

Weakly Supported Voltammetry

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Abstract

This thesis is concerned with dynamic electrochemical experiments with different concentrations of supporting electrolyte. Normally supporting electrolyte is added to a solution in order to avoid undesirable effects as migration and potential drop in solution. However, in the present thesis we focus on the study and understanding of such effects as the concentration of supporting electrolyte decreases.

First a theoretical treatment is proposed, based on numerical simulation using the Nernst-Planck-Poisson system of equations. The theoretical treatment is compared with previous works as electroneutrality, the differences between both models are explained. The model is also compared with theoretical results to validate the theoretical treatment. Experimental results of chronoamperometry and cyclic voltammograms are compared with theoretical results obtaining remarkable agreement. Is noteworthy that to the best of the author's knowledge this is the first time that experimental dynamic voltammetry under weakly supported conditions has been successfully modeled by a theoretical treatment.

The electrochemical reaction of a non-charged electroactive species is presented for the system ferrocene/ferrocenium in acetonitrile in which the oxidized and reduced species are soluble in solution, the reaction is studied at different concentrations of supporting electrolyte. Comparison is presented between theoretical simulations and experimental results, for which potential drop in solution is studied. Then systems involving charged electroactive species are treated, in these cases the decrease of supporting electrolyte influence the mass transport of the electroactive species due to migration, comparison between different experimental systems as hexaammineruthenium (III)/(II), cobaltocenium/cobaltocene and hexacyanoferrate (III)/(II) are presented in comparison with theoretical simulations.

More complex mechanistic paths are also investigated, such as deposition and stripping, in which it is established that the level of support required to achieve 'diffusion only' voltammetry is on dependence of the concentration of amalgamated electroactive species prior to the stripping step. Comparison between theoretical simulation and experimental results of the deposition and stripping of thallium at a mercury hemisphere are presented, and found to be in good agreement for either chronoamperometry and cyclic voltammetry

Simulations are also presented showing the necessary required amount of supporting electrolyte required to achieve 'diffusion only' cyclic voltammetry. This is obtained by comparison between diffusion only software and the simulation described in the present thesis. The required amount of supporting electrolyte is shown to depend on the concentration of the electroactive species and supporting electrolyte in the media, the electrode radius, the diffusion coefficient of species and the scan rate.

Finally, the cyclic voltammetry in weakly supporting media is used to obtain mechanistic information, by using the migration of electroactive species to differentiate the mass transport of electroactive species to the electrode. The two single electron reductions of anthraquinone in acetonitrile is presented, and the comproportionation mechanistic path is observed in weakly supported media, diffusion only voltammetry is normally unable to present whether this mechanism path takes place, due to the similarity in diffusion coefficients of the electroactive species. In contrast in weakly support conditions the diffusion controlled comproportionation mechanistic path is observed experimentally and constraints for the rate constant are discussed.

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Chapter 1

Introduction

Electrochemistry is dedicated to the study, application and measurement of charge exchange, normally between an electrode (a metal conductor or semiconductor) to a charge donor/acceptor (electroactive species) in a media (solution) containing ionic species (electrolyte). The charge exchanged at the interfacial region is normally studied as a function of the potential of the interface, and is therefore affected by the rate at which the electroactive couple is transported to the interface, the rate at which it is able to transfer the charge and any subsequent mechanistic path of conversion of the electroactive couple. Therefore, in the following we discuss the physics of the interface when a potential is applied, the mass transport that brings the electroactive species to the electrode/electrolyte interface, and the kinetic parameters influencing the rate at which the electron transfer occurs at the interfacial region.

1.1 Mass Transport

In an electrochemical experiment, the electroactive species react at the electrode/electrolyte interface. Mass transport brings a fresh supply of electroactive species to the interfacial region and removes part of the products. The mass transport in solution is composed of three factors diffusion, migration and convection. In a quiescent electrochemical experiment such as the ones treated in the present thesis only diffusion and migration are present in solution. However, convection has to be considered where there is either agitation of the solution or the experimental timescale is long enough for density gradients to develop.¹ Therefore diffusion and migration are considered in turn in the next sections.

1.1.1 Diffusion

In a quiescent chemical system in which neutral species are present in a solution, the only driving force for movement is a chemical potential gradient. Therefore, if two solutions of equal densities containing different concentrations of a neutral species are in contact, the chemical potential gradient

will be dissipated and eliminated as the solutions tend to equilibrium, by random molecular walk.² This phenomena was first described by Adolf Fick, who presented two laws describing diffusion by analogy to the conduction of heat.^{3,4}

$$J = -D\nabla C \quad (1.1)$$

$$\frac{\partial C}{\partial t} = D\nabla^2 C \quad (1.2)$$

The first of them Equation 1.1 shows that the flux of species (J) from a region which contains higher concentration (C) of species to a region with a lower concentration, and that the flux is proportional to the concentration gradient. The second law (equation 1.2) states that the variation of concentration with time is proportional to the spatial flux gradient. The constant of proportionality in both cases, D , is the diffusion coefficient of the species which depends on the nature of the species, the nature of the solvent and the interactions among them. The value of D is normally obtained experimentally, but there are also theoretical treatments such as the Stokes-Einstein^{4,5} equation and empirical such as the Wilke-Chang method,⁶ that correlate the diffusion coefficient with the nature of the species and the solvent.

In quiescent electrochemical systems containing neutral electroactive species that react at the electrode/electrolyte interface, mass transport is solely by diffusion. Therefore one can relate the charge exchanged at the interface to the diffusion coefficient of the electroactive species in the media as it will be explained in the following sections. If the electroactive species is charged then it will be influenced by any potential gradient in solution, if the concentration of supporting electrolyte is high enough to maintain the potential gradients in a very narrow region then the flux can be considered purely diffusional otherwise one should consider the influence of such potential gradients on the movement of the charged species.

1.1.2 Migration

Since an electrochemical system contains charged particles in the solution phase, one needs to consider not only diffusion, but migration as well, as all electrochemical systems are driven by electrical

forces which induce a field in solution. Therefore, an important part of electrochemical studies is focused on the importance of migration in solution, present just at the interfacial region or being part of the mass transport in solution.

