the reduction of V(III) in 0.1 M HCl plus 0.9 M KCl on mercury is inhibited but that the oxidation of V(II) is not. They attribute this to a reorganization reaction of the benzo-(f)-quinoline, where benzo-(f)-quinoline (a planar cation) lies perpendicular to the surface at cathodic potentials and causes inhibition, but lies flat on the surface at anodic potentials affording no inhibition. This is supported by their data showing a peak in the differential capacity-potential plot for the benzo-(f)-quinoline, which occurs at approximately the standard potential for the V(II)/V(III) reaction.

Radacanu and Lorenz (51,52) studied the inhibition by benzo-(f)-quinoline on platinum and gold in 0.5 M H₂SO₄ using triangular voltage sweep methods and found that in both cases the Fe(II)/Fe(III) reaction was inhibited by 5 x 10⁻³ M
benzo-(f)-quinoline. They also proposed on the basis of their data that the hydrogen evolution reaction was accelerated in the presence of benzo-(f)-quinoline.

It is due to this incomplete understanding of inhibition at electrode surfaces that the quantitative determination of the effect of benzo-(f)-quinoline adsorption at gold surfaces on the kinetics of the Fe(II)/Fe(III) and the quinone/hydroquinone system was undertaken.
CHAPTER II
THEORETICAL CONSIDERATIONS

The theoretical treatment presented here is that given by Delahay (53), Damaskin et al. (54), and Vetter (55).

The Double Layer

In order for a potential difference to develop across a phase boundary, there must be a separation of charge at the interface. The array of charged particles and of oriented dipoles which exist at an interface is termed the electric double layer. In order to obtain information about the ionic distribution of species in the double layer, a model is necessary. Though highly simplified, the first attempts to determine the structure of the double layer are due to Helmholtz (56) and Quincke (57). Here the double layer is considered as a parallel plate capacitor. A different model advocated independently by Gouy (58,59) and Chapman (60) is still, after modification by Stern (61), the basis of our present understanding of the electric double layer.

A schematic of a current model of the electric double layer is shown in Figure 1(62). The double layer is divided into two regions, the outer or diffuse double layer and the inner or compact double layer. The latter contains
Figure 1: Schematic Representation of the Current Model of the Electrical Double Layer. (Diffuse Layer not shown).
oriented solvent molecules and ions that have lost their hydration shells and are said to be specifically adsorbed on the electrode surface. The inner double layer consists of two planes of interest, the inner Helmholtz plane (IHP) which is defined as the plane through the centers of these specifically adsorbed ions and the outer Helmholtz plane (OHP) which is the plane through the center of charge of ions at their point of closest approach to the electrode when they are only electrostatically attracted to the electrode and have not lost their hydration shells. The diffuse layer has a thickness on the order of 10 nm, depending upon the solution composition, while that of the compact layer is only a few nanometers.

Under all conditions, the interface as a whole is electrically neutral; the net charge density of the electrode must be equal in magnitude and opposite in sign to the net charge density on the solution side. There will be a potential at which the charge density on the electrode is zero, and this potential is defined as the zero point of charge (ZPC). When the electrode is anodic to its ZPC, there is an excess of anions in the double layer. Conversely, when the electrode is cathodic to the ZPC, there is an excess of cations in the double layer.

Equilibrium can be assumed between any point in the double layer and the bulk of the solution for an ideal polarized electrode. Hence we have for ionic species $i$:

$$\bar{\mu}_i = \mu_i^s$$  \hspace{1cm} (4)
where $\bar{\mu}_i$ and $\bar{\mu}^S_i$ are the electrochemical potentials of species i in the double layer and in the bulk of the solution, respectively. The potential-distance function can be calculated according to the Gouy-Chapman theory (58-60) if we consider that in the diffuse double layer the concentration, $c_i^i$, of species i is given by the Boltzmann distribution:

$$c_i = c_i^S \exp (-Z_i f \phi) \quad (5)$$

where $f = F/RT$, $c_i^S$ is the concentration of species i in the bulk of the solution, $Z_i$ is the ionic valence of this species, $\phi$ is the potential with respect to the bulk of the solution at some distance, x, from the electrode surface, $F$ is Faraday's constant, $R$ is the ideal gas constant, and $T$ is the absolute temperature.

The Poisson equation gives the necessary correlation between the potential $\phi$ and the charge density $\rho$. For a planar electrode, this equation can be used in its one-dimensional form:

$$\frac{d^2 \phi}{dx^2} = -\frac{4\pi e \rho}{\varepsilon} \quad (6)$$

where $\varepsilon$ is the dielectric constant and e is the unit electron charge. The charge density is related to the concentration $c_i$ of species i by

$$\rho = \Sigma Z_i F c_i \quad (7)$$
Combining equations (4), (5), and (6) gives:

\[
\frac{d^2 \phi}{dx^2} = -\frac{4 \pi}{\varepsilon} \Sigma Z_i F c_i^S \exp (-Z_i f \phi) \quad (8)
\]

This equation can be solved for \( \phi \) if it is assumed that \( \varepsilon \) is independent of \( x \). Multiplying both sides of equation (8) by \( 2d\phi/dx \) and by integrating once we find, after noting that \( \phi \to 0 \) and \( d\phi/dx \to 0 \) for \( x \to \infty \):

\[
\left(\frac{d\phi}{dx}\right)^2 = \frac{8\pi RT}{\varepsilon} \Sigma Z_i c_i^S \{\exp (-Z_i f \phi) - 1\} \quad (9)
\]

The charge per unit area, \( q \), on an electrode is related to \( d\phi/dx \) by the Gauss theorem:

\[
4\pi q = -\varepsilon \left(\frac{d\phi}{dx}\right) x_2 \quad (10)
\]

Here we take the value of \( d\phi/dx \) at \( x = x_2 \), which is at the plane of closest approach of ions which are not specifically adsorbed. In this plane, the OHP, the potential is \( \phi = \Phi_2 \). Combining equations (9) and (10) we have

\[
q = -\left\{\frac{RT\varepsilon}{2\pi} \Sigma Z_i c_i^S \{\exp (-Z_i f \Phi_2) - 1\}\right\}^{\frac{1}{2}} \quad (11)
\]

This equation allows the calculation of \( q \) as a function of \( \phi \) or vice versa. For a Z-Z electrolyte of concentration \( c^S \), equation (11) can be written as

\[
q = +2A \sinh \left\{\frac{|Z| f \Phi_2}{2}\right\} \quad (12)
\]
where

$$A = + \left( \frac{RT \varepsilon c^S}{2 \pi} \right)^{1/2} \tag{13}$$

Unsymmetrical electrolytes have been reviewed by Grahame (63).

The Gouy-Chapman theory predicts the potential drop in the diffuse double layer to be exponential with distance from the electrode surface. The Stern modification to this theory postulates that solvated ions cannot reach the electrode beyond the plane of closest approach (OHP) and that the presence of dipoles and specifically adsorbed ions causes the potential to vary linearly with distance across the compact double layer. This is shown schematically in Figure 2 (62). The difference of potential $\phi_m$ between the metal and the solution ($\phi_s = 0$ by convention) can now be divided into two parts (62,63):

$$\phi_m = (\phi_m - \phi_2) + \phi_2 \tag{14}$$

Since normally a certain quantity of charge is in excess at the solution side of the interface and is matched by an equal and opposite charge on the electrode, the electrode-solution interface can be treated as a capacitor. The capacity varies with potential. It is convenient to define a differential capacity as (64)

$$C = \left( \frac{dq}{dE} \right)_{\mu,T,P} \tag{15}$$
Figure 2: Schematic of the Stern Modification of the Gouy-Chapman Theory Giving a Potential-Distance Function for the Double Layer.
where $P$ is the pressure and $E$ is the experimental electrode potential versus some reference electrode.

Hence it follows from equation (14) that

$$\frac{\delta \phi_m}{\delta q} = \frac{\delta (\phi_m - \phi_2)}{\delta q} + \frac{\delta \phi_2}{\delta q}$$

(16)

or

$$\frac{1}{C} = \frac{1}{C_{m-2}} + \frac{1}{C_{2-s}}$$

(17)

where $C$ is the double layer differential capacity and $C_{m-2}$ and $C_{2-s}$ are the differential capacities corresponding to the compact and diffuse double layers, respectively. It is seen that the double layer can be regarded as two capacitors in series. By differentiation of equation (12) with respect to potential, the Gouy-Chapman theory allows calculations of the capacity $C_{2-s}$. Therefore,

$$C_{2-s} = |Z| f A \cosh (|Z| f \phi_2 / 2)$$

(18)

Under conditions where $\phi_2$ is small (large electrolyte concentration) equation (18) shows that the capacity of the diffuse double layer becomes quite large. Equation (17) then indicates that the experimental total capacity is simply the capacity of the compact double layer alone.
Adsorption of Organic Compounds

If the adsorption of organic compounds at the electrode surface is reversible, and not complicated by formation of multimolecular layers and micellar films, the electrode potential, $\phi$, the electrode charge, $q$, and the degree of coverage, $\Theta$, of the surface by the organic substance are interconnected in a definite manner.

Several authors (65-68) have shown that the thermodynamic laws of Gibbs, which give the relation between the interfacial tension, $\sigma$, the electrode potential, and the adsorption and activity of ions and molecules ($\Gamma_i$ and $a_i$, respectively) in the solution, are applicable to the electrode-solution interface. At constant temperature and pressure, the fundamental electrocapillary equation can be written in the form

$$d\sigma = -q\,d\phi - \sum_i \Gamma_i\,d\mu_i$$

$$= -q\,d\phi - RT \sum_i \Gamma_i\,d\ln a_i$$

(19)

where $\mu_i$ is the chemical potential of component $i$, $\Gamma_i$ is the surface excess of adsorbate molecules $i$ and $a_i$ is the activity of species $i$.

Adsorption at a given potential can be determined from results of electrocapillary measurements with the aid of equation (19) from which it follows that

$$\Gamma_i = \frac{1}{RT} \left( \frac{\delta \sigma}{\delta \ln a_i} \right) \phi$$

(20)
In addition to electrocapillary measurements, measurements of the differential capacity may be used for obtaining data on the adsorption of organic substances at the electrode-solution interface. The thermodynamic method of using capacity data is based on the double integration of the differential capacity curves; this, in accordance with the Lippmann (69) equation, gives the dependence of the interfacial tension on the electrode potential:

\[ q = \int_{\phi=0}^{\phi} C \, d\phi \]  

(21)

and

\[ \sigma = \sigma_{\text{max}} - \int_{\phi=0}^{\phi} q \, d\phi \]  

(22)

The \( \sigma \) versus \( \phi \) curves obtained in this manner are subsequently used for calculating adsorption of the components as described in equation (20).

If the potential \( \phi \) is taken as the independent electrical variable, then, for a dilute solution of organic substance, the fundamental electrocapillary equation may be written in the form

\[ d\sigma = -q \, d\phi - RT \, \Gamma \, d\ln c \]

\[ = -q \, d\phi - A' \, \theta \, d\ln c \]  

(23)

where \( A' = RT \, \Gamma_m \) (\( \Gamma_m \) is the maximum adsorption). Since \( d\sigma \) in this equation is an exact differential, the reciprocal relation gives
\[ \frac{1}{A^*} \left( \frac{\delta q}{\delta \ln c} \right) \phi = \left( \frac{\delta \theta}{\delta \phi} \right) c \]  

(24)

From this equation, which was originally derived by Gouy (70), it follows that

\[ \left( \frac{\delta \ln c}{\delta \phi} \right) \theta = - \left( \frac{\delta \ln c}{\delta \theta} \right) \phi \left( \frac{\delta \theta}{\delta \phi} \right) c = - \frac{1}{A^*} \left( \frac{\delta q}{\delta \phi} \right) \phi \]  

(25)

If \( B \), the adsorption equilibrium constant, is of the form \( B c = f(\theta) \) and \( f(\theta) \) is a definite function of \( \theta \), it follows that

\[ \frac{d\ln B}{d\phi} = - \left( \frac{\delta \ln c}{\delta \phi} \right) \theta \]  

(26)

then from equations (25) and (26) we have

\[ \left( \frac{\delta q}{\delta \theta} \right) \phi = A' \frac{d\ln B}{d\phi} \]  

(27)

Hence

\[ q = A' \left( \frac{d\ln B}{d\phi} \right) \theta + q_o \]  

(28)

where \( q_o \) is the integration constant, equal to the electrode charge when \( \theta = 0 \).

We denote the charge at \( \theta = 1 \) and a given potential by \( q_1 \); then

\[ q_1 = A' \frac{d\ln B}{d\phi} + q_o \]  

(29)

Combining equations (28) and (29) we see that
\[ q = q_0 (1 - \theta) + q_1 \theta \]  
\[ (30) \]

This result corresponds to the model of two parallel capacitors proposed by Frumkin (71) with the respective capacities being given by

\[ C_1 = \frac{dq_1}{d\phi} \quad \text{and} \quad C_0 = \frac{dq_0}{d\phi} \]

showing that the coverage, \( \theta \), can be calculated from the experimentally determined values of the differential capacity.

It is useful to classify the organic substances' behavior in terms of an adsorption isotherm. It is important to find the adsorption isotherm which agrees best with the experimental data, since the fundamental assumptions that are made in deriving these isotherms give further insight into the nature of the metal-solution interface. Some of the adsorption isotherms are listed below.

1) The Henry isotherm (72)
\[ Bc = \theta \]

2) The Freundlich isotherm (73)
\[ Bc^n = \theta \quad \text{where} \quad 0 \leq n \leq 1 \]

3) The Langmuir isotherm (74)
\[ Bc = \frac{\theta}{1 - \theta} \]
4) The Volmer isotherm (75)

\[ B_c = \frac{\theta}{1 - \theta} \exp \left( \frac{\theta}{1 - \theta} \right) \]

5) The Amagat isotherm (76)

\[ B_c^n = \frac{\theta}{1 - \theta} \exp \left( \frac{\theta}{1 - \theta} \right) \]

6) The Helfand-Frisch-Lebowitz isotherm (77)

\[ B_c = \frac{\theta}{1 - \theta} \exp \left\{ \frac{2 - \theta}{(1 - \theta)^2} \right\} \]

7) The Frumkin isotherm (78)

\[ B_c = \frac{\theta}{1 - \theta} \exp (-2\alpha \theta) \]

where \( \alpha \) characterizes the interaction between the adsorbed particles.

8) The Hill-de Boer isotherm (79)

\[ B_c = \frac{\theta}{1 - \theta} \exp \left( \frac{\theta}{1 - \theta} \right) \exp (-2\alpha \theta) \]

9) The Parsons isotherm (80)

\[ B_c = \frac{\theta}{1 - \theta} \exp \left\{ \frac{2 - \theta}{(1 - \theta)^2} \right\} \exp (-2\alpha \theta) \]

10) The isotherm with virial coefficients (see reference (76))

\[ B_c = \theta \exp (-2\alpha \theta) \]

where \( \alpha < 0 \) (repulsive interaction only)
11) The Temkin isotherm (81)

\[ Bc = \frac{\exp(a\Theta) - 1}{1 - \exp(-a(1 - \Theta))} \]

12) The Lorenz isotherm (82)

\[ \Theta = \frac{(1 + 1/Bc)^{V-1} + K_{as}}{(1 + 1/Bc)^V + K_{as}} \]

where \( K_{as} = V_{as}/V_{dis} \) is the equilibrium constant for association of the adsorbed molecules,

\[ v_{M} = \frac{V_{as}}{V_{dis}} \]

\( v \) is the "degree of association", i.e., the number of organic molecules in an associated group.