Migration occurs to charged molecules in presence of an electric field gradient. Any charged species in solution will experience a force in a electric field, the phenomena is described by Coulomb's law;

$$\mathbf{F} = q\mathbf{E} \quad (1.3)$$

which states that the force vector $\mathbf{F}$ experienced by a particle is proportional to the charge of the particle q and the field vector in the medium $\mathbf{E}$. Therefore the flux of ions in solution is given by;

$$\mathbf{J}_i = -z_i u_i C_i \nabla \phi \quad (1.4)$$

relating the flux of an ion i in solution $\mathbf{J}_i$ to its mobility u_i , charge z_i , concentration C_i with the gradient of electric field in solution $\nabla \phi$. Einstein related the ionic mobility with the diffusion coefficient⁷ as;

$$u = \frac{RT}{F} D \quad (1.5)$$

where R , T and F are the universal gas constant, absolute temperature and the Faraday constant respectively. For cases in which a chemical gradient ∇C and electric field $\nabla \phi$ are present in solution the Nernst-Planck equation is used,

$$\mathbf{J} = -D\nabla C - zDC \frac{F}{RT} \nabla \phi \quad (1.6)$$

which include the both diffusion and migration contributions in the overall flux. The importance of such equation in electrochemical systems is fundamental as electrochemical experiments are likely to generate both concentration gradients and electric field due to the exchange of charge and charging near the electrode.

The electric field in solution is calculated by the Poisson equation;

$$\nabla^2 \phi = -\frac{\rho}{\epsilon_r \epsilon_0} \quad (1.7)$$

which relates the electric field gradient $\nabla^2 \phi$ to the charge density in a medium ρ and the dielectric constant of the medium (ϵ_r) and the permittivity of space (ϵ_0). The charge density is related with the local concentration of charged species by;

$$\rho = F \sum_i z_i C_i \quad (1.8)$$

1.2 Electrochemical Processes

Having reviewed the forms in which species can be transported in electrolytic solution, we now analyze how the species interact and exchange charge at the electrode/electrolyte interface.

At the electrode interface there are two processes that generate electric flow in electrochemical systems, these processes are called non faradaic and faradaic processes. The first is concerned with the charging effects at the electrode interfaces and its dependence of the accumulation/distortion of charge (ions) near or at the electrode when the potential of the electrode is varied. The latter, faradaic processes, are concerned with the charge that is exchanged between the electrode and species in the media modifying the oxidation state of the such species in solution. The name given to those electrochemical processes is because they are in agreement with Faraday's law;

$$Q = F n_e m \quad (1.9)$$

which states that, the amount of charge passed (Q) through an electrochemical system is proportional to the moles of material (m) reacted at an electrode by the number of electrons exchanged by each species (n_e). Dividing by time yields;

$$I = n_e F A J \quad (1.10)$$

In which the current (I) is proportional to the flux of reacted species (J) by the number of electrons they exchange.

1.2.1 Non faradaic processes

The non faradaic processes generate current due to a change in potential at the interface or the nature of the interfacial region, but they do not exchange charge across the interface, some examples of these processes are electrode charging, ion adsorption and desorption. These processes are characterized by the accumulation of charge at the electrode/electrolyte interface as the charge does not cross the boundary, but instead, is accumulated depending on the potential applied to the electrode. In a charging process, the charge accumulated at the interfaces is normally presented in an analogous manner to a capacitor in an electric circuit,¹ in which charge is accumulated along metal plates separated by a dielectric material, the accumulation of charge in both plaques is of equal magnitude but opposite sign.

$$q_s = -q_m \quad (1.11)$$

For an electrochemical interface, the charge accumulated at the solution interface (q_s) will depend on the magnitude and the sign of the potential applied to the electrode (q_m). The conceptual similarity between a electric capacitor and the charging of the interface has led to the application of electric circuit equations to electrochemical systems, experimental evidence shows good agreement in some cases. The electric circuit is modeled expressing the charging of the interfacial region as a capacitor ;

$$\frac{q}{E} = Cd \quad (1.12)$$

where the charge of the capacitor (q), equals the potential between the interface (E) times the capacitance of the system (Cd). The charge of the metal will represent a excess/lack of electrons and the solution represents a excess/lack of anions/cations in the interfacial part of the electrolyte solution. The region of charge in solution is called the electrical double layer.

1.2.2 The electrical double layer

The earliest description of the double layer was presented by Helmholtz,⁸ in which the charge at the electrode is confined in the outermost region. The charge at the electrode is counter-balanced by layer of solvated ions of opposite charge. This charge of solvated ions is confined to region called Outer

Helmholtz Plane (OHP) as presented in figure 1.1. The model equivalent to a parallel capacitor in a electrical circuit. The drop in potential across the OHP is linear leading to a electric field discontinuity at the edge of the plane. The assumption of a constant capacitance is not experimentally valid, but is presents a good first aproximation.

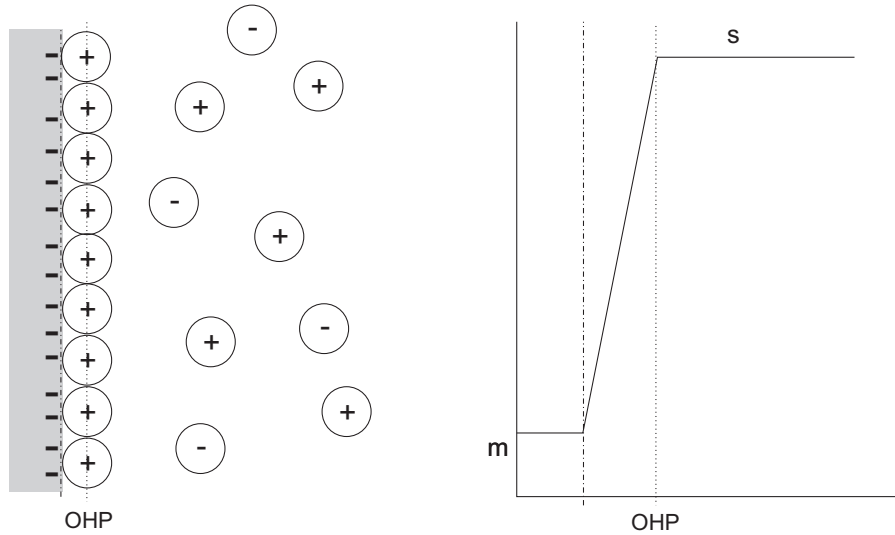


Figure 1.1: schematic representation of the electrical double layer as postulated by Helmholtz

A more descriptive model was presented by Gouy⁹ and Chapman.¹⁰ In this model, the electrode is also considered to have charge confined to its surface, whilst in the solution phase, in the Gouy-Chapman model the charge at the interface is presented as a balance of electrostatic forces between the ions and the electrode and the thermal energy of the ions allowing the ions to move away from the electrode surface. Thus leading to a more disperse and continuous distribution of the solvated charge as shown in the Figure 1.2. The highest concentration of charge is next to the electrode surface. The region containing the counterbalancing charge is called the *diffuse layer*. The ions are in thermal equilibrium therefore the distribution of the diffuse layer follows the Boltzmann distribution.

$$C_i = C_i^* \exp\left(\frac{-z_i F \phi}{RT}\right) \quad (1.13)$$

In which the concentration of species at i (C_i) depends on the bulk concentration (C^*), their charge (z_i) and the potential ϕ . Where the potential is measured in comparison to the bulk solution, this approach considers the ions as a point charges in solution ignoring their size, shape and the solvent. The variation in potential along the diffuse layer is obtained by applying the Poisson equation.

$$\nabla^2 \phi = -\frac{F}{\epsilon_r \epsilon_0} \sum_i C_i^* \exp\left(\frac{-z_i F \phi}{RT}\right) \quad (1.14)$$

The solution of Poisson-Boltzmann equations for such a system when just single charged species (X^- and M^+) are present in solution yields;

$$\frac{\tanh\left(\frac{F\phi}{4RT}\right)}{\tanh\left(\frac{F\phi_m}{4RT}\right)} = \exp\left(-\left(\frac{2F^2 C^*}{\epsilon_0 \epsilon_r RT}\right)^{1/2} x\right) \quad (1.15)$$

where x , is the distance from the electrode.

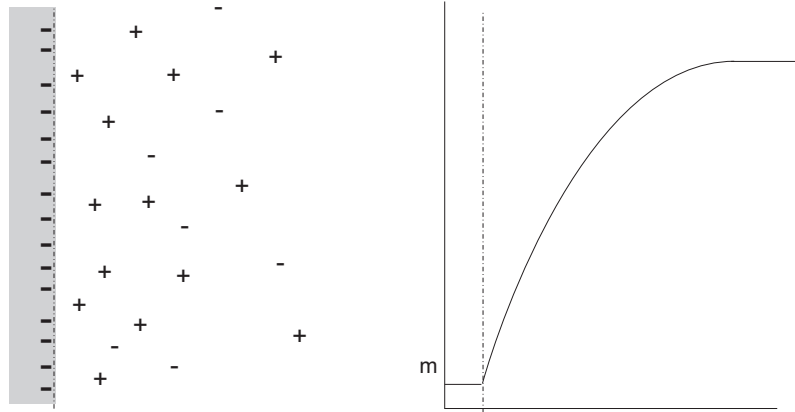


Figure 1.2: Schematic representation of the electrical double layer as postulated by Gouy and Chapman

The result is that the length of the diffuse double layer varies inversely with the square root of concentration, the Gouy-Chapman model gives the double layer capacitance as a function of the electrode potential, but it has been found to overestimate the values of the capacitance at high electrode overpotentials, due to the high concentrations of ions very close to the electrode surface. Other mod-

els, as proposed by Stern¹¹ have overcome with the problem in presenting an extra plane next to the metal surface, which is the ‘plane of closest approach’ for the ionic centers as they remain solvated in solution the limiting distance from the electrode it is the ionic radius (the plane of closest approach resembles the OHP). In the Stern model all the charge resides in the diffuse layer as in the Gouy-Chapman model. The Stern model gives predictions that account for the behavior of real systems and is in better agreement with experiment, this provided that the ions are not adsorbed to the electrode.

1.2.3 Faradaic processes

We next consider how the charge is exchanged between the electrode surface and the electrolyte interface. These processes are termed Faradaic, as the current that they produce is proportional to the extent of oxidation/reduction of electroactive species in the electrolyte media.

The faradaic processes are either galvanic or electrolytic. The former are spontaneous reactions that occur when electrodes are connected, examples are fuel cells, batteries among others. Electrolytic cells instead require an external source of voltage to initiate the reaction. The electrolytic process is an heterogeneous process and takes place just at the electrode/electrolyte interfacial region and the rate in which this reaction occurs is affected by electron transfer kinetics, mass transport and surface effects among other factors.

1.2.4 Electrode kinetics

Electrolytic cells require an external source of potential to initiate the heterogeneous reaction. The heterogeneous electron transfer reaction can be made more or less thermodynamically favorable varying the cell potential. This can be explained in terms of the energy levels of the reacting species and of the electrode.

First consider a solution containing species A in solution, A being able to electrochemically reduce by electron exchange to B.



In the reaction electrons are exchanged by quantum mechanical tunneling between electroactive species in solution A, and the electrode surface. At the electrode surface a continuum of energy levels

exists that forms a conduction band, the energy levels are filled as high as an energy maximum is known as Fermi level, in case of a reduction the process involves an electron transfer from of the electrode to the lowest unoccupied molecular orbital (LUMO) of species A see figure 1.3. When the electrode potential is made more negative, the Fermi level increases its energy relative to the LUMO of the A species, and the reduction of A is thermodynamically more favorable, therefore electrons will flow from the electrode to the electroactive species A in solution (cathodic process). If then, a more positive potential is applied to the electrode the Fermi energy level decreases its energy relative to the Highest Occupied Molecular Orbital (HOMO) of B, and the oxidation of B is more favorable; electrons will flow from the solution to the electrode surface (anodic process). These processes are exemplified in the figure 1.3.