13) The Blomgren-Bockris isotherm (83)

\[ Bc = \frac{\Theta}{1 - \Theta} \exp(p\Theta^{3/2} - q\Theta^3) \]

and for the adsorption of organic ions,

\[ Bc = \frac{\Theta}{1 - \Theta} \exp(p_{1}\Theta^{3/2} - q\Theta^3) \]

In these equations \( p > 0, p_{1} > 0, \) and \( q < 0 \) are constants, expressed in terms of the dipole moment (or charge), the area occupied by an adsorbed molecule or ion, and the dielectric constant of the surface layer.
It is known from experimental data \((82,84)\) that the adsorption isotherms of organic substances may be either sigmoid or logarithmic, depending upon whether attractive or repulsive interaction predominates between the adsorbed particles. Of the equations considered above, the most suitable for representation of adsorption of organic substances on electrodes are isotherms \(7)\) through \(9)\), in which an arbitrary constant, \(a\), is used to represent two-dimensional interaction between the adsorbed particles. Depending upon the sign of this attraction constant, isotherms \(7)\) through \(9)\) may describe both attractive \((a > 0)\) and repulsive \((a < 0)\) interaction.

**Electrochemical Kinetics**

**Introduction**

The overall electrode reaction, which can be determined by a chemical analysis of the electrochemical products, generally consists of a series of reaction steps. An overall electrode reaction differs from an overall chemical reaction in that at least one reaction step of the overall electrode reaction must be a charge transfer reaction in which a charge carrier (ion or electron) is transported against a potential controlled activation energy, from one phase into another phase across the electrical double layer.

The aim of electrochemical kinetics is to explain the sequence of reaction steps constituting the overall electrode reaction, as well as determining the electrode reaction
rates which are proportional to the current density, $i$, the electrode potential, $E$, and the concentration, $c_j$, of reactants $s_j$.

The potential of an electrode measured against a standard hydrogen electrode, $E$, through which current flows differs from the equilibrium potential, $E_e$, established when no current passes through the electrode. The difference between the potentials is defined as the overvoltage, $\eta$, which was originally introduced by Nernst, and by Caspari (85). The concept of overvoltage is important since in electrochemical kinetics, as in chemical kinetics, the slowest reaction step is rate determining for the total reaction, and the magnitude and type of overvoltage is therefore governed by the slowest reaction step. After deducting any ohmic resistance drop which might have been included in a measurement, the total overvoltage can be divided into charge transfer, diffusion, reaction, and crystallization overvoltage according to the four possible types of rate control (86).

If only the charge transfer reaction is hindered and none of the other preceding or following reactions, there exists only a charge transfer overvoltage, $\eta_t$. If a chemical reaction is hindered, there exists a reaction overvoltage, $\eta_r$. In this case, the chemical reaction may proceed either homogeneously in the electrolyte or heterogeneously at the surface.
Pure diffusion overvoltage, $\eta_d$, is encountered if mass transport by diffusion to and from the electrode surface is the slowest process among the partial reactions involved.

Hindrance of the process by which atoms are incorporated into or removed from the crystal lattice leads to crystallization overvoltage, $\eta_c$. If several of the reactions have low reaction rates of similar orders of magnitude, the corresponding overvoltages are superimposed to form the total overvoltage, $\eta$.

The total overvoltage can be determined by measuring the alternating current polarization impedance of the system under consideration. An alternating current density $i = I \sin \omega t$ of the frequency $(\omega/2\pi)$ (Hz) gives rise to an overvoltage

$$\eta = Z_{I,p} I \sin (\omega t - \delta)$$

(31)

the frequency of which equals that of the current, but which has a phase lag, $\delta$, with respect to the current. The quantity $Z_{I,p}$ has the dimensions of "impedance" and is called the polarization impedance, corresponding to the diffusion impedance, $Z_{I,d}$, the reaction impedance, $Z_{I,r}$, the charge-transfer impedance, $Z_{I,t}$, and the crystallization impedance, $Z_{I,c}$. This polarization impedance of the electrode can be described by an ohmic resistance $R_p$ and a series (or parallel) capacitance $C_p$. $R_p$ represents the polarization resistance and $C_p$ the polarization capacitance of the electrode.
The total overvoltage \( \eta \) behaves as though the electrode consisted of a charge transfer resistance, \( R_t \), a diffusion impedance, \( Z_{I,d} \), and a reaction impedance, \( Z_{I,r} \), and a crystallization impedance, \( Z_{I,c} \), all connected in series. The capacitive partial current density, \( i_c \), which is consumed through the double layer capacitance, \( C_d \), together with the charge transfer current density, \( i_t \), yields the total current density \( i \). Thus, in place of the electrode, a circuit of different ohmic resistances and capacitances may be substituted as is shown in Figure 3. Each of these impedances will be considered separately.

**Charge Transfer Overvoltage**

The charge transfer reaction is of fundamental importance in electrochemical kinetics, since it is the only reaction directly affected by the electrode potential. For the development of charge transfer resistance, the simple case of a charge transfer reaction,

\[
0 + n \text{e}^- \xrightarrow{Z} R
\]  

(32)

taking place at a smooth, homogeneous electrode surface, neither preceded nor followed by any other reaction, will be considered. The integer \( n \) represents the number of electrons consumed in the reaction and is called the stoichiometric factor.

Generally there are two ways in which the current is carried across a metal-electrolyte interface, the faradaic and the non-faradaic path. In the former, current crosses
Figure 3. Equivalent-circuit diagram of an electrode with charge-transfer overvoltage \( (R_t) \), diffusion overvoltage \( (R_d, C_d) \), and reaction overvoltage \( (R_r, C_r) \).
the interface by virtue of an electrochemical reaction such as a reduction or oxidation of an electroactive species. In the latter case, charged particles do not cross the interface, and the current is carried by the charging and discharging of the electrical double layer.

For a sinusoidal signal, the faradaic current may be written

\[ i_f = i_{ct} + I \sin \omega t \]  \hspace{1cm} (33)

where \( I \) is the amplitude and \( i_{ct} \) is the constant component of the current. The faradaic current is also some function of the electrode potential \( E \) and the concentration of the reactants at the electrode surface

\[ i_f = f(E, c_o, c_r) \]  \hspace{1cm} (34)

or in the equivalent form

\[ E = g(i_f, c_o, c_r) \]  \hspace{1cm} (35)

where \( c_o \) and \( c_r \) are the concentration at the electrode surface of species \( O \) and \( R \) respectively.

Differentiating equation (35) with respect to time we have

\[ \frac{dE}{dt} = \left( \frac{\delta E}{\delta i_f} \right) \frac{di_f}{dt} + \left( \frac{\delta E}{\delta c_o} \right) \frac{dc_o}{dt} + \left( \frac{\delta E}{\delta c_r} \right) \frac{dc_r}{dt} \]  \hspace{1cm} (36)

and for equation (33)
Combining equations (36) and (37) we have

\[
\frac{\partial E}{\partial t} = \left( \frac{\partial E}{\partial i_f} \right) I_{f} \cos \omega t + \left( \frac{\partial E}{\partial c_o} \right) \frac{\partial c_o}{\partial t} + \left( \frac{\partial E}{\partial c_r} \right) \frac{\partial c_r}{\partial t}
\]

(38)

Since the faradaic response of an electrode can be represented as a series combination of a resistance and capacitance (37) we can write

\[
\frac{\partial E}{\partial t} = R_f \frac{\partial i_f}{\partial t} + \frac{i_f - i_{ct}}{C_f}
\]

\[
= R_f I_{f} \cos \omega t + \frac{I}{C_f} \sin \omega t
\]

(39)

By equating quantities \(dE/dt\) from equation (38) and (39), we obtain the general equation for the faradaic impedance

\[
R_f I_{f} \cos \omega t + \frac{I}{C_f} \sin \omega t =
\]

\[
\left( \frac{\partial E}{\partial i_f} \right) I_{f} \cos \omega t + \left( \frac{\partial E}{\partial c_o} \right) \frac{\partial c_o}{\partial t} + \left( \frac{\partial E}{\partial c_r} \right) \frac{\partial c_r}{\partial t}
\]

(40)

By using diffusion equations for each specific case with prescribed boundary conditions, it is possible to determine the derivative \(dc/dt\) which will always contain the terms \(\sin \omega t\) and \(\cos \omega t\). By equating the coefficients for the sine and cosine terms, the expressions for \(R_f\) and \(C_f\) may
be obtained which relate to the kinetic parameters for the electrochemical reaction.

If we consider the reaction described in equation (32), Fick's diffusion equation can be solved. The solution for $c_0(x,t)$ is

$$c_0(x,t) = f(x,t) + \frac{I}{nF(2D_0 \omega)^{1/2}} \exp \left\{ -\left(\frac{\omega}{2D_0}\right)^{1/2}x \right\}$$

$$\sin \{\omega t - \left(\frac{\omega}{2D_0}\right)^{1/2}x\} - \cos \{\omega t - \left(\frac{\omega}{2D_0}\right)^{1/2}x\}$$

(41)

where $f(x,t)$ is a function which describes the change in concentration related to the constant component of the current, $i_{ct}$. At $x = 0$, equation (41) becomes

$$c_0(0,t) = f(0,t) + \frac{I}{nF(2D_0 \omega)^{1/2}} (\sin \omega t - \cos \omega t)$$

(42)

and

$$\frac{dc_0(0,t)}{dt} = \frac{df(0,t)}{dt} + \frac{I}{nF} \left(\frac{\omega}{2D_0}\right)^{1/2}$$

$$(\cos \omega t + \sin \omega t)$$

(43)

Similarly, we can write

$$\frac{dc_r(0,t)}{dt} = \frac{df(0,t)}{dt} + \frac{I}{nF} \left(\frac{\omega}{2D_r}\right)^{1/2}$$

$$(\cos \omega t + \sin \omega t)$$

(44)
By substituting equations (43) and (44) into equation (40) and by equating the coefficients for the sine and cosine terms, we obtain

$$ R_f = \frac{\delta E}{\delta l_f} + \frac{\beta}{\omega^2} $$  \hspace{1cm} (45)

and

$$ C_f = \frac{1}{\beta \omega^2} $$  \hspace{1cm} (46)

where

$$ \beta = \frac{1}{2^{1/2} nF} \left\{ \frac{\delta E/\delta c_O}{D_O^{1/2}} - \frac{\delta E/\delta c_r}{D_r^{1/2}} \right\} $$  \hspace{1cm} (47)

From well established principles of reaction kinetics (53-55) it can be shown that the rate of the forward electrochemical reaction (reduction) is given by

$$ \dot{i} = - nF c_O k_o \exp\left(-\alpha nFE/RT\right) $$  \hspace{1cm} (48)

and for the backward reaction (oxidation)

$$ \dot{i} = nF c_r k_r \exp\left\{ (1 - \alpha) nFE/RT \right\} $$  \hspace{1cm} (49)

where $k_o$ and $k_r$ are the reaction rate constants and $\alpha$ is the charge transfer coefficient. The net current at any potential is given by

$$ i_f = \dot{i} + \dot{i} $$  \hspace{1cm} (50)

and hence
\[
\frac{\delta i_f}{\delta E} = (c_O k_O \alpha n^2 F^2/RT) \exp(\alpha nF/RT)
\]
\[
+ \{c_r k_r (1 - \alpha) n^2 F^2/RT\} \exp\{(1 - \alpha) nF/RT\}
\]

(51)

and therefore

\[
\frac{\delta i_f}{\delta E} = (nF/RT)(\alpha i_f + \bar{i})
\]

(52)

and if \( E = E_e \), the equilibrium potential, \( i_f = 0 \) and \( \bar{i} = \bar{i} = i_o \), the exchange current density, then equation (52) reduces to

\[
\frac{\delta i_f}{\delta E} = nF i_o/RT
\]

(53)

or

\[
\frac{\delta E}{\delta i_f} = RT/nF i_o
\]

(54)

Hence it can be seen that the exchange current density can be obtained from equation (54) if \( \delta E/\delta i_f \) is known. The latter can be determined by plotting \( R_f \) versus \( 1/\omega_b^i \) as indicated by equation (45). The intercept of this straight line yields the charge transfer resistance \( R_t = RT/nF i_o \).

It can further be shown that, if the exchange current density can be obtained as a function of the concentration of one of the reacting species, then the standard rate constant, \( k^0 \) and \( \alpha \) can be determined from the following equation:

\[
i_o = nF k^0 c_r^{1-\alpha} c_o^\alpha
\]

(55)
If we are working at the equilibrium potential, the Nernst equation may be employed to determine \( \frac{\delta E}{\delta c_o} \) and \( \frac{\delta E}{\delta c_r} \). These functions then reduce to

\[
\frac{\delta E}{\delta c_o} = \frac{RT}{nF} \frac{1}{c_o}
\]

and

\[
\frac{\delta E}{\delta c_r} = -\frac{RT}{nF} \frac{1}{c_r}
\]

where \( c_o \) and \( c_r \) are concentrations in the bulk of the solution, since the change in surface concentration is caused only by the alternating current. By substituting equations (56) and (57) into equation (47), we obtain

\[
\beta = \frac{RT}{2^{k_2} n^2 F^2} \left\{ \left( \frac{1}{c_o^k D_o^k} \right) + \left( \frac{1}{c_r^k D_r^k} \right) \right\}
\]

If the potential is not the equilibrium potential, the expression for \( \beta \) is greatly complicated since the changes in the surface concentrations are then caused not only by the alternating current but also by the direct current. Qualitatively it is possible to conclude that the faradaic impedance sharply increases with an increase in the difference between the electrode potential and the equilibrium potential. This occurs because the surface concentration of one of the reactive species decreases and, consequently, the measured cell impedance approaches the impedance of the double layer. Therefore, the study of the electrochemical reaction kinetics
by the faradaic impedance method has to be carried out at the equilibrium potential, $E_e$.

For an electrochemical reaction which is governed by charge transfer overvoltage only, the entire electrode behaves like an ohmic resistance, $R_t$, in parallel with a condenser of capacitance, $C_{dl}$, as shown below,

![Diagram showing $R_t$ and $C_{dl}$ in parallel]

where $C_{dl}$ is the double layer capacitance.

**Diffusion Overvoltage**

Diffusion overvoltage, $\eta_d$, appears when the supply of reactants at the electrode or the removal of products is rate determining when current flows. If all chemical processes are in equilibrium, only diffusion overvoltage is present. This condition for the appearance of pure diffusion overvoltage indicates that the calculation of the potential of an electrode with current flow is possible using the Nernst equation with the concentrations of the components directly at the surface rather than those in the interior of the solution.

Upon application of the alternating current to an electrode, a certain time is required to reach a steady-state
concentration gradient. Also, after a change in current density, a steady state is reached asymptotically with time. Therefore, a current having a time-variable density will lead to a concentration distribution which is also variable with time, and which fluctuates at the same frequency as the current.

The calculation of the concentration distribution when applying a sinusoidal alternating current leads to a damped concentration wave going from the electrode surface into the electrolyte. The concentration at the surface has a phase shift of 45° with respect to the current. This means that the concentration maximum appears one eighth of an oscillation period after the current maximum.

The derivation of the concentration wave according to Warburg (88) and Kruger (89) uses Fick's second law to relate the change in concentration $c_j$ with time, $t$, and distance, $x$, from the surface.

$$\frac{\delta c_j}{\delta t} = D_j \frac{\delta^2 c_j}{\delta x^2} \quad (59)$$

$D_j$ is the diffusion coefficient of species $j$.