The semi-empirical Butler-Volmer^{12,13} equation has been found to be in good agreement with experimental results and the electric flux (J) in dependence with the potential at the interface (E) ;

$$J = k_A C_A - k_B C_B \quad (1.17)$$

In which the flux of electrons (J) is equal to flux of electrons due to oxidation minus the flux due to reduction, the heterogeneous rate constants k_A and k_B describe the cathodic and anodic processes. And C_a and C_b are the concentrations of electroactive species at the electrode surface. The constants k_a and k_b are in dependence of applied potential E in respect with the formal potential E_f° , k^0 is the standard rate constant;

$$k_A = k^0 \exp \left(-\alpha \frac{F}{RT} (E - E_f^\circ) \right) \quad (1.18)$$

$$k_B = k^0 \exp \left(\beta \frac{F}{RT} (E - E_f^\circ) \right) \quad (1.19)$$

where E is the cell potential, E_f^0 is the formal cell potential, k^0 is the standard rate constant, and these latter two parameters have the same values in both expressions. E_f^0 approximates to E^0 , which is the formal potential. E_f^0 is defined as the potential measured when the species A and B are in equal and unitary concentrations, no net electron flux is passed by the interface and the temperature and

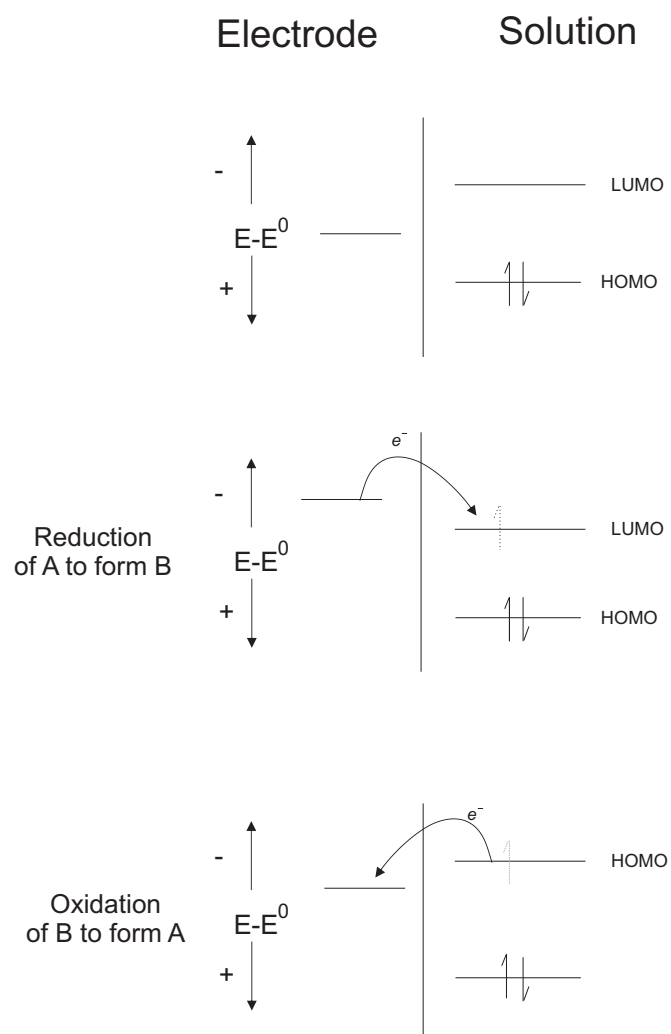


Figure 1.3: Schematic representation of the electron exchange by the potential of the electrode and the vacant and occupied potentials of the molecular orbitals.

pressure are under standard conditions. E^0 potential is referred to a potential of a standard electrode. α and β are the charge transfer coefficients and relates the transition state of the reaction on the potential, the sum of α and β is equal to the number of electrons transferred in a single mechanistic step.

When $k^0 C^*$ is infinitely greater than the flux J , the previous equations could be simplified yielding;

$$E = E^0 + \frac{RT}{F} \ln \frac{C_A}{C_B} \quad (1.20)$$

which is the Nernst equation.¹⁴ Therefore, if the kinetics of the reaction are infinitely faster in comparison with the flux driven, the concentrations at the electrode surface are in 'equilibrium'.

1.3 The Electrochemical Cell

Hither to the current chapter, we have investigated how species can move in solution, how an ionic fluid responds to a charge and how species react at the electrode/electrolyte interface. In this section we explain the electrochemical practices for obtaining data from the potential/current responses of the interfacial region.

In a normal electrochemical experiment we are interested to obtain, information about the current while a potential is established at an interface, this in order to derive the desired information about the system of study. And we cannot solely obtain such information with a single electrode,^{15,16} as we have to close a electric circuit in order to the potential to be measured and the current to flow. Therefore the minimum number of electroactive interfaces is two, as there is no way of isolating an absolute potential at one single interface. The measurement of potential at a single electrode has been compared by Albery with the Zen Buddhists idea of the noise of a single hand clapping.¹⁷ The required second interface is called counter electrode (CE), which is the one that closes the electrical circuit and therefore the same magnitude of current but opposite sign is driven at this interface.

But as we are interested on understanding the conditions at the working electrode. Particularly in the potential difference applied at the interface, in such a set-up the potential is dependent on the nature of both interfacial regions, as the potential depends on the electrolysis rates at both electroactive

surfaces, making the desired measurement inaccurate and undesirable for analysis. In order to avoid the problem of a fluctuating potential another electrode is set in the analyte solution. This electrode 'reference electrode' is set in order to control the potential of the working electrode. The stability of the potential reference electrode potential is usually reached by employing a reversible redox system with constant concentrations of the reaction participants and passing little current ($\frac{J}{C_a K^0} \approx 0$) in order to establish a potential following Nernst equation. Common examples of reference electrodes are Calomel and Ag/Ag^+ which are immersed in a solution containing defined concentrations and porous frit in order to avoid contaminations to the analyte solution. In some systems the two electrode arrangement is preferable, this is when the current driven at the working electrode is small enough to affect the potential response at counter-reference electrode.

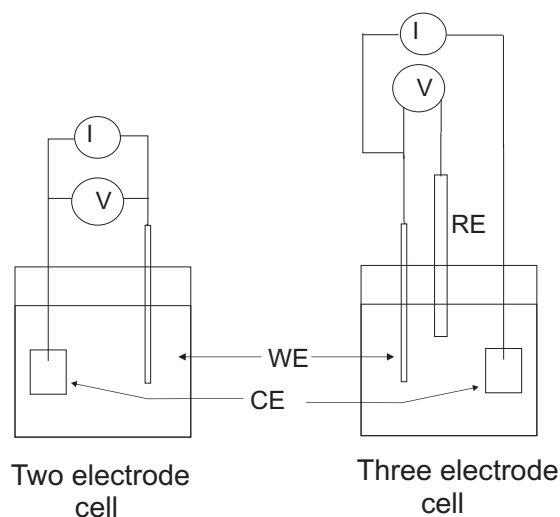


Figure 1.4: Schematic representation of a two and three electrodes electrochemical cell; WE, CE and RE refers to working, counter and reference electrodes respectively, ΔV refers the application of potential difference and I refers to the current measurement.

The electrodes in solution are controlled by a device called a potentiostat, that applies a desired potential or potential function with time and measures the current response. The potential applied to the working electrode is controlled in respect to the reference electrode, and the current response from the working electrode is facilitated by the counter electrode, which moves to whatever poten-

tial is required to ‘drive’ the current through the working electrode. Both current and potential are measured and plotted in the desired fashion. The current that is passed at the working electrode as a function of time and potential in respect to the reference electrode. The current is actually the sum of all the process occurring at the interface both Faradaic and non Faradaic, sometimes it is hard to separate the contributions of both processes as they are often interrelated.¹

1.3.1 Electrode size

A common electrochemical experiment uses electrodes whose dimensions are greater than $100\ \mu\text{m}$. However since the discovery of microelectrodes it has become common to miniaturize the working electrode. Electrodes which have dimensions of less than $10\ \mu\text{m}$ have become routinely used. This trend to go smaller has been facilitated by improvements on the electrode fabrication¹⁸ but it has been encouraged particularly by the numerous advantages of using electrodes of such small dimensions.^{19–21}

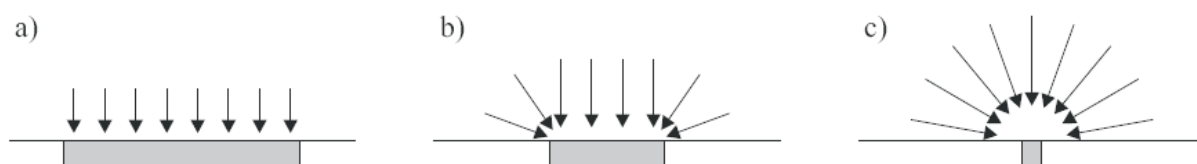


Figure 1.5: Schematic representation of diffusional behaviour for different sized electrodes

The main differences between macroelectrodes and microelectrodes results from the nature of the diffusion of electroactive species to the electrode surface. The differences in diffusion are presented in the figure 1.5, which illustrates that for a) macroelectrode the planar diffusion dominates. This is because the diffusion layer of the electrolyte is small in respect to the electrode size. The same behavior is found at a microdisc electrode but only at very short timescales. On conventional timescales the diffusion layer grows and the diffusion to the microelectrode changes from that shown on b) to that presented in c). In 1.5c convergent diffusion from spherical direction gives to the electrode a higher current density compared to a macroelectrode. This change of behaviour enables more information

to be extracted from the system.

At a microelectrode non-faradaic currents occur on a much faster timescale because the capacitance of an electrode surface depends on the electrode area.²¹ This means that the potential difference at the interfacial region is attained at shorter timescales. This allows the accurate measurement of shorter timescales, this enables the electrochemist to obtain more reliable data from the system, for example fast kinetics.²²

While in the use of a conventional macroelectrode, the shape is not important because the electrode is always significantly bigger than the thickness of the diffusion layer. Whereas using a microelectrode, the shape of the diffusive layer and its evolution along time will depend on the electrode shape. Therefore a well defined geometry is important to record and interpret data with good accuracy. The simplest system is the spherical microelectrode, as the derivation of mathematical equations for such a geometry depends only on radial diffusion. Other geometries of microelectrodes such as band and discs have normally more than one . Therefore most experiments presented in this thesis utilize hemispherical microelectrodes due to the theoretical simplicity of solving the flux equations.

1.4 Electrochemical Methods

The controlling potentiostat can be set to apply the potential at an interface of interest in several different ways; maintaining a potential constant with time, varying the applied potential according to the chosen waveform. The most commonly used measurements are called cyclic voltammetry and chronoamperometry. But there are more complex methods of applying potential in order to derive information about the electrochemical couple under study. The some common examples include; impedance, differential pulse voltammetry, squarewave voltammetry among others. In the present thesis the attention is focused on cyclic voltammetry and chronoamperometry, but readers may find further information about other methods in the standard electrochemistry literature.^{1, 15, 16, 23, 24}

1.4.1 Chronoamperometry

In this electrochemical method, the potential of the working electrode is stepped and maintained at a desired potential. The current passed in the circuit is recorded along time. In Figure 1.6 an example of chronoamperometry is presented, considering the reaction 1.16 and just A present in solution. The

potential E_0 is maintained at a point in which no reduction takes place in solution (the potential being considerably positive than E_f^0). Then at $t = 0$, the potential is set to a potential value negative enough from E_f^0 , so that the reduction of A occurs at a diffusion controlled rate (the potential is set so negative that the rate of reduction of species A is much greater than the rate of oxidation of B). A schematic representation of diffusion controlled chronoamperometry is presented in figure 1.6