For an alternating current density given by

$$i = I \sin \omega t \quad (60)$$

and for the boundary condition

$$\left( \frac{\delta c_j}{\delta x} \right)_{x=0} = - \frac{Iv_j}{nF D_j} \sin \omega t \quad (61)$$
where $v_j$ is the stoichiometric factor of $s_j$ in the overall electrode reaction. Equation (59) can be solved on the basis of Faraday's law and Fick's first law (88).

$$c_j(x,t) = \overline{c}_j + A \exp(-x/x_0) \sin (\omega t - \frac{2\pi x}{\lambda} + \beta)$$

(62)

where $\overline{c}_j$ is the concentration of species $j$ when no current flows. Equation (62) constitutes the damped concentration wave in the electrolyte with the phase shift $\beta$ at the surface $x = 0$.

The equations for $x_0$ and $\lambda$ are obtained by partial differentiation of equation (62) with respect to $x$ and $t$ and substitution into equation (59). If this is done, it is seen that $x_0 = \lambda/2\pi$, where

$$x_0 = (2D/\omega)^{\frac{1}{2}}$$

(63)

$$\lambda = 2\pi (2D/\omega)^{\frac{1}{2}}$$

(64)

The distance of penetration of the concentration wave at which the amplitude has dropped to the fraction $1/e = 0.372$ is $x_0$. The wavelength of the concentration wave is $\lambda$.

The first partial derivative of $x$ for $x = 0$ provides the value of $\beta$ and $A$ by comparison of the coefficients with the boundary condition expressed in equation (61).

$$\beta = -\pi/4$$

(65)

and

$$A = I v_j/nF (D_j \omega)^{\frac{1}{4}}$$

(66)
Therefore, the concentration wave is given by

\[ c_j(x,t) = \overline{c_j} + \frac{I v_j}{nF (D_j \omega)^{\frac{1}{2}}} \exp \left\{ -\frac{(\omega/2D_j)^{\frac{1}{2}}x}{\frac{\omega}{2D_j}} \right\} \sin \left\{ \omega t - (\omega/2D_j)^{\frac{1}{2}}x - \frac{\pi}{4} \right\} \]  

This equation is valid only in the case where the thickness \( x \) of the diffusion layer is large in comparison with the depth of penetration.

The change in concentration \( \Delta c_j = c_j(0,t) - \overline{c_j} \) leads to a diffusion overvoltage \( \eta_d(t) \) whose value fluctuates sinusoidally with time. For a single substance, \( s_j \), one obtains for \( \Delta c_j \ll \overline{c_j} \)

\[ \eta_d = \frac{v_j}{nF} \frac{RT}{\ln \left\{ \frac{c_j}{\overline{c_j}} \right\}} = \frac{I RT v_j^2}{n^2 F^2 \overline{c_j} (D_j \omega)^{\frac{1}{2}}} \sin \left( \omega t - \frac{\pi}{4} \right) \]  

If more than one component is present in the overall electrode reaction, the total diffusion overvoltage at small amplitudes \( \eta_d \ll v_j RT/nF \) is

\[ \eta_d = \frac{I}{n^2 F^2} (\omega)^{-\frac{1}{2}} \sum_j \left( \frac{v_j}{\overline{c_j} (D_j)^{\frac{1}{2}}} \right)^2 \sin \left( \omega t - \frac{\pi}{4} \right) \]  

Thus, the diffusion overvoltage lags the current by a phase angle of \( \pi/4 = 45^\circ \). The direction of the phase shift corresponds to that of an equivalent RC circuit. The
amplitude of the overvoltage, \( \eta_{d,\text{max}} \) through the current
density maximum results in a diffusion impedance \( Z_{I,d} = \eta_{d,\text{max}}/I \) (also called the Warburg impedance) with the capac-
tance phase angle \( \phi = \pi/4 \). Then, \( Z_{I,d} \) is given by

\[
Z_{I,d} = \frac{RT}{n^2 F^2} (\omega)^{-\frac{1}{2}} \sum_j \frac{\nu_j^2}{C_j (D_j)^{\frac{1}{2}}} \tag{70}
\]

Accordingly, this diffusion impedance may be composed of an ohmic resistance, \( R_d \), and a diffusion capacitance, \( C_d \),
connected in series according to the equivalent circuit diagram shown below.

\[ \begin{array}{c}
\text{R}_d \\
\hline
\text{C}_d \\
\end{array} \]

However, since the alternating current overvoltage lags the
current by 45° in every case, then

\[
R_d = \frac{1}{\omega C_d} \tag{71}
\]

This relation must exist between the diffusion resistance
and the diffusion capacitance, since the impedance value of
the ohmic component must be equal to that of the capacitive
component in order to satisfy the 45° requirement.

From \( R_d \) and \( C_d \), the impedance of the equivalent circuit
diagram can be obtained.
\[ Z_{I,d} = \left( R_d^2 + \frac{1}{\omega^2 C_d^2} \right)^{\frac{1}{2}} = 2^{\frac{1}{2}} R_d = \frac{2^{\frac{1}{2}}}{\omega C_d} \]  

(72)

and the elements in the equivalent circuit diagram are

\[ R_d = \frac{RT}{n^2 F^2} \left( \frac{1}{(2\omega)^{\frac{1}{2}}} \sum_j \frac{v_j^2}{c_j (D_j)^{\frac{1}{2}}} \right) \]  

(73)

\[ C_d = \frac{n^2 F^2}{RT} \left( \frac{1}{(2\omega)^{\frac{1}{2}}} \sum_j \left( \frac{v_j^2}{c_j (D_j)^{\frac{1}{2}}} \right)^{-1} \right) \]  

(74)

The diffusion resistance is an inverse function of the square root of the angular frequency. The slope of the line passing through the origin depends upon the sum in equations (73) and (74) and thus on the concentration, \( c_j \), of the components of the overall electrode reaction and their diffusion coefficients, \( D_j \). For \( \omega \to \infty \) the diffusion resistance \( R_d \) tends toward zero, as does the total diffusion impedance, \( Z_{I,d} \).

**Reaction Overvoltage**

The reaction overvoltage, \( \eta_r \), is a phenomenon resulting from the existence of a slow (rate determining) chemical step in the overall electrode reaction. This reaction overvoltage is dominant when the other component steps of the overall reaction, such as charge transfer and diffusion of the substance, \( s_j \), are not rate determining. By definition, this chemical step is a reaction whose rate constant does not depend on the electrode potential.
If only reaction overvoltage occurs, the charge transfer equilibrium for the transfer of charge carriers through the double layer must be maintained during the flow of the current, even though an electrochemical reaction takes place in accordance with Faraday's law. The charge transfer equilibrium remains undisturbed during the flow of the current only when the exchange current density, \( i_0 \), is infinitely high. However, it is sufficient that the current density \( i \ll i_0 \), since in that case the deviation of the charge transfer equilibrium is negligibly small.

The rate determining chemical reaction may proceed homogeneously in a thin layer of liquid at the surface of the electrode, or, as in many cases, as a heterogeneous reaction in an adsorption layer at the surface. Both of these cases will be considered individually.

**Reaction overvoltage with a rate determining homogeneous reaction**

An alternating current causes a reaction overvoltage which fluctuates with an identical frequency. This reaction overvoltage, as in the case of diffusion rate control, has a phase shift with respect to the alternating current. The resistance resulting from the current and the overvoltage is an impedance. This "reaction impedance" consists of an ohmic component, \( R_r \), and a capacitive component, \( C_r \), which determine the magnitude of the phase shift. The phase shift is not constant, as in the case of the diffusion overvoltage, but is a function of the frequency and the rate of the
chemical reaction. Therefore, the relationships are more complicated than with alternating current diffusion over-voltage.

For the derivation, Fick's second law in the form

\[
\frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2} + \nu \tag{75}
\]

is applied for the change with time, \( t \), and distance, \( x \), of concentration \( c \) at the electrode surface. For the formulation of the homogeneous reaction rate, \( \nu \), the relation (55)

\[
\nu = \nu_0 \left\{ 1 - \left( \frac{c}{\bar{c}} \right)^p \right\} \tag{76}
\]

with reaction order \( p \) will be used. For the evaluation of the reaction impedance, only the current and overvoltage range in which a linear relationship exists between \( i \) and \( \eta \) is of interest. Thus, it is that range in which an undistorted purely sinusoidal time-function of the overvoltage results when a purely sinusoidal alternating current is used. This is true only for relatively small concentration changes. Then, because

\[
\left( \frac{c}{\bar{c}} \right)^p = (1 - \frac{c - \bar{c}}{\bar{c}})^p \approx 1 + p \frac{c - \bar{c}}{\bar{c}} \tag{77}
\]

the following is approximately valid:

\[
\nu = \frac{\nu_0}{\bar{c}} \Delta c = -k \Delta c \tag{78}
\]

where \( \Delta c = c - \bar{c} \), and \( k = \nu_0 \frac{p}{\bar{c}} \).
Substituting equation (78) for the reaction rate into equation (75) gives the partial differential equation

\[ \frac{\delta (\Delta c)}{\delta t} = D \frac{\delta^2 (\Delta c)}{\delta x^2} - k \Delta c \]  

(79)

for the concentration difference \( \Delta c(x,t) = c(x,t) - \bar{c} \).

An alternating current density \( i = I \sin \omega t \) of frequency, \( \omega/2\pi \), which satisfies the boundary condition

\[ \left\{ \frac{\delta (\Delta c)}{\delta x} \right\}_{x=0} = - \frac{\nu}{nF} I \sin \omega t \]  

(80)

on the basis of Faraday's law and Fick's first law, leads to the solution

\[ \Delta c = \{ \Delta c_\Omega \sin (\omega t - \frac{2\pi x}{\lambda}) - \Delta c_k \cos (\omega t - \frac{2\pi x}{\lambda}) \} \times \exp \left( - \frac{x}{x_\Omega} \right) \]  

(81)

of the differential equation (79). Equation (81) represents a damped concentration wave traveling into the electrolyte, which displays a phase shift with respect to the current density at the surface \( x = 0 \).

By partial differentiation of equation (81) with respect to \( x \) and \( t \), and by substitution into equations (79) and (80) the values of \( x_\Omega \), \( \lambda \), \( \Delta c_\Omega \) and \( \Delta c_k \) are obtained by coefficient comparison. For the damping factor, the following is obtained:

\[ x_\Omega = \{ (2D/\omega) \left( (1 + k^2/\omega^2)^{1/2} - (k/\omega) \right) \}^{1/2} \]  

(82)
and for the wavelength

$$\lambda = 2\pi \{(2D/\omega) \left[ (1 + k^2/\omega^2)^{1/2} + (k/\omega) \right] \}^{1/2} \quad (83)$$

For $k = 0$, i.e., without reaction, equations (82) and (83) become the corresponding equations (63) and (64) for pure diffusion.

The concentration oscillation at the surface $x = 0$ is constituted additively of two terms with a phase shift of $\pi/2$. The first term, with an amplitude $\Delta c_\Omega$, has the same phase as the current and leads to an ohmic component, $R_I$, of the alternating current reaction impedance, $Z_{I,r}$. The second term has a phase lag of $-\pi/2$ with respect to the current and likewise leads to a capacitive component $1/\omega C_I$ of $Z_{I,r}$.

The amplitudes $\Delta c_\Omega$ and $\Delta c_k$ are

$$\Delta c_\Omega = \frac{\nu I}{nF (2D\omega)^{1/2}} \left( \frac{k/\omega + \{1 + (k/\omega)^2\}^{1/2}}{1 + (k/\omega)^2} \right)^{1/2} \quad (84)$$

and

$$\Delta c_k = \frac{I}{nF (2D\omega)^{1/2}} \left( \frac{\{1 + (k/\omega)^2\}^{1/2} - k/\omega}{1 + (k/\omega)^2} \right)^{1/2} \quad (85)$$

with $\nu > 0$ or $\nu < 0$

The alternating current reaction overvoltage $\eta_r$ follows from the Nernst equation, using the concentration $c = \bar{c} + \Delta c$ for $\nu < 0$. The concentration difference $c$ is obtained from equation (81). Then
\[ \eta_r = \nu \frac{RT}{nF} \ln \frac{C}{c} = \nu \frac{RT}{nF} \frac{\Delta c}{c} \quad (86) \]

After substituting equation (81) into equation (85) the reaction overvoltage is obtained:

\[
\begin{align*}
\eta_r &= \frac{RT}{n^2 F^2} \frac{\nu^2}{C} \frac{1}{(2D)^\frac{1}{2}} \frac{1}{\omega^\frac{1}{2}} \left( \frac{\left(1 + \left(\frac{k}{\omega}\right)^2\right)^\frac{1}{2}}{1 + \left(\frac{k}{\omega}\right)^2} \right) I \sin \omega t - \frac{RT}{n^2 F^2} \frac{\nu^2}{C} \frac{1}{(2D)^\frac{1}{2}} \frac{1}{\omega^\frac{1}{2}} \\
&+ \left( \frac{\left(1 + \left(\frac{k}{\omega}\right)^2\right)^\frac{1}{2}}{1 + \left(\frac{k}{\omega}\right)^2} - \frac{k}{\omega} \right) I \cos \omega t \quad (87)
\end{align*}
\]

The alternating current reaction overvoltage \( \eta_r \) consists additively of an ohmic component \( \eta_{r,\Omega} \) and a capacitive component \( \eta_{r,k'} \), as already indicated. Both \( R_r \) and \( C_r \) are functions of frequency. The ohmic component of the reaction impedance \( Z_{r,r} \) is obtained from \( \eta_{r,\Omega}/i \) and the capacitive component \( 1/i \omega C_r \) from \( \eta_{r,k'/i} \cos \omega t \), i.e.,

\[
\begin{align*}
R_r &= \frac{RT}{n^2 F^2} \frac{\nu^2}{C} \frac{1}{(2D)^\frac{1}{2}} \frac{1}{\omega^\frac{1}{2}} \left( \frac{\left(1 + \left(\frac{k}{\omega}\right)^2\right)^\frac{1}{2}}{1 + \left(\frac{k}{\omega}\right)^2} + \frac{k}{\omega} \right) \quad (88) \\
C_r &= \frac{n^2 F^2}{RT} \frac{\nu^2}{C^2} \frac{1}{\omega^\frac{1}{2}} \left( 1 + \left(\frac{k}{\omega}\right)^2 \right)^\frac{1}{2} \left( \frac{1}{\left(1 + \left(\frac{k}{\omega}\right)^2\right)^\frac{1}{2}} - \frac{k}{\omega} \right) \quad (89)
\end{align*}
\]

Equations (88) and (89) correspond to equations (73) and (74) for diffusion impedance. Equations (88) and (89)
without the square root expression would be a diffusion impedance for a single substance, s. It is this expression (the square root) which takes into account the formation and depletion of s as a result of the rate determining step.

The magnitude of $R_r$ and $C_r$ depends not only on $\omega^{1/2}$, but also greatly on the ratio $k/\omega$. For $\omega << k$, the ohmic component tends toward a constant value. The capacitive component $1/\omega C_r$, on the other hand, approaches zero as $\omega \to \infty$. Figure 4 illustrates the dependence of the two components of the reaction impedance on $1/\omega^{1/2}$ in units of the limiting value $R_r$ as $\omega \to 0$. The abscissa is in units of $(k/\omega)^{1/2}$. The dashed line represents $R_r$ and $1/\omega C_r$ at very high frequencies $\omega >> k$ which corresponds to pure diffusion control.