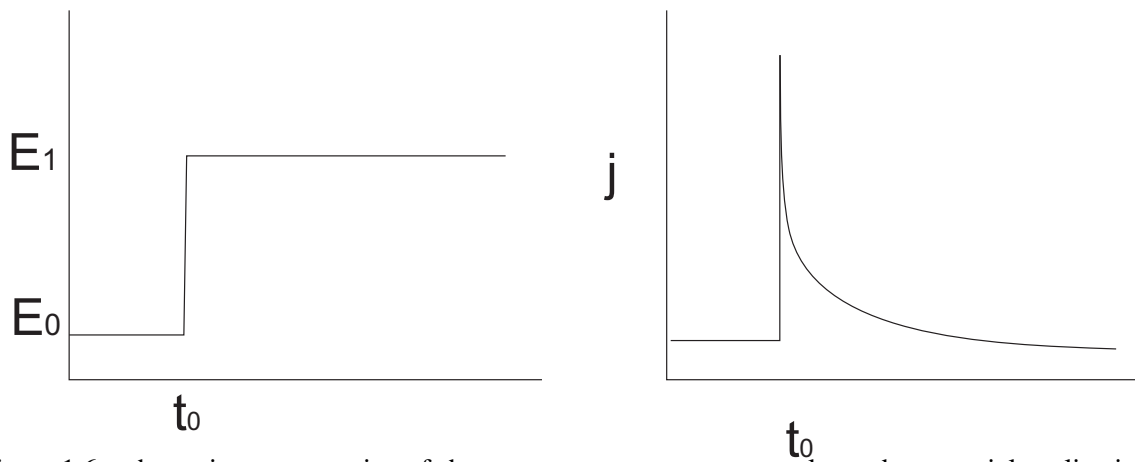


Figure 1.6: schematic representation of chronoamperometry at a macroelectrode, potential application and current response in a diffusion controlled system

For this case the Fick's laws of diffusion was solved for planar diffusion under such conditions by Cottrell²⁵ for a macroelectrode, here a more descriptive equation for the case of a hemispherical microdisk electrode is presented.

$$j = D_A C_A^* \left(\frac{1}{\sqrt{D_A \pi t}} + \frac{1}{r_e} \right) \quad (1.21)$$

where the flux at the electrode surface J is in dependence of D_A is the diffusion coefficient of the electroactive species A, C_A^* the bulk concentration of A and r_e the electrode radius.

This equation is obtained by solving Fick's laws of diffusion for a single radial coordinate flux in spherical coordinates, the full derivation of this equation is presented elsewhere.¹⁵ The implication of this equation is that the flux will depend on the electrode radius. For microelectrode behavior the second term will predominate as the diffusion layer is much bigger than the radius, therefore steady state flux predominates, whereas for a macroelectrode the dependence of the flux relies just on the

increase of the diffusion layer as the second term is negligibly small as the electrode radius is much greater than the size of the depletion layer.

The importance of such transients is that using microelectrodes, one is able to observe transient and steady state voltammetry, and as the dependence of the diffusion coefficient under transient and steady state behaviour is different, one has two degrees of freedom in this equation. Therefore in an experiment while the concentration and diffusion coefficient of the analyte are unknown, one can obtain both by obtaining a chronoamperogram.

1.4.2 Cyclic voltammetry

This electrochemical method consists of applying a linearly varying potential from a potential E_1 to a potential E_2 and then back. Normally the first potential E_1 is such that no faradaic process occurs and the potential is increased until the process is diffusion controlled. The rate at which the potential is varied with time is called the scan rate v . An example of the applied potential waveform and the resulting current vs potential response is presented in figure 1.7 for the process in equation 1.16 and infinitely fast k^0 .

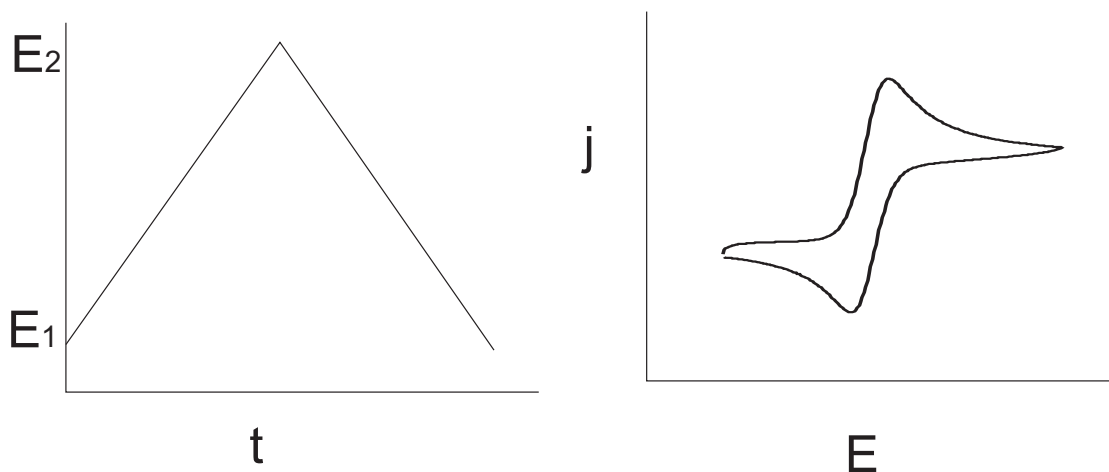


Figure 1.7: schematic representation of cyclic voltammetry, potential application and current response in a diffusion controlled system

Cyclic voltammetry is one of the most used methods in electrochemistry. The advantage of the method relies on the observation of peaks that are related to the concentration of the electroactive

species. Moreover the method can give concentration, diffusive, kinetic and mechanistic information about the electroactive species in the media.

In a simple system at a macroelectrode and using the electrochemical couple system in equation 1.16, assuming that both species are soluble in the media and that the kinetics of the couple are infinitely fast ('reversible'), the peak to peak separation will be of 57 mV at 25⁰C and the peak height of the cyclic voltammogram will follow the equation;

$$i_p = 2.69 \times 10^{-5} n_e^{3/2} A D_A^{1/2} C_A^* \nu^{1/2} \quad (1.22)$$

This equation is commonly called Randles-Sevcik,²⁶ and describes the dependence of the peak current in concentration (C_A), diffusion coefficient (D_A), number of electrons tranfered (n_e), scan rate (ν) and electrode area (A). A similar equation has been solved for conditions in which the kinetics are non-reversible¹⁵. For the cases in which the kinetics are in the intermediate region between both cases one has to simulate the process to obtain the kinetic parameters from the cyclic voltammogram.

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Chapter 2

Foundations and previous studies of weakly supported voltammetry

2.1 The supporting electrolyte

A well known common practice in electrochemistry is to add inert salts to the solution under study. These salts are called supporting electrolyte. The aim of adding this inert charged species is to give charge mobility to the solutions, so when charge transfer occurs at the electrode-solution interface, the induced electric field in solution can be easily dispersed by ionic movement, avoiding the creation of significant potential loss in solution.

If the concentration of supporting electrolyte is high relative to that of the analyte, the overall migration of any charged species in solution is negligible, and the potential drop due to the concentration gradients is minimized. Accordingly the potential applied by the controlling electrochemical instrument (potentiostat) tends to the potential raised at the solution-electrode interface.

A more precise description of recommended ratios of supporting electrolyte to analyte is presented in a later chapter of this thesis. However an approximate concentration of 100 mM of supporting electrolyte is normally recommended,¹ a more precise treatment will show that in some cases particularly with macroelectrodes this amount is insufficient.

By adding supporting electrolyte, the migration contribution of the flux of the electroactive species is decreased up to a point that the mass transport via migration can be considered negligible. Therefore in a quiescent electrochemical experiment only transport via diffusion needs to be considered, which simplifies considerably the mathematical treatment of experimental results. This allows the electrochemist to use the well established diffusion only equations such as Randles-Sevcik, Cottrell, Steady state, among others.

The ideal supporting electrolyte should have the following characteristics;

1. A high diffusion coefficient

2. A high molar solubility
3. It should be fully dissociated in solution
4. It should have high purity
5. Ideally is composed of highly charged ions
6. It would be inert to the electroactive species and its products of the electrochemical reaction
7. It should not modify the nature of the solution (for example, viscosity or acidity)

The most common used salts as supporting electrolyte in aqueous systems, contains cations as K^+ or Na^+ and anions as Cl^- , F^- , ClO_4^- , NO_3^- and SO_4^{2-} among others. For non-aqueous solvent normally organic tetra-alkylammonium cations are commonly used as: tetra-n-butylammonium and tetraethylammonium. Anions like hexafluorophosphate and perchlorate are normally preferred.²⁻⁴ Also the dissolution of ionic liquids in organic solvents is encouraged in some cases.⁵ When using organic solvents special care should be taken, as some solvents are of very low polarity and the effective concentration of dissociated species in solution is not equivalent to that of the bulk concentration of the salt in in solution, due to ion pairing effects.

The adding of supporting electrolyte, can sometimes lead to undesirable features. The added salts increase considerably the ionic strength of solution which intrinsically and significantly affects the activities of ions and mobility of the desired analyte, modifying the normal environment of the analyte. Also, the supporting electrolyte may interact with either the electroactive species or its products physically or chemically i.e. ion paring, complexation, denaturation of the sample.

Moreover, added salt can cause an intrinsic contamination of the sample if there are contaminating impurity traces present in the salt, as the salt is normally added in much higher concentration (normally 1-3 higher orders of magnitude) so that the 'trace' impurity become considerable in respect to the analyte concentration.

The use of salty conditions make electrochemistry highly undesirable for some samples for example, biological or biochemical samples that are structurally modified by the salt concentrations in solution.

In the present thesis we present a model based on the Nernst-Planck-Poisson system of equations that allow the electrochemist to study analytes under very low or zero added supporting electrolyte, in which migration and potential drop in solution are considered, studied and explained.

2.1.1 Previous work on electrochemistry under low supporting electrolyte concentrations

The first attempts to make an experiment with low concentrations of supporting electrolyte were made by Heyrovsky more than 80 years ago. It involved analyzing ionic species.⁷ But in the late decades of the 20th century the use of voltammetry in weakly supported conditions became a fashionable topic due to the discovery of microelectrodes,^{8–12} which reduce the potential drop in solution, making possible to obtain reliable data from experiments under conditions of absence of added supporting electrolyte. Ionic contaminations at the solvent were able to disperse the field created in solution in order to allow the charge transfer at the electrode-solution interfaces and to provide relatively reliable voltammetric data. The first published results of a neutral charged electroactive species without any intentionally added supporting electrolyte was presented in 1984 by Fleischmann et al. and later duplicated by others.^{13–15} In which it was shown experimentally that the limiting current of a neutral electroactive species does not depend upon the concentration of supporting electrolyte. As a neutral species is not affected by migration, its mass transport to the electrode remains constant regardless of the quantity of supporting electrolyte.

The difficulty of studying an experiment under weakly supported conditions is due to the fact that the bulk concentrations of all charged species in solution are highly distorted by migration near to the electrode interface, and consequently, the ionic strength, the solution resistance, etc cannot be considered constant.

Different mechanistic pathways have been experimentally considered in the absence of supporting electrolyte, as the lack of supporting electrolyte opens a window for elucidating mechanisms based on charge migration and not solely on diffusion as constrained by (fully supported) electrochemistry with added salt. Studies have been successful undertaken on the interpretation of ion pairing effects, and on homogeneous reactions among others. Such mechanistic paths are normally blind to diffusion only electrochemistry. A more detailed description of this phenomena is presented later in this thesis.

Voltammetry under these conditions also permits more accurate description of colloidal suspensions, polyelectrolytes and gels, as the electrostatic interactions of such systems are strongest at low ionic concentrations. More detailed descriptions of the experimental cases in which supporting electrolyte is undesirable for the analysis of electrochemical systems have been presented in reviews by Stojek et al.^{16,17}

2.2 The Principle of electroneutrality

The first theoretical attempts to study systems in which the concentration of supporting electrolyte was not in excess in solution, were done by Amatore et al.¹⁸ providing a theory for a neutral electroactive species under steady state conditions. This approach was based on the principle of electroneutrality which states that all points in the solution will have the same concentration of positive and negative charge, therefore no net charge will be accumulated. Later Oldham and Mayland presented a general theoretical treatment of steady state voltammetry for almost all experimentally (possible and impossible) electrochemical single step mechanisms in which analytical solutions were presented for potential drop and migration under steady state conditions.²⁰

Norton et al. in a later study presented a theoretical treatment stating that the principle will hold for all steady state conditions when the depletion layer is larger than the double layer.¹⁹ (typically the double layer is of ca. 100 Angstroms)

The theoretical approximation for weakly supported electrochemistry based on the principle of electroneutrality varies among the authors. The one stated here is mainly based on the Amatore approach for steady state electrochemistry.^{18,21} The principal assumption is that the solution remains electrically neutral at all times and position, and the electrical double layer is considered to be negligible compared to the electrode size therefore not intervening in the voltammetric predictions..