**Reaction overvoltage with a rate determining heterogeneous reaction**

The complex reaction resistance $Z_{i,\nu}$ in the case of a rate determining heterogeneous reaction, displays a simpler behavior than that of the reaction impedance in the homogeneous reaction case. Here, though, the reaction always occurs on the surface, independent of current density, reaction rate, and frequency. Therefore, in the case of pure heterogeneous reaction overvoltage, diffusion processes in the electrolyte need not be considered.

The current amplitude $I$ of the alternating current $i = I \sin \omega t$ will be taken to be so small in the present case that there exists a linear relationship between $i$ and $\eta_r$. This condition is fulfilled as in the previous section when the
Resistance, \( R/R_\infty = 0 \)

Dependence of the ohmic component \( R_d \) and the capacitive component \( 1/\omega C_d \) of the complex reaction impedance \( z_\text{I} \) with frequency \( \omega \).

Figure 4.
relative change in surface concentration of the species \( s \) remains small. This means that \( \Delta c / \bar{c} = (c - \bar{c}) / \bar{c} \ll 1 \). This equation results in the following equation for the formation rate \( \nu \) (mole cm\(^{-2}\) s\(^{-1}\)) of \( s \),

\[
\nu = \left( \frac{\nu_o p}{c} \right) \Delta c = -k \Delta c
\]  

(78)

which is also valid in the case of a rate determining homogeneous reaction. Here \( \nu_o \) is the heterogeneous reaction exchange rate at equilibrium with the surface concentration \( \bar{c} \). The value \( p \) is the reaction order relative to \( s \) for the depletion of \( s \).

The surface concentration \( c \) determines the overvoltage \( \eta_r \) according to

\[
\eta_r = \nu \frac{RT}{nF} \ln \frac{c}{\bar{c}} = \nu \frac{RT}{nF} \frac{\Delta c}{\bar{c}}
\]  

(90)

In order to calculate the time dependence of the overvoltage, \( \Delta c \) must first be determined as a function of time, \( t \). In the zero current case \( d(\Delta c)/dt = \nu \). With current flow \( \frac{vi}{nF} \) (mole cm\(^{-2}\)) are formed of the species \( s \) in addition. The following differential equation can be written:

\[
\frac{d(\Delta c)}{dt} = \nu \frac{i}{nF} + \nu = \nu \frac{i}{nF} - k \Delta c
\]  

(91)

with \( i = I \sin \omega t \), the form of the differential equation which is to be integrated is

\[
\frac{d(\Delta c)}{dt} = \nu \frac{I}{nF} \sin \omega t - k \Delta c
\]  

(92)
which gives

$$\Delta c = \Delta c_\Omega \sin \omega t - \Delta c_k \cos \omega t$$  \hspace{1cm} (93)

with an ohmic ($\Delta c_\Omega$) and a capacitive ($\Delta c_k$) component.

Upon differentiation of equation (93) with respect to $t$, the following is obtained:

$$\omega \Delta c_k = \frac{\nu I}{nF} - k \Delta c_\Omega$$  \hspace{1cm} (94)

and

$$\omega \Delta c_\Omega = k \Delta c_k$$  \hspace{1cm} (95)

The amplitude of the ohmic and capacitive components of the surface concentration change follows:

$$\Delta c_\Omega = \frac{\nu I}{nF} \frac{k}{k^2 + \omega^2}$$  \hspace{1cm} (96)

$$\Delta c_k = \frac{\nu I}{nF} \frac{\omega}{k^2 + \omega^2}$$  \hspace{1cm} (97)

Substituting equation (96) into equation (93) and this once again into equation (90), yields the reaction overvoltage, $\eta_r$,

$$\eta_r = \eta_{r,\Omega} + \eta_{r,k} = \frac{\nu^2 RT}{n^2 F^2} \frac{I}{c} \frac{k}{k^2 + \omega^2} \sin \omega t$$

$$- \frac{\nu^2 RT}{n^2 F^2} \frac{I}{c} \frac{\omega}{k^2 + \omega^2} \cos \omega t$$  \hspace{1cm} (98)
The ohmic and the capacitive components of the reaction impedance connected in series are

\[
R_r = \frac{\nu^2 RT}{n^2 F^2} \frac{1}{ck} \frac{1}{1 + (\omega/k)^{\frac{1}{2}}} \tag{99}
\]

\[
\frac{1}{C_r} = \frac{\nu^2 RT}{n^2 F^2} \frac{1}{ck} \frac{\omega/k}{1 + (\omega/k)^{\frac{1}{2}}} \tag{100}
\]

Figure 5 shows the variation of the normalized reaction resistance with \(k/\omega\).

For low frequencies \(\omega \ll k\), \(R_r\) approaches a limiting value as in the homogeneous reaction case and \(1/\omega C_r\) decreases inversely with the frequency, and eventually becomes insignificant at extremely low frequency. For high frequency \(\omega \gg k\) both values approach zero. The reaction resistance proceeds to zero quadratically while \(1/\omega C_r\) varies linearly with \(1/\omega\). The reaction impedance \(Z_{I,r}\) is largely ohmic at low frequency and behaves like a capacitance at high frequencies. In contrast to reaction impedance with a rate determining homogeneous reaction, the phase shift can vary between 0° and 90°, whereas the variation for the heterogeneous case is between 0° and 45°.

**Crystallization Overvoltage**

With metal/metal ion electrodes, overvoltage is observed which is due not to transport and to reaction but also to crystallization. Crystallization overvoltage is caused by a hindrance in the inclusion or the release of the "ad-atoms", into and from, the ordered lattice of the solid metal electrode.
Figure 5: Dependence of Ohmic Component, $R_r$, and Capacitive Component, $1/\omega C_r$, on Reciprocal Frequency for a Rate Determining Heterogeneous Reaction.
The ad-atom state is the final state of the metal ion prior to going into solution during the anodic charge transfer reaction or the final state of the metal ion prior to incorporation into the lattice during the cathodic charge transfer reaction. Due to the nature of the charge transfer reactions chosen for this study, it is not possible by definition for crystallization overvoltage to occur and it will not be treated here.
CHAPTER III
EXPERIMENTAL

Experimental Design

Cell Design

The electrochemical cell used here is shown in Figure 6. It was constructed of Pyrex with the reference compartment separated from the main cell by a closed ground glass stopcock to prevent contamination of the test solution by chloride ions.

Electrode Design

A four electrode system was used consisting of a reference electrode, test electrode, polarizing electrode, and an auxiliary electrode.

The polarizing electrode was a platinum wire (1.0 mm in diameter) bent into a circle such that the test electrode was in the center and in the same horizontal plane as the polarizing electrode. This electrode was mounted on the side of the electrochemical cell using a glass tube which was sealed around the electrode just below the circular configuration. The auxiliary electrode was a platinum cylindrical gauze (Engelhard Industries) of approximately 500 cm² apparent surface area. It was suspended from the top of the electrochemical cell. Both of these electrodes were plated with gold from a thiosulfate bath prepared according
Figure 6: Schematic Diagram of Experimental Electrochemical Cell Composed of a Four Electrode System.

Electrodes:  
A Auxiliary  
B Polarizing  
C Test  
D Reference
to Zak (90). The plating solution contained 50 g/L citric acid, 10 g/L sodium tetraborate, and 20 g/L gold in the form of a thiosulfate complex. The pH of the plating solution was adjusted to 10 and the electrodeposition was carried out at room temperature using a gold wire anode. The auxiliary electrode was plated for two hours at a current of 50 mA and the polarizing electrode was plated for two hours at a current of 5 mA.

The test electrode is shown in Figure 7. It was a gold bead of 0.13 cm$^2$ apparent (geometric) area made by heating a 7.9 x 10$^{-3}$ cm diameter wire of fine gold (Engelhard Industries) in a hydrogen-air flame. The electrode was then inserted into a Teflon holder and connected to a spring which in turn was connected to a 0.016 cm diameter copper wire. This assembly was inserted into a 0.31 cm i.d. thick walled glass tube which was crimped at one end. The assembly was held firmly in place by securing the copper wire in a chuck at the top of the glass tube. To insure that there was no leaking of the solution into the electrode holder, the glass-Teflon junction was backed with a Kel-F wax seal (3M Company). The glass tube was inserted into a 1.5 cm i.d. glass sleeve fitted with a 24/40 ground glass joint which could be mounted in the top of the cell.

The test electrode was cleaned with warm chromic-sulfuric acid solution and rinsed thoroughly with triply distilled water. No further treatment of the electrode was found to be necessary since this treatment gave a smooth, bright, reproducible surface. The reference electrode was a saturated calomel electrode.
Figure 7: Schematic Diagram of the Gold Bead Test Electrode.
Solution Preparation

All solutions were prepared from triply distilled water. The water was initially distilled from alkaline permanganate and then twice distilled from a Heraeus-Schott quartz still.

Supporting electrolytes were 1.0 M perchloric acid, and 0.1 M and 1.0 M sulfuric acid. Perchloric acid solutions were made from Mallinckrodt analytical reagent grade 70% perchloric acid. Sulfuric acid solutions were made from Mallinckrodt ACS grade 98% sulfuric acid. All supporting electrolytes were further purified by electrolyzing between two gold electrodes. This was carried out in a two liter flask fitted with two gold wire electrodes 3.8 cm long, separated by 3.8 cm. The solutions were electrolyzed for 12 hours at a current of 10 mA (applied potential of 2.3 V), using a Beckman Electroscan 30 as power source. This procedure improved the reproducibility of the capacitance measurements. Further purification was not deemed necessary.

Ferric sulfate and ferrous sulfate stock solutions, 0.1 M each, were prepared from Fisher Scientific Company certified reagent ferric sulfate and ferrous sulfate, respectively. The stock solutions were standardized by amperometric titration (91) with two polarized platinum electrodes using a standard potassium dichromate solution. The concentration of ferrous ions in each stock solution was determined by titrating known aliquots, whereas the determination of ferric ions was performed by first passing known aliquots through a Jones reductor (92) and then titrating, yielding the total iron concentration in each solution. The test solutions were
prepared volumetrically from the stock solutions using de-aerated, electrolyzed 1.0 M sulfuric acid for dilution. The amount of ferrous ion in the ferric sulfate solution and of the ferric ion in the ferrous sulfate solution was taken into consideration. After all experiments were completed, the stock solutions were again standardized as described above. No appreciable change in concentration was observed.

Quinone and hydroquinone test solutions were prepared gravimetrically just prior to each experiment from Fisher Scientific Company purified grade quinone and J. T. Baker purified grade hydroquinone. It was determined that in 1 M sulfuric acid quinone rapidly reacted to form semiquinone making the use of stock solutions impossible.

R.S.A. Corporation 0.1 M benzo-(f)-quinoline stock solution was prepared gravimetrically without further purification. Recrystallized benzo-(f)-quinoline showed no difference in its fluorescence spectrum when compared to "as received" benzo-(f)-quinoline. Test solutions were made volumetrically from the stock solutions.

Experimental Technique

The electrochemical cell was purged of oxygen with a constant stream of helium (99.99%). The helium was initially passed through a glass fritted wash bottle containing electrolyzed supporting electrolyte to insure that it was saturated with water vapor before entering the electrochemical cell. Prior to making measurements, the helium was directed for at
least 30 minutes into the electrochemical cell through a glass frit located at the base of the cell. During measurements helium was passed over the test solution. The helium also exited the cell through a wash bottle, thus completely isolating the cell from the ambient air. All glass lines were made of Pyrex glass with Teflon swagelocks.

The electrochemical cell was cleaned daily with warm chromic-sulfuric acid and thoroughly rinsed with electrolyzed supporting electrolyte. The test solution was replaced at least three times a day with fresh solution. This procedure produced reproducible results indicating that more frequent cleaning was not necessary.

**Differential Capacitance**

To measure the total impedance of the cell, as a series or parallel combination of resistance and capacitance, the AC bridge method was used. The test and auxiliary electrodes formed one of the arms of the impedance bridge (General Radio 1608-A) (Figure 8). Measurements were made between 350 and 10,000 Hz (usually at five frequencies) using an external oscillator (General Radio 1310-A). The amplitude of the alternating current applied to the electrode was less than 5 mV RMS and was monitored with a Hewlett-Packard model 400 HR vacuum tube voltmeter. An external null detector (General Radio model 1232-A) was used for bridge balance. Since the test electrode was grounded, the bridge was operated in the floating mode. Polarization of the test electrode was
Figure 8. Block diagram of the AC bridge method setup.

**ELECTRODES**
A - Auxiliary  
B - Polarizing  
C - Test  
D - Reference
accomplished using a Sensitive Research Instrument Corp. potentiometer/voltmeter.

A 10 Henry choke was inserted in series with the potentiometer to keep A.C. current out of the D.C. polarizing circuit. Potentials were measured versus the saturated calomel electrode (SCE) using a Keithley Instruments 610 BR electrometer ($10^{14}$ ohm input impedance). At times, the bridge could not be balanced due to the impedance of the cell being larger than the equivalent impedance in the corresponding bridge arm. In cases such as this, a decade resistor (General Radio 1432-J) was used in series with the internal resistor of the bridge. This only occurred at low frequencies.

Capacitance measurements were made at 17 different potentials between -0.20 V and 1.40 V versus SCE. The test solution was potentiostated at -0.20 V and deaerated for one-half hour. Measurements were taken every ten minutes (20 minutes for high concentrations of benzo-(f)-quinoline) at 100 mV intervals in quiescent solutions and were made in the anodic direction only. At the end of each run, the solution was replaced with fresh solution and the procedure repeated.

Faradaic Impedance

The total impedance of the test electrode in the presence of the electroactive species at various concentrations was measured between 20 and 800 Hz. The same experimental configuration was used as shown in Figure 8 except that the potentiometer/voltmeter (Sensitive Research Instruments) was removed from the circuit since all of the measurements were
made at the equilibrium potential as determined by the relative amounts of the oxidized and reduced species in solution.

Prior to faradaic impedance measurements, the differential capacity as a function of applied potential was measured using supporting electrolyte solution. These measurements were made to just below the expected equilibrium potential for the electrochemically active test solution. The supporting electrolyte solution was then replaced by the electrochemically active test solution. The test solutions were stirred for 15 minutes prior to the taking of any impedance measurements. Measurements of the equilibrium potential were made using a Keithley 610 BR electrometer.

D.C. Polarization

For these measurements, the experimental configuration shown in Figure 9 was used and the auxiliary electrode was removed from the electrochemical cell. The desired potential was maintained using a Wenking 61TRS potentiostat. Potentials could be set to 0.1 mV using a Keithley 660 guarded differential voltmeter. The resulting current was determined by placing a standard resistor (±0.1%) across the recorder output of the potentiostat and measuring the potential drop across it with a Keithley 602 electrometer. The solutions were stirred to minimize diffusion impedance. Measurements were made by lowering the potential to about 10 mV below $E_e$ as estimated by the Nernst equation and the current was measured at 2.5 mV intervals over a range of 20 mV through $E_e$. The apparent exchange current was then calculated from the slope of the potential-current curve.
Figure 9. Block diagram of the setup for DC polarization measurements.
CHAPTER IV
RESULTS AND DISCUSSION

Introduction

It is well known that the differential capacitance of a metal solution interface is frequency dependent (93,94). In all cases studied here the capacitance was found to vary linearly with the inverse square root of the angular frequency. This being the case, all differential capacities presented are those which have been extrapolated to infinite frequency using a least squares fit of the experimental data. A typical plot is shown in Figure 10. The reproducibility of the differential capacity was always better than ±10% and generally improved as the concentration of benzo-(f)-quinoline increased.

The structure of benzo-(f)-quinoline is shown below.

![Structure of Benzo-(f)-Quinoline]

The base dissociation constant in aqueous solution for benzo-(f)-quinoline is $7.76 \times 10^{-6}$ (95) comparable to the basicity of ammonia. Hence in acidic solutions this compound will be protonated forming the quinoline cation.
Figure 10: Differential Capacitance in 1.0 M HClO₄. (E = 0.30 V versus SCE).
Adsorption of Benzo-(f)-quinoline in 1 M Perchloric Acid Solutions

Differential capacity versus potential data obtained in 1.0 M perchloric acid with various concentrations of benzo-(f)-quinoline are shown in Figure 11. The 1.0 M HClO₄ curve is characterized by having a broad peak centered around +0.5 V followed by a sharp depression in the capacitance at +1.1 V which then rises quickly due to oxygen adsorption. The capacity-potential curve is similar in magnitude and slope to that determined by Schmid and Hackerman (96) although their broad maximum occurs at more cathodic potentials than was found here. Also, their minimum is higher in magnitude than that determined here but does occur at the same potential. The work of Laitinen and Chao (97) and Bonewitz (98) show the capacitance to be larger by a factor of 2 to 3 over the potential range covered, although the general shape of the curve was similar.

Upon the addition of small quantities of benzo-(f)-quinoline suppression of the capacitance curve occurs indicating the adsorption of benzo-(f)-quinoline. It is seen that for 1.32 x 10⁻⁶ M benzo-(f)-quinoline, the peak is still centered at 0.5 V but the cathodic side of the capacitance curve is suppressed to a greater extent than the anodic side of the curve. This is further exemplified by the data for 1.97 x 10⁻⁶ M benzo-(f)-quinoline where the curve is essentially flat in the potential range from -0.2 V to +0.40 V and then rises to form a maximum centered at +0.7 V. This might indicate that at cathodic potentials, the electron cloud of
Figure 11: Differential Capacitance versus Potential in 1.0 M HClO₄ with Various Concentrations of Benzo-(f)-quinoline.

Curve A: 1.0 M HClO₄
Curve B: 1.0 M HClO₄ plus 1.3 x 10⁻⁶ M Benzo-(f)-quinoline
Curve C: 1.0 M HClO₄ plus 2.0 x 10⁻⁶ M Benzo-(f)-quinoline
Curve D: 1.0 M HClO₄ plus 4.0 x 10⁻⁶ M Benzo-(f)-quinoline
Curve E: 1.0 M HClO₄ plus 1.3 x 10⁻⁵ M Benzo-(f)-quinoline
Curve F: 1.0 M HClO₄ plus 5.3 x 10⁻⁵ M Benzo-(f)-quinoline
Curve G: 1.0 M HClO₄ plus 2.6 x 10⁻⁴ M Benzo-(f)-quinoline
the benzo-(f)-quinoline interacts with the d-band of the
gold electrode producing an attraction. As the potential
is raised this attraction is countered by the repulsive
interaction occurring between the positive electrode and
the positive charge on the benzo-(f)-quinoline making desorp-
tion likely. In 4 x 10^{-6} M benzo-(f)-quinoline, the peak
is very much less noticeable at +0.7 V with a substantial
decrease in capacitance occurring up to +1.2 V. Subsequent
concentration increases yield curves which decrease through-
out the potential range until +1.1 V.

The highest concentration used for this study was 2.6
x 10^{-4} M benzo-(f)-quinoline since at higher concentrations
precipitation of benzo-(f)-quinolinium perchlorate occurred.
Since concentrations larger than this could not be obtained,
it is not known if subsequent reductions in the capacitance-
potential curve would occur. It is for this reason that 1 M
HClO_4 was not chosen for kinetic work.

If it is assumed that near full coverage is reached at
the solubility limit then the fractional coverages can be
calculated according to equation (30). These are shown in
Figure 12 for the concentrations indicated between 0.0 V and
1.0 V. It is seen that for the three lowest concentrations,
the fractional coverage starts from zero and increases to a
maximum at around +0.2 V and then gradually decreases as the
potential is increased. The two largest concentrations show
a similar behavior except that the fractional coverage at
0.0 V is 1.0 and decreases steadily as the potential increases.
Figure 12: Fractional Coverage versus Potential in 1.0 M HClO₄ with Various Concentrations of Benzo-(f)-quinoline.

Curve B: 1.0 M HClO₄ plus 1.3 x 10⁻⁶ M Benzo-(f)-quinoline
Curve C: 1.0 M HClO₄ plus 2.0 x 10⁻⁶ M Benzo-(f)-quinoline
Curve D: 1.0 M HClO₄ plus 4.0 x 10⁻⁶ M Benzo-(f)-quinoline
Curve E: 1.0 M HClO₄ plus 1.3 x 10⁻⁵ M Benzo-(f)-quinoline
Curve F: 1.0 M HClO₄ plus 5.3 x 10⁻⁵ M Benzo-(f)-quinoline
Potential, (Volts versus SCE)
For all five concentrations, there is a maximum in the fractional coverage-potential curve at about +0.9 V.

At constant potential, the variation of fractional coverage with concentration can be described by an adsorption isotherm. It was determined using a least squares linear regression program that the data fit the Langmuir isotherm between 0.2 V and 0.9 V, with an average correlation coefficient of 0.991. These results are shown in Table 1. The adsorption equilibrium constant, B, remained essentially constant over the potential range studied but did show a slight tendency to decrease. This decrease may be expected since as the potential is increased, the electrostatic interaction between the electrode and the benzo-(f)-quinoline cation will become more repulsive in nature, making the adsorption process a less favored reaction. The adsorption equilibrium constant was found to be 6.83 x 10^5 at +0.2 V and 1.36 x 10^5 at +0.9 V, which represent the maximum and minimum values, respectively. The standard free energy of adsorption was found to be -33.3 kJ/mole at +0.2 V and -29.3 kJ/mole at +0.9 V.

**Adsorption of Benzo-(f)-quinoline in 1 M Sulfuric Acid Solutions**

Differential capacitance versus potential data obtained in 1 M H_2SO_4 with various concentrations of benzo-(f)-quinoline are shown in Figure 13. The 1 M H_2SO_4 curve is characterized by an ever increasing capacitance up to +0.6 V where a small maximum occurs followed by a slight decrease in capacitance.
Table 1. Calculated values of $B$, the equilibrium constant, and $\Delta G_{ads}^0$, the standard free energy of adsorption using the Langmuir isotherm

<table>
<thead>
<tr>
<th>$E$ (V)</th>
<th>$B \times 10^{-5}$</th>
<th>$\Delta G_{ads}^0$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>6.83</td>
<td>-33.3</td>
</tr>
<tr>
<td>0.3</td>
<td>3.97</td>
<td>-31.9</td>
</tr>
<tr>
<td>0.4</td>
<td>3.59</td>
<td>-31.7</td>
</tr>
<tr>
<td>0.5</td>
<td>3.11</td>
<td>-31.3</td>
</tr>
<tr>
<td>0.6</td>
<td>2.47</td>
<td>-30.8</td>
</tr>
<tr>
<td>0.7</td>
<td>2.24</td>
<td>-30.5</td>
</tr>
<tr>
<td>0.8</td>
<td>2.56</td>
<td>-30.9</td>
</tr>
<tr>
<td>0.9</td>
<td>1.36</td>
<td>-29.3</td>
</tr>
</tbody>
</table>
Figure 13: Differential Capacitance versus Potential in 1.0 M H₂SO₄ with Various Concentrations of Benzo-(f)-quinoline.

Curve A: 1.0 M H₂SO₄
Curve B: 1.0 M H₂SO₄ plus 1.0 x 10⁻⁵ M Benzo-(f)-quinoline
Curve C: 1.0 M H₂SO₄ plus 1.0 x 10⁻⁴ M Benzo-(f)-quinoline
Curve D: 1.0 M H₂SO₄ plus 1.0 x 10⁻³ M Benzo-(f)-quinoline
Curve E: 1.0 M H₂SO₄ plus 1.0 x 10⁻² M Benzo-(f)-quinoline
Curve F: 1.0 M H₂SO₄ plus 1.0 x 10⁻¹ M Benzo-(f)-quinoline
up to +1.0 V. At this point a rapid decrease in capacitance occurs indicating the adsorption of water as was seen in the case of 1 M HClO₄. For an equivalent electrode surface area, the capacitance for 1 M H₂SO₄ is about two times greater than that for 1 M HClO₄ indicating a greater amount of adsorption in 1 M H₂SO₄ than in 1 M HClO₄. The capacitances at +1.3 V and +1.4 V are nearly equal in both cases indicating that the principal effect is due to adsorption of water and is not a function of the supporting electrolyte.

Upon the addition of benzo-(f)-quinoline to the sulfuric acid solution, a substantial reduction in the differential capacitance is seen for each concentration until a 0.1 M benzo-(f)-quinoline a virtually flat capacitance-potential curve is obtained between +0.2 V and +1.2 V. At concentrations of benzo-(f)-quinoline greater than 1.0 x 10⁻⁵ M it is seen that even at +1.4 V the capacitance does not attain the same magnitude as that found in 1 M H₂SO₄ indicating that the adsorption of water is hindered by the presence of the benzo-(f)-quinoline.

The fractional coverage for each concentration studied of benzo-(f)-quinoline between -0.2 V and +1.0 V was calculated and is shown in Figure 14. The data taken in 0.1 M benzo-(f)-quinoline were assumed to represent full coverage. This is probably a very good assumption since the capacitance data for 0.01 M and 0.1 M benzo-(f)-quinoline did superimpose for the potentials between 0.6 V and 1.0 V and were very similar over the remainder of the potential region covered. Each of the
Figure 14: Fractional Coverage versus Potential in 1.0 M H₂SO₄ with Various Concentrations of Benzo-(f)-quinoline.

Curve B: 1.0 M H₂SO₄ plus 1.0 x 10⁻⁵ M Benzo-(f)-quinoline
Curve C: 1.0 M H₂SO₄ plus 1.0 x 10⁻⁴ M Benzo-(f)-quinoline
Curve D: 1.0 M H₂SO₄ plus 1.0 x 10⁻³ M Benzo-(f)-quinoline
Curve E: 1.0 M H₂SO₄ plus 1.0 x 10⁻² M Benzo-(f)-quinoline
fractional coverage curves show a small minimum centered at +0.1 V. Only the \(10^{-5}\) M benzo-(f)-quinoline curve shows a decreasing fractional coverage with increasing potential. The remaining three higher concentrations increase with increasing potential which is not in agreement with the fractional coverage-potential curves found in 1 M HClO₄, in which all curves tended to decrease with increasing potential after an initial maximum.

It was determined that the fractional coverage-concentration curves could be fitted to the Frumkin isotherm (78) and the isotherm with virial coefficients (76) between -0.2 V and +0.5 V. The results are shown in Table 2. Both isotherms have an arbitrary constant, a, which represents the two-dimensional interaction between the adsorbed particles. In all cases, the constant is less than zero, indicating a repulsion between adsorbed molecules. Both isotherms show the same variation in the parameters a and B with a maximum occurring at +0.1 V which is then followed by values becoming more positive with increasing potentials. The average value for a determined from the Frumkin isotherm is -3.70 and that for the isotherm with virial coefficients is -5.34. The value of B, the adsorption equilibrium constant, shows much more variability in the case of the Frumkin isotherm than the isotherm with virial coefficients. In the latter case, B is essentially constant over the potential range having an average value of \((1.35 \pm 0.38) \times 10^6\). This gives an average free energy of adsorption of -35.0 kJ/mole. In the case of
Table 2. Calculated values of $a$, $B$, and $\Delta G^o_{\text{ads}}$ for the Frumkin isotherm and the isotherm with virial coefficients.

<table>
<thead>
<tr>
<th>$E$ (V)</th>
<th>$a$</th>
<th>$B \times 10^{-5}$</th>
<th>$\Delta G^o_{\text{ads}}$ (kJ/mole)</th>
<th>$a$</th>
<th>$B \times 10^{-6}$</th>
<th>$\Delta G^o_{\text{ads}}$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.2</td>
<td>-3.51</td>
<td>4.08</td>
<td>-32.0</td>
<td>-5.12</td>
<td>0.927</td>
<td>-34.0</td>
</tr>
<tr>
<td>-0.1</td>
<td>-3.95</td>
<td>6.61</td>
<td>-33.2</td>
<td>-5.51</td>
<td>1.44</td>
<td>-35.1</td>
</tr>
<tr>
<td>0.0</td>
<td>-4.42</td>
<td>8.39</td>
<td>-33.8</td>
<td>-5.82</td>
<td>1.56</td>
<td>-35.3</td>
</tr>
<tr>
<td>0.1</td>
<td>-4.58</td>
<td>9.03</td>
<td>-34.0</td>
<td>-5.97</td>
<td>1.67</td>
<td>-35.5</td>
</tr>
<tr>
<td>0.2</td>
<td>-3.91</td>
<td>4.28</td>
<td>-32.1</td>
<td>-5.36</td>
<td>0.824</td>
<td>-33.7</td>
</tr>
<tr>
<td>0.3</td>
<td>-3.66</td>
<td>5.88</td>
<td>-32.9</td>
<td>-5.39</td>
<td>1.52</td>
<td>-35.3</td>
</tr>
<tr>
<td>0.4</td>
<td>-3.19</td>
<td>6.22</td>
<td>-33.1</td>
<td>-5.02</td>
<td>1.82</td>
<td>-35.7</td>
</tr>
<tr>
<td>0.5</td>
<td>-2.36</td>
<td>2.60</td>
<td>-30.9</td>
<td>-4.55</td>
<td>1.02</td>
<td>-34.3</td>
</tr>
</tbody>
</table>

Frumkin isotherm: $Bc = \frac{\theta}{1-\theta} \exp (-2a\theta)$

Isotherm with virial coefficients: $Bc = \theta \exp (-2a\theta)$
the Frumkin isotherm, the average value of $B$ was determined to be $(5.89 \pm 2.2) \times 10^5$ which gives a free energy of adsorption of -32.9 kJ/mole.

Comparison of the adsorption data for benzo-(f)-quinoline on gold in the two electrolytes shows that the equilibrium adsorption constant, $B$, and hence the standard free energy of adsorption are essentially the same. In 1 M HClO$_4$ the adsorption fits the Langmuir isotherm indicating that lateral interactions between the molecules are not important and that a uniform surface exists, these being inherent assumptions in the derivation. An alternate explanation would be that complete coverage was not attained at the solubility limit of benzo-(f)-quinolium perchlorate. If this were the case, the data could follow the Langmuir isotherm at low coverages with substantial deviations at higher coverages going undetected due to the inability of making measurements at these coverages.

In the case of adsorption in 1 M H$_2$SO$_4$, a different phenomenon is observed. The experimental data could only be fitted to an isotherm containing a term which accounts for lateral interaction between adsorbed molecules. This interaction term was found to be negative and constant over the potential range studied indicating the nature of the adsorption process did not change with potential. The repulsive interaction between adsorbed molecules is to be expected since they will be positively charged in acid solutions.
Electrochemical Kinetics of the Quinone-Hydroquinone System in 1 M H₂SO₄

The electrochemical kinetics of the quinone-hydroquinone system have been determined from current density measurements at low applied overvoltages. These measurements were made at varying concentrations of one of the components while the concentration of the other component was held constant. Either the concentration of quinone was varied while the concentration of hydroquinone was held constant or the concentration of hydroquinone was varied while the concentration of quinone was held constant. Two plots of the current density versus overpotential are shown in Figure 15. These plots are typical for all of the concentrations of quinone and hydroquinone studied. A least squares analysis of these data was carried out resulting in the best fit for the straight line. From this analysis an average correlation coefficient of 0.9959 was calculated indicating a very good fit between overvoltage and current density. From the slope of these straight lines the apparent exchange current density was calculated using the low-overvoltage approximation (see equation (53)) (99). These results are shown in Table 3 along with the experimentally determined equilibrium potential.

The charge transfer coefficient, α, and the standard rate constant, k°, were determined by rearranging equations (48) and (49) and noting that at \(E = E_e\) (the equilibrium potential), \(\dot{i} = \dot{i} = i_o\). This results in the following expressions:
Figure 15: Typical Plots of Current Density versus Overpotential for the Quinone-Hydroquinone Electrochemical System in 1.0 M H$_2$SO$_4$.

\[ \Delta : \ 7.47 \times 10^{-4} \text{ M quinone plus } 9.79 \times 10^{-4} \text{ M hydroquinone} \]

\[ \bigcirc : \ 7.47 \times 10^{-4} \text{ M quinone plus } 2.40 \times 10^{-4} \text{ M hydroquinone} \]
$i \times 10^6 \ (A \ cm^{-2})$

$\eta \ (mV)$
### Table 3. Exchange Current Densities, $i_a$, and Equilibrium Potentials at Various Quinone and Hydroquinone Concentrations in 1.0 M $\text{H}_2\text{SO}_4$.

<table>
<thead>
<tr>
<th>Solution</th>
<th>$i_a \times 10^6$ (A cm$^{-2}$)</th>
<th>$E_e$ (V vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.81 \times 10^{-4}$ M Q</td>
<td>182</td>
<td>0.6759</td>
</tr>
<tr>
<td>$5.18 \times 10^{-4}$ M Q</td>
<td>222</td>
<td>0.6893</td>
</tr>
<tr>
<td>$1.11 \times 10^{-4}$ M Q</td>
<td>309</td>
<td>0.6935</td>
</tr>
<tr>
<td>$1.68 \times 10^{-4}$ M Q</td>
<td>409</td>
<td>0.6981</td>
</tr>
</tbody>
</table>

Hydroquinone concentration = constant = $7.55 \times 10^{-4}$ M

<table>
<thead>
<tr>
<th>Solution</th>
<th>$i_a \times 10^6$ (A cm$^{-2}$)</th>
<th>$E_e$ (V vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.40 \times 10^{-4}$ M $\text{H}_2\text{Q}$</td>
<td>195</td>
<td>0.7024</td>
</tr>
<tr>
<td>$4.70 \times 10^{-4}$ M $\text{H}_2\text{Q}$</td>
<td>266</td>
<td>0.6948</td>
</tr>
<tr>
<td>$9.79 \times 10^{-4}$ M $\text{H}_2\text{Q}$</td>
<td>345</td>
<td>0.6854</td>
</tr>
<tr>
<td>$2.01 \times 10^{-3}$ M $\text{H}_2\text{Q}$</td>
<td>472</td>
<td>0.6767</td>
</tr>
</tbody>
</table>

Quinone concentration = constant = $7.47 \times 10^{-4}$ M
\[
\ln \left( \frac{i_o}{c_Q} \right) = -\alpha nF_e/RT + \ln nF^0_k_a \quad (101)
\]

\[
\ln \left( \frac{i_o}{c_{H_2Q}} \right) = (1 - \alpha) nF_e/RT + \ln nF^0_k_a \quad (102)
\]

From these equations it is seen that the plots of \( \ln \left( \frac{i_o}{c_Q} \right) \) or \( \ln \left( \frac{i_o}{c_{H_2Q}} \right) \) versus \( E_e \) should yield straight lines from which the charge transfer coefficient can be determined from the slopes and the standard rate constant from the intersection of the two lines. At this point of intersection, \( \ln \left( \frac{i_o}{c_Q} \right) = \ln \left( \frac{i_o}{c_{H_2Q}} \right) \), and this specifies the formal potential, \( E^0_F \), which is defined as the equilibrium potential where the concentration of quinone and hydroquinone are equal. This potential is not equivalent to the standard potential, \( E^0 \), because the concentration of the two species is not necessarily at unit activity. The formal potential also reflects the unique experimental conditions in this work.

The plot for the determination of the standard rate constant, the formal potential and the charge transfer coefficient is shown in Figure 16. From this plot the standard rate constant was found to be equal to \( 1.98 \times 10^{-3} \) cm s\(^{-1}\) with a formal potential of 0.6870 V. The charge transfer coefficient for the variation of the quinone concentration was found to be 0.57. The charge transfer coefficient for the variation of the hydroquinone concentration was found to be 0.38.

As a consistency check, the formal potential can also be determined from the concentration-potential data for
Figure 16: Plot of $\ln \left( \frac{i_0}{c_Q} \right)$ and $\ln \left( \frac{i_0}{c_{H_2Q}} \right)$ versus $E_e$ for the Variation of the Concentration of Quinone, $\bigcirc$, with constant Hydroquinone Concentration, and for the Variation of the Concentration of Hydroquinone, $\bigtriangleup$, with constant Quinone Concentration in 1.0 M Sulfuric Acid.
both the variation of the quinone and the variation of the hydroquinone concentration. This plot is shown in Figure 17. The formal potential for the variation of the quinone concentration was found to be 0.6885 and for the variation of the hydroquinone concentration the formal potential was found to be 0.6888 V. These values are in good agreement with 0.6879 V determined above.

The values determined for the charge transfer coefficient are different for the variation of the quinone concentration and for the variation of the hydroquinone concentration indicating that the oxidation of hydroquinone and the reduction of quinone proceed as two one electron steps and not as a concerted two electron transfer. This result is not unexpected and has been observed by other investigators as is discussed below.

Vetter (55,86) has studied the quinone-hydroquinone system using overvoltage techniques to determine the anodic and cathodic Tafel lines and found that these lead to different exchange current densities and charge transfer coefficients. Quinone and hydroquinone, $1 \times 10^{-3}$ M each, were used with 1 M HCl as supporting electrolyte on platinum electrodes. Vetter determined the charge transfer coefficient for the reduction of quinone to be 0.54 and for the oxidation of hydroquinone to be 0.46. These values compare favorably with those determined in this work. Based upon his experiments, Vetter (55) proposed the following mechanism for the electrochemical behavior of the quinone-hydroquinone system in acid solution:
Figure 17: Determination of the Formal Potential, $E_p^0$, for the Quinone/Hydroquinone System in 1.0 M \( H_2SO_4 \).

\( \odot \): Variation of the Concentration of Quinone

\( \Delta \): Variation of the Concentration of Hydroquinone
In $C_Q$ or $C_{H_2O}$ against $E_{e'}$ (Volts)
This mechanism indicates that the quinone-hydroquinone system consists of two one-electron steps where the rate determining step for the reductive charge transfer reaction is reaction (4) and for the oxidative charge transfer reaction is reaction (2) listed above. This work supports the conclusion that the oxidation and reduction of the quinone-hydroquinone system occurs as a two step reaction.

K. G. Everett et al. (100) have studied the quinone-hydroquinone system in 1.0 M HClO₄ on rhodium electrodes and found the charge transfer coefficient to be 0.61 with the standard rate constant equal to $2.42 \times 10^{-4}$ cm s$^{-1}$. Very good agreement is found for the charge transfer coefficient but almost an order of magnitude difference is found when standard rate constants are compared.

Hale and Parsons (101) have studied this reaction at a dropping mercury electrode in 1 M NH₄NO₃ solutions buffered at pH 3.9. They find the charge transfer coefficient to be equal to 0.58 and the standard rate constant equal to $1.41 \times 10^{-3}$ cm s$^{-1}$ in good agreement to those values determined here. They also report that the cathodic reaction is probably composed of two one-electrode steps, supporting Vetter's (55) conclusion.
Electrochemical Kinetics of the Quinone-Hydroquinone System in 1.0 M H_2SO_4 with Benzo-((f))-quinoline

The results for the variation of the concentration of quinone at constant hydroquinone concentration in the presence of benzo-((f))-quinoline are summarized in Table 4. The results for the variation of the hydroquinone concentration at constant quinone concentration in the presence of benzo-((f))-quinoline are shown in Table 5. From Tables 4 and 5 the values of ln (i_0/c_Q) and ln (i_0/c_H2Q) have been calculated and are plotted in Figures 18-20 versus E_e for the determination of the charge transfer coefficients, the standard rate constant, and the formal potential. These results are presented in Table 6 together with the 1.0 M H_2SO_4 data. It is seen that the charge transfer coefficient is essentially constant with an exception at 1.0 x 10^{-3} M benzo-((f))-quinoline for the variation of the quinone concentration. It is felt that the decrease in \( \alpha \) at this latter concentration does not represent a change in mechanism but rather results from the limited data available. The average value of the charge transfer coefficient for the variation of the quinone concentration was found to be 0.54 ± 0.09, and for the variation of the hydroquinone concentration the charge transfer coefficient was found to be 0.44 ± 0.05. The formal potential was found to be independent of the concentration of benzo-((f))-quinoline indicating that its presence does not affect the quinone-hydroquinone reaction mechanism. The average value of the formal potential was found to be 0.6877 ± 0.0017 V. The standard rate constant
Table 4. Exchange Current Density, $i^a$, versus Fractional Coverage for the Quinone-Hydroquinone System in 1.0 M H$_2$SO$_4$ with Various Coverages, $\Theta$, of Benzo-(f)-quinoline.

Hydroquinone concentration = constant = 7.5 x 10$^{-4}$ M

<table>
<thead>
<tr>
<th>Solution moles/liter</th>
<th>$E_E$ V vs. NHE</th>
<th>$\Theta$</th>
<th>$i^a \times 10^6$ A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.81 x 10$^{-4}$</td>
<td>0.6759</td>
<td>0</td>
<td>182</td>
</tr>
<tr>
<td>2.71 x 10$^{-4}$</td>
<td>0.6762</td>
<td>0.05</td>
<td>133</td>
</tr>
<tr>
<td>2.50 x 10$^{-4}$</td>
<td>0.6758</td>
<td>0.20</td>
<td>73.2</td>
</tr>
<tr>
<td>2.53 x 10$^{-4}$</td>
<td>0.6769</td>
<td>0.40</td>
<td>22.3</td>
</tr>
<tr>
<td>5.18 x 10$^{-4}$</td>
<td>0.6839</td>
<td>0</td>
<td>222</td>
</tr>
<tr>
<td>5.14 x 10$^{-4}$</td>
<td>0.6838</td>
<td>0.05</td>
<td>201</td>
</tr>
<tr>
<td>5.03 x 10$^{-4}$</td>
<td>0.6837</td>
<td>0.20</td>
<td>113</td>
</tr>
<tr>
<td>5.18 x 10$^{-4}$</td>
<td>0.6852</td>
<td>0.40</td>
<td>35.5</td>
</tr>
<tr>
<td>1.11 x 10$^{-3}$</td>
<td>0.6935</td>
<td>0</td>
<td>309</td>
</tr>
<tr>
<td>1.03 x 10$^{-3}$</td>
<td>0.6927</td>
<td>0.05</td>
<td>226</td>
</tr>
<tr>
<td>1.01 x 10$^{-3}$</td>
<td>0.6930</td>
<td>0.20</td>
<td>132</td>
</tr>
<tr>
<td>1.04 x 10$^{-3}$</td>
<td>0.6945</td>
<td>0.40</td>
<td>50.0</td>
</tr>
<tr>
<td>1.68 x 10$^{-3}$</td>
<td>0.6981</td>
<td>0</td>
<td>409</td>
</tr>
<tr>
<td>1.99 x 10$^{-3}$</td>
<td>0.7014</td>
<td>0.05</td>
<td>345</td>
</tr>
<tr>
<td>2.08 x 10$^{-3}$</td>
<td>0.7011</td>
<td>0.20</td>
<td>185</td>
</tr>
<tr>
<td>2.08 x 10$^{-3}$</td>
<td>0.7032</td>
<td>0.40</td>
<td>78.2</td>
</tr>
</tbody>
</table>
Table 5. Exchange Current Density, $i_0^a$, versus Fractional Coverage for the Quinone-Hydroquinone System in 1.0 M H$_2$SO$_4$ with Various Coverages, $\Theta$, of Benzo-(f)-quinoline.

Quinone concentration = constant = $7.5 \times 10^{-4}$ M

<table>
<thead>
<tr>
<th>Solution moles/liter</th>
<th>$E_e$ V vs. NHE</th>
<th>$\Theta$</th>
<th>$i_0^a \times 10^6$ A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.40 \times 10^{-4}$</td>
<td>0.7028</td>
<td>0</td>
<td>195</td>
</tr>
<tr>
<td>$2.47 \times 10^{-4}$</td>
<td>0.7021</td>
<td>0.05</td>
<td>163</td>
</tr>
<tr>
<td>$3.11 \times 10^{-4}$</td>
<td>0.7008</td>
<td>0.20</td>
<td>81.0</td>
</tr>
<tr>
<td>$2.34 \times 10^{-4}$</td>
<td>0.7052</td>
<td>0.40</td>
<td>30.0</td>
</tr>
<tr>
<td>$4.69 \times 10^{-4}$</td>
<td>0.6948</td>
<td>0</td>
<td>266</td>
</tr>
<tr>
<td>$5.01 \times 10^{-4}$</td>
<td>0.6947</td>
<td>0.05</td>
<td>229</td>
</tr>
<tr>
<td>$5.82 \times 10^{-4}$</td>
<td>0.6936</td>
<td>0.20</td>
<td>91.4</td>
</tr>
<tr>
<td>$4.75 \times 10^{-4}$</td>
<td>0.6970</td>
<td>0.40</td>
<td>45.5</td>
</tr>
<tr>
<td>$9.79 \times 10^{-4}$</td>
<td>0.6854</td>
<td>0</td>
<td>345</td>
</tr>
<tr>
<td>$1.01 \times 10^{-3}$</td>
<td>0.6854</td>
<td>0.05</td>
<td>339</td>
</tr>
<tr>
<td>$1.05 \times 10^{-3}$</td>
<td>0.6861</td>
<td>0.20</td>
<td>147</td>
</tr>
<tr>
<td>$1.02 \times 10^{-3}$</td>
<td>0.6872</td>
<td>0.40</td>
<td>58.6</td>
</tr>
<tr>
<td>$2.01 \times 10^{-3}$</td>
<td>0.6767</td>
<td>0</td>
<td>472</td>
</tr>
<tr>
<td>$2.01 \times 10^{-3}$</td>
<td>0.6772</td>
<td>0.05</td>
<td>438</td>
</tr>
<tr>
<td>$2.01 \times 10^{-3}$</td>
<td>0.6779</td>
<td>0.20</td>
<td>217</td>
</tr>
<tr>
<td>$2.05 \times 10^{-3}$</td>
<td>0.6780</td>
<td>0.40</td>
<td>79.4</td>
</tr>
</tbody>
</table>
Figure 18: Plot of $\ln \left( i_0/c_q \right)$ and $\ln \left( i_0/c_{H2Q} \right)$ versus $E_e$ for the Variation of the Concentration of Quinone, $\bigcirc$, with Constant Hydroquinone Concentration, and for the Variation of the Concentration of Hydroquinone, $\triangle$, with Constant Quinone Concentration in $1.0 \times 10^{-5}$ M Benzo-(f)-quinoline.
Figure 19: Plot of \( \ln \left( \frac{i_0}{c_Q} \right) \) and \( \ln \left( \frac{i_0}{c_{H_2Q}} \right) \) versus \( E_e \) for the Variation of the Concentration of Quinone, \( \Theta \), with Constant Hydroquinone Concentration, and for the Variation of the Concentration of Hydroquinone, \( \Delta \), with Constant Quinone Concentration in \( 1.0 \times 10^{-4} \) M Benzo-(f)-quinoline.
Figure 20: Plot of $\ln (i_0/c_Q)$ and $\ln (i_0/CH_2Q)$ versus $E_e$ for the Variation of the Concentration of Quinone, $\Theta$, with Constant Hydroquinone Concentration, and for the Variation of the Concentration of Hydroquinone, $\Delta$, with Constant Quinone Concentration in $1.0 \times 10^{-3}$ M Benzo-(f)-quinoline.
Table 6. Summary of Results: Charge Transfer Coefficient, Standard Rate Constant, and Formal Potential for the Quinone-Hydroquinone System.

<table>
<thead>
<tr>
<th>Concentration of benzo-(f)-quinoline in 1.0 M H₂SO₄</th>
<th>Θ</th>
<th>α_Q</th>
<th>α_H₂O</th>
<th>kₐ⁰ x 10³ cm/s</th>
<th>Eₑ V vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.57</td>
<td>0.38</td>
<td>1.98</td>
<td>0.6870</td>
</tr>
<tr>
<td>1.0 x 10⁻⁵ M</td>
<td>0.05</td>
<td>0.56</td>
<td>0.45</td>
<td>1.70</td>
<td>0.6858</td>
</tr>
<tr>
<td>1.0 x 10⁻⁴ M</td>
<td>0.20</td>
<td>0.62</td>
<td>0.50</td>
<td>0.815</td>
<td>0.6898</td>
</tr>
<tr>
<td>1.0 x 10⁻³ M</td>
<td>0.40</td>
<td>0.42</td>
<td>0.42</td>
<td>0.316</td>
<td>0.6881</td>
</tr>
</tbody>
</table>

\[ \bar{\alpha}_Q = 0.54 \pm 0.09 \]

\[ \bar{\alpha}_{H₂O} = 0.44 \pm 0.05 \]

\[ \bar{E}_F = 0.6877 \pm 0.0017 \text{ V} \]
is seen to decrease with increasing concentrations of benzo-(f)-quinoline. This effect is shown graphically in Figure 21.

In $1.0 \times 10^{-2}$ M benzo-(f)-quinoline ($\Theta = 0.75$) and in $1.0 \times 10^{-1}$ M benzo-(f)-quinoline ($\Theta = 1.0$), the experimentally determined values of the current density with applied over-voltage were not different from those determined in $1.0$ M $\text{H}_2\text{SO}_4$ with no electroactive species added. The overvoltage range was $\pm 10$ mV from the equilibrium potential. Over this range of potentials the background current density was approximately $3 \, \mu\text{A} \, \text{cm}^{-2}$. Hence the values of the charge transfer coefficient and the standard rate constant could not be determined for these two concentrations of benzo-(f)-quinoline.

Everett et al. (100) studied the quinone-hydroquinone system on rhodium in $1.0$ M $\text{HClO}_4$. The standard rate constant was determined at various coverages of oxygen and was found to decrease linearly up to $\Theta = 0.75$ and remain constant at higher coverages. This behavior was explained as being due to the geometric blocking model showing that the charge transfer reaction is much more rapid at free rhodium than at oxygen covered rhodium. The levelling off effect at fractional coverages above $\Theta = 0.75$ rather than at $\Theta > 1.0$ was suggested to be due to steric hindrance. This is to be expected if it is assumed that either quinone or hydroquinone lie flat on the free electrode surface in order to react.
Figure 21: Variation of the Standard Rate Constant with Fractional Coverage for the Quinone-Hydroquinone System.
A geometric blocking mechanism cannot explain the results observed here since it predicts linearity between the standard rate constant and the fractional coverage. A change in reaction mechanism does not seem likely to have caused the observed results since $\alpha$ is constant over the range of fractional coverage studied.

Due to the adsorption of the benzo-(f)-quinoline, the potential at the outer Helmholtz plane, $\phi_2$, will change as the concentration is varied. Parsons (36) first suggested that this change in potential needs to be taken into account when interpreting electrochemical kinetic data. The change in potential, $\Delta \phi_2$, can be calculated using equation (36):

$$\frac{k_\alpha^0}{k_a} = \exp\left\{-(Z + \alpha) \frac{F}{RT} \Delta \phi_2\right\}$$

where $k_\alpha^0$ is the standard rate constant at some fractional coverage $\Theta$. The charge of the oxidized or reduced species is $Z$. The results of these calculations are shown in Table 7.

If this mechanism is responsible for the observed decrease in the standard rate constant with increasing fractional coverage, the effect should be independent of the electrochemical reaction studied. With this in mind, a comparison of these results to those obtained for the Fe(III)/Fe(II) reaction discussed in the following section can be made.

In addition to the mechanisms discussed above for the observed inhibition behavior, changes in the surface layer
Table 7. Calculation of the Change in Potential at the Outer Helmholtz Plane ($\Delta \phi_2$) as a Function of Fractional Coverage.

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$\Delta \phi_2(Q)$ (mV)</th>
<th>$k_a^0 \times 10^3$ (cm/s)</th>
<th>$\Delta \phi_2(H_2O)$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
<td>1.98</td>
<td>-</td>
</tr>
<tr>
<td>0.05</td>
<td>7.7</td>
<td>1.70</td>
<td>9.5</td>
</tr>
<tr>
<td>0.20</td>
<td>41.0</td>
<td>0.815</td>
<td>50.4</td>
</tr>
<tr>
<td>0.40</td>
<td>87.6</td>
<td>0.316</td>
<td>107.5</td>
</tr>
</tbody>
</table>

structure need to be considered. As pointed out in the Introduction (Chapter I), one can expect a change in the interaction between electroactive species and the surface layer as solvent molecules are replaced by adsorbate molecules. This interaction will change the free energy of activation resulting in the inhibition or acceleration of the electrochemical reaction. Afanas'ev and Ternovskoi (46) and Avilova et al. (45) have suggested that in the presence of adsorbed molecules, the concentration of the electroactive species within the surface layer is determined by an additional free energy term associated with the transfer of electroactive molecules from the bulk of the solution into the structured surface layer. They suggested (46) the equation

$$k_a^\theta = k_a^0 \exp (-2a\gamma\theta)$$

where $a$ is a constant characterizing the interaction between
the adsorbate molecules and $\gamma$ is a constant describing the degree to which the surface layer is disturbed when an electroactive molecule is incorporated into the surface layer. Incorporation of the electroactive species is considered to be reversible, with the rate of the entire process being limited by the rate of the electron transfer step.

From the equation above it is seen that a plot of $\ln \left( \frac{k_a^{\theta}}{k_a^{O}} \right)$ versus $\theta$ should yield a straight line with a slope of $-2\alpha\gamma$. This plot for the experimental data is shown in Figure 22. The least squares fit for this line is

$$\ln \left( \frac{k_a^{\theta}}{k_a^{O}} \right) = -4.80 \theta + 0.09$$

It has already been determined (see Table 2) that the interaction between adsorbed benzo-(f)-quinoline molecules is repulsive in nature and essentially constant throughout the potentials studied. This will necessitate $\gamma$ to be negative and constant indicating that both the quinone and the hydroquinone molecules will have difficulty penetrating the surface layer in order for an electrochemical reaction to occur.

**Kinetics of the Fe(II)/Fe(III) System in 1.0 M H$_2$SO$_4$**

The Fe(II)/Fe(III) system was studied using the faradaic impedance technique described in Chapter III. The total impedance of the cell was measured as a function of the frequency while the concentrations of Fe(II) and Fe(III) were held constant. Thirteen frequency measurements between
Figure 22: Plot of $\ln \left( \frac{k_a^\Theta}{k_a^\circ} \right)$ versus $\Theta$ for the Quinone-Hydroquinone Electrochemical System.
20 and 800 Hz were made for each solution. The number of measurements in this frequency range was increased from five for differential capacitance since the variation in impedance with reciprocal angular frequency is expected to be linear if only faradaic and diffusion impedance occurs. Should homogeneous or heterogeneous chemical reactions play a significant role in the electrochemical reaction then non-linearity would be observed (see Chapter II).

Once the total impedance had been obtained, the solution resistance and the differential capacitance were subtracted using the method of Damaskin (102) leaving the series resistive and capacitive components of the reaction impedance. A typical plot of these two components is shown in Figure 23.

It is seen that the two components of the faradaic impedance are linear with the reciprocal angular frequency, and are nearly parallel. As was pointed out in Chapter II, the charge transfer resistance is not a function of frequency whereas when pure diffusion impedance is present, the resistive and capacitive components are equal at any given frequency \( R_d = \frac{1}{\omega C_d} \). With this in mind, it is obvious that \( R_r \) in Figure 23 is the summation of charge transfer and diffusion impedance and \( \frac{1}{\omega C_r} \) is due solely to diffusion impedance. The charge transfer resistance can then be determined by extrapolating the reaction resistance to infinite frequency, \( \frac{1}{\omega R} = 0 \), since the diffusion impedance goes to zero.

Figure 24 shows the reaction resistance for five different Fe(III) concentrations while the concentration of
Figure 23: Least Squares Plot of the Resistive and Capacitive Components of the Faradaic Impedance for $4.75 \times 10^{-3}$ M Fe(II) and $1.29 \times 10^{-2}$ M Fe(III) in 1.0 M Sulfuric Acid.
Figure 24: Plot of Reaction Resistance versus the Reciprocal of Angular Frequency for Five Fe(III) Solutions with the Concentration of Fe(II) Being Constant at 4.75 x 10^{-3} M.

Curve A: 1.25 x 10^{-3} M Fe(III)
Curve B: 2.01 x 10^{-3} M Fe(III)
Curve C: 3.57 x 10^{-3} M Fe(III)
Curve D: 6.66 x 10^{-3} M Fe(III)
Curve E: 1.29 x 10^{-2} M Fe(III)
Fe(II) remains constant. Figure 25 shows the reaction resistance for five Fe(II) concentrations while the concentration of Fe(III) is held constant. The respective capacitive components representing diffusion have been omitted from these graphs for the sake of clarity. It is seen that for all concentrations of Fe(II) and Fe(III) studied, good linearity is found. It should also be noted that as the total concentration of iron is increased, the resistive and capacitive components of the total reaction impedance decrease indicating that the contribution from diffusion is smaller at the higher concentration. This is to be expected. The charge transfer resistances, as determined by extrapolation to infinite frequency, and the calculated exchange current densities for the variation of Fe(III) and Fe(II) are shown in Tables 8 and 9, respectively.

As was done for the quinone-hydroquinone system for the determination of the charge transfer coefficient, standard rate constant, and the formal potential, \( \ln (i_0//c_\text{Fe(III)}) \) and \( \ln (i_0//c_\text{Fe(II)}) \) have been calculated from Tables 8 and 9 and are plotted versus \( E_e \) in Figure 26. From this graph the charge transfer coefficient was found to be 0.58 for the variation of the Fe(III) concentration at constant Fe(II) concentration, and 0.51 for the variation of the Fe(II) concentration at constant Fe(III) concentration. The standard rate constant was found to be \( 1.30 \times 10^{-2} \text{ cm s}^{-1} \) at the formal potential of 0.6678 V. As a check to the consistency of the formal potential, the natural logarithm of the concentration
Figure 25: Plot of Reaction Resistance versus the Reciprocal of Angular Frequency for Five Fe(II) Solutions with the Concentration of Fe(III) Being Constant at $3.57 \times 10^{-3}$ M.

- Curve A: $1.19 \times 10^{-3}$ M Fe(II)
- Curve B: $2.38 \times 10^{-3}$ M Fe(II)
- Curve C: $4.75 \times 10^{-3}$ M Fe(II)
- Curve D: $9.50 \times 10^{-3}$ M Fe(II)
- Curve E: $1.90 \times 10^{-2}$ M Fe(II)
Table 8. Charge Transfer Resistance and Exchange Current Densities versus Fe(III) Concentration in 1.0 M H$_2$SO$_4$. The Fe(II) Concentration is Constant at 4.75 x 10$^{-3}$ M.

<table>
<thead>
<tr>
<th>Concentration of Fe(III) mole/liter</th>
<th>Charge Transfer Resistance $\Omega$</th>
<th>Exchange Current Density $A \text{ cm}^{-2}$</th>
<th>Equilibrium Potential V vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25 x 10$^{-3}$</td>
<td>58.6</td>
<td>$3.37 \times 10^{-3}$</td>
<td>0.6283</td>
</tr>
<tr>
<td>2.01 x 10$^{-3}$</td>
<td>40.7</td>
<td>$4.86 \times 10^{-3}$</td>
<td>0.6427</td>
</tr>
<tr>
<td>3.57 x 10$^{-3}$</td>
<td>33.0</td>
<td>$5.98 \times 10^{-3}$</td>
<td>0.6605</td>
</tr>
<tr>
<td>6.66 x 10$^{-3}$</td>
<td>27.9</td>
<td>$7.08 \times 10^{-3}$</td>
<td>0.6749</td>
</tr>
<tr>
<td>1.29 x 10$^{-2}$</td>
<td>24.3</td>
<td>$8.15 \times 10^{-3}$</td>
<td>0.6940</td>
</tr>
</tbody>
</table>

Table 9. Charge Transfer Resistance and Exchange Current Densities versus Fe(II) Concentration in 1.0 M H$_2$SO$_4$. The Fe(III) Concentration is Constant at 3.57 x 10$^{-3}$ M.

<table>
<thead>
<tr>
<th>Concentration of Fe(II) mole/liter</th>
<th>Charge Transfer Resistance $\Omega$</th>
<th>Exchange Current Density $A \text{ cm}^{-2}$</th>
<th>Equilibrium Potential V vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.19 x 10$^{-3}$</td>
<td>69.5</td>
<td>$2.84 \times 10^{-3}$</td>
<td>0.6940</td>
</tr>
<tr>
<td>2.38 x 10$^{-3}$</td>
<td>52.3</td>
<td>$3.78 \times 10^{-3}$</td>
<td>0.6785</td>
</tr>
<tr>
<td>4.75 x 10$^{-3}$</td>
<td>33.0</td>
<td>$5.98 \times 10^{-3}$</td>
<td>0.6608</td>
</tr>
<tr>
<td>9.50 x 10$^{-3}$</td>
<td>25.6</td>
<td>$7.72 \times 10^{-3}$</td>
<td>0.6443</td>
</tr>
<tr>
<td>1.90 x 10$^{-2}$</td>
<td>20.6</td>
<td>$9.58 \times 10^{-3}$</td>
<td>0.6290</td>
</tr>
</tbody>
</table>
Figure 26: Plot of $\ln \left( \frac{i_0/C_{\text{Fe(III)}}}{i_0/C_{\text{Fe(II)}}} \right)$ versus $E_e$ for the Determination of the Standard Rate Constant, the Formal Potential, and the Charge Transfer Coefficient.

- $\Theta$: Variation of the Fe(III) Concentration
- $\Delta$: Variation of the Fe(II) Concentration
of the two species was plotted against the equilibrium potential. These results are shown in Figure 27. For the variation of Fe(III) concentration with constant Fe(II) concentration the formal potential was determined to be 0.6664 V and equal to 0.6696 V for the variation of Fe(II) concentration with constant Fe(III) concentration. Both of these values are in good agreement with the formal potential determined from Figure 26. The observed deviations (1.4 and 1.8 mV) are well within the expected experimental accuracy.

The two values determined for the charge transfer coefficient are in good agreement for the variation of the concentration of Fe(III) at constant Fe(II) concentration and for the variation of Fe(II) concentration at constant Fe(III) concentration.

The Fe(II)/Fe(III) system is a well studied reaction due to its simplicity (55). Gerischer (103) found the charge transfer coefficient to be equal to 0.58 for the iron system on platinum electrodes in 1.0 M H₂SO₄. He used direct current polarization resistance measurements from which the standard rate constant was found to be 3 x 10⁻³ cm s⁻¹. Randles and Somerton (104) using the faradaic impedance method, found the standard rate constant to be equal to 5 x 10⁻³ cm s⁻¹. Their measurements were made on platinum electrodes in 1.0 M HClO₄. The charge transfer coefficient was not determined. Anson (105) using chronopotentiometric methods on platinum electrodes, determined the standard rate constant for the iron system in 1.0 M H₂SO₄, 1.0 M NaHSO₄, and 1.0 M
Figure 27: Plot of $\ln c_{\text{Fe(III)}}$ and $\ln c_{\text{Fe(II)}}$ versus $E_\text{f}$ for the Determination of the Formal Potential, $E_\text{F}^\circ$.

○: Variation of the Fe(III) Concentration

△: Variation of the Fe(II) Concentration
NaHSO₄ plus 1.0 M Na₂SO₄. He found that the rate constant was highest in 1.0 M H₂SO₄ solution, having a value of 5.3 x 10⁻³ cm s⁻¹ and decreased to 2.7 x 10⁻³ cm s⁻¹ and 1.4 x 10⁻³ cm s⁻¹ for the 1.0 M NaHSO₄ and 1.0 M NaHSO₄ plus 1.0 M Na₂SO₄ electrolytes, respectively. The decrease in rate was explained by assuming that the greater degree of complexation between the Fe(III) and sulfate species in solution leads to a slower rate.

Angell and Dickinson (106) found the standard rate constant to be equal to 7 x 10⁻³ cm s⁻¹ for the iron system in 0.5 M H₂SO₄ on platinum electrodes. Samec and Weber (107) using platinum rotating disc electrodes, found the standard rate constant to be 3.2 x 10⁻³ cm s⁻¹ in 0.5 M H₂SO₄ and 8.0 x 10⁻³ cm s⁻¹ in 0.5 M Na₂SO₄ which had a pH of 2.2 by dilution with H₂SO₄. Everett et al. (100) studied the iron system in 1.0 M HClO₄ using low overvoltage direct current measurements on rhodium. The charge transfer coefficient was found to be equal to 0.59 and the standard rate constant equal to 4.60 x 10⁻⁴ cm s⁻¹. This rate constant is generally lower than usually found for the Fe(II)/Fe(III) system but this is probably due to the electrode material used.

From the discussion above it is seen that the charge transfer coefficient determined in this work is in agreement with those values determined by other investigators. The standard rate constant determined here is generally two to three times larger than those values reported in the literature.
The use of gold as the electrode material may be responsible for this discrepancy since direct comparison is only possible when all experimental conditions are identical.

Kinetics of the Fe(II)/Fe(III) System in the Presence of Benzo-(f)-quinoline

The effect of small additions of benzo-(f)-quinoline to inhibit the corrosion of iron or to decrease the rate of the Fe(II)/Fe(III) electrochemical reaction at inert electrodes has been discussed previously (see Chapter I). This investigation was undertaken to elucidate the mechanism by which this inhibition occurs.

From the total experimentally determined impedance, the reaction impedance was calculated in the same manner as for the experimental solutions in 1.0 M $\text{H}_2\text{SO}_4$. The reaction resistance versus the reciprocal of the square root of angular frequency is shown in Figure 28 for the variation of Fe(II) concentration at constant Fe(III) concentration in $1.0 \times 10^{-5}$ M benzo-(f)-quinoline, and in $1.0 \times 10^{-4}$ M benzo-(f)-quinoline in Figure 29. It is seen that all experimental solutions yield straight lines indicating that the reaction resistance is made up exclusively of charge transfer and diffusion resistance. Extrapolation to infinite frequency yields the charge transfer resistance. These results together with the experimentally determined equilibrium potential and the calculated exchange current density are shown in Tables 10 and 11 for $1.0 \times 10^{-4}$ M
Figure 28: Plot of Reaction Resistance versus the Reciprocal of Angular Frequency for Four Fe(II) Solutions with the Concentration of Fe(II) Being 1.0 x 10^{-5} M Benzo-(6)-quinoline.

Curve A: 1.19 x 10^{-3} M Fe(II)
Curve B: 2.38 x 10^{-3} M Fe(II)
Curve C: 4.75 x 10^{-3} M Fe(II)
Curve D: 9.50 x 10^{-3} M Fe(II)
Curve E: 1.90 x 10^{-2} M Fe(II)
Figure 29: Plot of Reaction Resistance versus the Reciprocal of Angular Frequency for Five Fe(II) Solutions with the Concentration of Fe(III) Being Constant at 3.57 x 10^{-3} M. Supporting Electrolyte 1.0 M H_{2}SO_{4} plus 1.0 x 10^{-4} M Benzo-(f)-quinoline.

- Curve A: 1.19 x 10^{-3} M Fe(II)
- Curve B: 2.38 x 10^{-3} M Fe(II)
- Curve C: 4.75 x 10^{-3} M Fe(II)
- Curve D: 9.50 x 10^{-3} M Fe(II)
- Curve E: 1.90 x 10^{-2} M Fe(II)
Table 10. Charge Transfer Resistance and Exchange Current Densities versus Fe(II) Concentration in $1.0 \times 10^{-5} \text{ M}$ Benzo-(f)-quinoline. The Fe(III) Concentration is Constant at $3.57 \times 10^{-3} \text{ M}$.

<table>
<thead>
<tr>
<th>Concentration of Fe(II) mole/liter</th>
<th>Charge Transfer Resistance $\Omega$</th>
<th>Exchange Current Density $A \text{ cm}^{-2}$</th>
<th>Equilibrium Potential $V \text{ vs. NHE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.19 \times 10^{-3}$</td>
<td>59.7</td>
<td>$3.30 \times 10^{-3}$</td>
<td>0.6915</td>
</tr>
<tr>
<td>$2.38 \times 10^{-3}$</td>
<td>50.4</td>
<td>$3.92 \times 10^{-3}$</td>
<td>0.6738</td>
</tr>
<tr>
<td>$4.75 \times 10^{-3}$</td>
<td>23.5</td>
<td>$8.39 \times 10^{-3}$</td>
<td>0.6585</td>
</tr>
<tr>
<td>$9.50 \times 10^{-3}$</td>
<td>24.2</td>
<td>$8.15 \times 10^{-3}$</td>
<td>0.6420</td>
</tr>
<tr>
<td>$1.90 \times 10^{-2}$</td>
<td>19.8</td>
<td>$9.99 \times 10^{-3}$</td>
<td>0.6245</td>
</tr>
</tbody>
</table>

Table 11. Charge Transfer Resistance and Exchange Current Densities versus Fe(II) Concentration in $1.0 \times 10^{-4} \text{ M}$ Benzo-(f)-quinoline. The Fe(III) Concentration is Constant at $3.57 \times 10^{-3} \text{ M}$.

<table>
<thead>
<tr>
<th>Concentration of Fe(II) mole/liter</th>
<th>Charge Transfer Resistance $\Omega$</th>
<th>Exchange Current Density $A \text{ cm}^{-2}$</th>
<th>Equilibrium Potential $V \text{ vs. NHE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.19 \times 10^{-3}$</td>
<td>152</td>
<td>$1.30 \times 10^{-3}$</td>
<td>0.6913</td>
</tr>
<tr>
<td>$2.38 \times 10^{-3}$</td>
<td>108</td>
<td>$1.83 \times 10^{-3}$</td>
<td>0.6744</td>
</tr>
<tr>
<td>$4.75 \times 10^{-3}$</td>
<td>80.2</td>
<td>$2.46 \times 10^{-3}$</td>
<td>0.6590</td>
</tr>
<tr>
<td>$9.50 \times 10^{-3}$</td>
<td>52.3</td>
<td>$3.78 \times 10^{-3}$</td>
<td>0.6418</td>
</tr>
<tr>
<td>$1.90 \times 10^{-2}$</td>
<td>44.1</td>
<td>$4.48 \times 10^{-3}$</td>
<td>0.6295</td>
</tr>
</tbody>
</table>
benzo-(f)-quinoline, respectively. From these data the formal potential was calculated for the two solutions of benzo-(f)-quinoline from the plots of ln $c_{Fe(II)}$ versus $E_e$. In the presence of $1.0 \times 10^{-5}$ M benzo-(f)-quinoline the formal potential was found to be 0.6704 V and for $1.0 \times 10^{-4}$ M benzo-(f)-quinoline the formal potential was 0.6708 V. These values are in good agreement with the formal potential calculated in 1.0 M $H_2SO_4$ ($E_F^O = 0.6696$ V) for the variation of Fe(II) concentration. To calculate the kinetic parameters, plots of ln ($i_o/c_{Fe(II)}$) versus $E_e$ were made and are shown in Figure 30. From the slope of these lines, the charge transfer coefficient was determined whereas the standard rate constant was calculated with the aid of the formal potentials determined above. In $1.0 \times 10^{-5}$ M benzo-(f)-quinoline, the charge transfer coefficient was found to be 0.48 and 0.51 in $1.0 \times 10^{-4}$ M benzo-(f)-quinoline. These two values are generally lower than those found in the literature but agree well with the charge transfer coefficient found in 1.0 M $H_2SO_4$ for the variation of Fe(II) concentration ($\alpha = 0.51$). The standard rate constant decreased from the value found in 1.0 M $H_2S\)_4 with increasing benzo-(f)-quinoline concentration. The standard rate constant found in 1.0 M $H_2SO_4$, $1.30 \times 10^{-2}$ cm s$^{-1}$, decreased to $1.01 \times 10^{-2}$ cm s$^{-1}$ in 1.0 x $10^{-5}$ M benzo-(f)-quinoline and was found to be $4.21 \times 10^{-3}$ cm s$^{-1}$ in 1.0 x $10^{-4}$ M benzo-(f)-quinoline. This decrease in rate is logarithmic with fractional coverage as was found in the quinone-hydroquinone system indicating that both systems are inhibited by similar mechanisms in the presence
Figure 30: Plot of $\ln \left( \frac{i_0}{C_{Fe(II)}} \right)$ versus $E_e$ for the Variation of the Concentration of Fe(II) in $1.0 \times 10^{-5} \text{ M Benzo-(f)-quinoline, \bigcirc}$, and in $1.0 \times 10^{-4} \text{ M Benzo-(f)-quinoline, \bigtriangleup}$. 
of benzo-(f)-quinoline. A comparison of the rate of decrease in the two rates is shown below.

\[
\ln \left( \frac{k_a^0}{k_a^0} \right) = -4.80 \theta + 0.09 \quad Q/H_2O \text{ System}
\]

\[
\ln \left( \frac{k_a^0}{k_a^0} \right) = -5.68 \theta + 0.01 \quad \text{Fe(II)/Fe(III) System}
\]

The two inhibition mechanisms which predict a logarithmic decrease in the rate with fractional coverage are changes in \( \phi_2 \) due to the adsorption of the inhibiting species and an increase in the free energy of activation due to the interaction of the adsorbate molecules and the electroactive species. If it is assumed that the Fe(II) species in 1.0 M \( H_2SO_4 \) is hydrated but not appreciably complexed with the sulfate species in solution, then the predicted changes in the \( \phi_2 \) potential would be approximately two times greater for the Fe(II)/Fe(III) reaction than for the quinone-hydroquinone reaction. This would indicate that changes in the \( \phi_2 \) potential are not the principal cause for the reduction in the standard rate constant.

The explanation that the adsorption of benzo-(f)-quinoline increases the free energy of activation due to the interaction of the adsorbed layer and the electroactive species is reasonable since the adsorbed layer is expected to increase the positive charge of the electrode surface by elimination of sulfate species during adsorption. This effectively increases the electrostatic repulsion between the positively charged surface layer and the electroactive species (assumed positively charged). This same effect
was suggested for the reduction in the standard rate constant for the quinone-hydroquinone system due to an increase in difficulty of the electroactive species to penetrate the adsorbed layer as a result of steric hindrance.
The adsorption of benzo-(f)-quinoline on gold in 1.0 M perchloric acid and 1.0 M sulfuric acid has been investigated using alternating current impedance methods. In 1.0 M perchloric acid the adsorption between 0.20 V and 0.90 V versus the saturated calomel electrode could be described using the Langmuir isotherm. The adsorption equilibrium constant was found to decrease with increasing potential due to the increased electrostatic interaction between the positively charged benzo-(f)-quinoline cation and the electrode. Due to the limited solubility of the benzo-(f)-quinoline in perchloric acid this electrolyte was not chosen for the electrochemical kinetic work. In 1.0 M sulfuric acid the adsorption was found to fit the Frumkin isotherm the isotherm with virial coefficients equally well between -0.20 V and 0.50 V versus the saturated calomel electrode. Both isotherms indicated a repulsion between adsorbed benzo-(f)-quinoline molecules and gave an adsorption equilibrium constant which did not appreciably vary with potential.

The 1.0 M sulfuric acid electrolyte system was used to study the electrochemical kinetics of the quinone-hydroquinone and the Fe(III)/Fe(II) reaction at various benzo-(f)-quinoline concentrations. The quinone-hydroquinone system
was studied using direct current measurements at low over-voltages. The average charge transfer coefficient for the variation of the concentration of quinone was found to be 0.54 ± 0.09 and was 0.44 ± 0.05 for the variation of the hydroquinone concentration. This result indicates that the quinone-hydroquinone reaction is composed of two one-electron steps rather than one two-electron step. The standard rate constant was found to decrease logarithmically with increasing fractional coverage.

The Fe(III)/Fe(II) electrochemical system was studied using the Faradaic impedance method. The average charge transfer coefficient was found to be equal to 0.52 ± 0.04 and constant for the variation of the Fe(III) concentration with constant Fe(II) concentration and for the variation of the Fe(II) concentration with constant Fe(II) concentration. The standard rate constant decreased logarithmically with increasing fractional coverage.

The decrease in the standard rate constant with fractional coverage was explained as being due to an increase in the free energy of activation for the electroactive species with increasing coverage. The change in potential at the Outer Helmholtz Plane was evaluated but the observed standard rate constants resulted in inconsistent changes in this potential.
REFERENCES


2. Ibid., Vol. 1, pp. 1.52 - 1.113.

3. Ibid., Vol. 2, pp. 18.34 - 18.41.


BIOGRAPHICAL SKETCH

Thomas Allen Holmes was born in Newport, Rhode Island, on July 3, 1951. After completing his elementary education, he graduated from Churchland High School in Portsmouth, Virginia. The author entered Virginia Wesleyan College in the Fall of 1969 and was granted a Bachelor of Arts degree in chemistry from there in June of 1973. He was married to Whitney Allison Smith on December 21, 1974.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Gerhard M. Schmid, Chairman
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Ellis D. Verink, Jr.
Professor of Materials Science and Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 1980

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Dean, Graduate School