For electroneutrality;^{18,21}

$$\sum_i z_i C_i = 0 \quad (2.1)$$

where C_i and z_i are respectively the concentration and charge of the i species in solution. The mass transport of the species in solution follows the Nernst-Planck equation;

$$J_i = -D_i \frac{\partial C_i}{\partial r} - z_i D_i C_i \frac{F}{RT} \frac{\partial \phi}{\partial r} \quad (2.2)$$

Amatore showed that, using the principle of electroneutrality implies, that the sum of the concentrations of all species in solution is constant at any time or position;¹⁸

$$\sum_i c_i = \gamma \quad (2.3)$$

where γ is the total concentration of species at any point. The flux, J , of electroactive species thorough the electrode is described using the Butler-Volmer equation ;

$$J = k^0 C_{A,r=r_e} \exp\left(\frac{-\alpha F}{RT} (E - E_f^\circ - \phi_e)\right) - k_{B,r=r_e}^0 \exp\left(\frac{\beta F}{RT} (E - E_f^\circ - \phi_e)\right) \quad (2.4)$$

The potential at the electrode surface will be that applied to the electrode E minus the potential consumed in solution ϕ_e , in respect of the formal potential of the electroactive couple (E_f°). Therefore, the potential profile along the solution renders from that which can satisfy simultaneously the electroneutrality condition, the Butler-Volmer kinetics and the Nernst-Planck equation. Here is noteworthy to state that the model based on the electroneutrality does not necessarily satisfy Maxwell equations nor the Poisson equation. In the Amatore model the potential gradient at any point in solution is derived and related to the faradaic flux at the electrode-solution interface. For example, for a reduction of neutral equation 2.5 or singly charged electroactive equation 2.6 species;

$$\frac{\partial \theta}{\partial y} = \frac{J_A}{\gamma - c_B} \quad (2.5)$$

$$\frac{\partial \theta}{\partial y} = \frac{J_A}{\gamma - c_A} \quad (2.6)$$

The variation of concentration of the electroactive species and potential are obtained simultaneously from the Nernst-Planck equation and equation 2.5 or 2.6.

Last, Bond et al.^{16,17} have published a series of papers using the principle of electroneutrality for cyclic voltammetry at dynamic conditions and a clear departure between theory and experiment is observable. To the best of the author's knowledge that has been the only prior attempt to present a theoretical treatment of voltammetric data under dynamic conditions and with low concentrations of supporting electrolyte.

2.3 The Nernst-Planck-Poisson Model

The work described along the present thesis models dynamic voltammetry varying the concentration of supporting electrolyte, using the Nernst-Planck-Poisson System of equation, as we have said in the introduction the Nernst-Planck equation relates the mass transport of species depending upon the chemical potential and electric field gradients. The Poisson equation relates charge concentration

with field gradients in solution. The Nernst-Planck-Poisson set of equations have been previously applied to faradaic processes in conditions of potential gradients in solution.

As the previous methodology based on the principle of electroneutrality, has failed to predict the features of dynamic voltammetry, this new route is presented in comparison with experiment in the present thesis as a way to overcome the problem.

2.3.1 Establishment of the model

We have a solution containing a cationic electroactive species A^z , which is capable of undergoing electron transfer to form a species B :



The solution is additionally supported by a concentration C_{sup} of a monovalent inert salt MX, which is presumed to be completely dissociated. An extra equivalent of X^- is initially present as the counter-ion of the electroactive species.

The continuum Nernst-Planck equation is used to describe the flux of any species i at any point in solution. Assuming convection to be negligible, this equation has a contribution from diffusion and from migration:

$$\mathbf{J}_i = -D_i \left(\nabla C_i + \frac{z_i F}{RT} C_i \nabla \phi \right) \quad (2.8)$$

where for species i , $\mathbf{J}_i$ is the flux vector, D_i is the diffusion coefficient, C_i is concentration, z_i is the species charge, ϕ is potential, F is the Faraday constant, R is the gas constant and T is temperature. Conservation of mass then requires that the space-time evolution of the concentration of i obeys:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{J}_i \quad (2.9)$$

And the Poisson equation is used to calculate the difference in the electric field in the solution, depending on the concentration of charge along the solution.

$$\nabla^2 \phi = -\frac{F}{\epsilon_s \epsilon_0} \sum_i z_i C_i \quad (2.10)$$

where ϕ is the potential in solution, ϵ_0 and ϵ_s are respectively the permittivity of free space and

the relative permittivity of the solution. The Poisson equation is preferred over the electroneutral approximation originally postulated by Planck. As the Poisson equation obeys Maxwell's equation for electric field. Whereas the electroneutral system just present a particular solution for the system and its foundation is just based on the observation of the lack of separation of charge in solution.

2.3.2 Dimensionless coordinates

Having established the Poisson equation as most appropriate, we may hence write, in a hemispherically symmetric space surrounding the electrode and extending into bulk solution, with spatial coordinate r , for $i = A^+, B^0, M^+, X^-$:

$$\frac{\partial C_i}{\partial t} = D_i \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} + \frac{z_i F}{RT} \left(\frac{\partial C_i}{\partial r} \frac{\partial \phi}{\partial r} + C_i \frac{\partial^2 \phi}{\partial r^2} + C_i \frac{2}{r} \frac{\partial \phi}{\partial r} \right) \right) \quad (2.11)$$

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} = - \frac{F}{\epsilon_s \epsilon_0} \sum_i z_i C_i \quad (2.12)$$

A range of conventional normalisations are introduced to simplify these equations and reduce the number of independent variables in the system such that the most general possible conclusions may be drawn:

$$c_i = \frac{C_i}{C_A^*} \quad (2.13)$$

$$\theta = \frac{F \phi}{RT} \quad (2.14)$$

$$R = \frac{r}{r_e} \quad (2.15)$$

$$\tau = \frac{D_A}{r_e^2} t \quad (2.16)$$

where C_A^* is the bulk concentration of species A and r_e is the electrode radius.

The resulting set of dimensionless Nernst-Planck-Poisson (NPP) equations are then:

$$\frac{\partial c_i}{\partial \tau} = \frac{D_i}{D_A} \left(\frac{\partial^2 c_i}{\partial R^2} + \frac{2}{R} \frac{\partial c_i}{\partial R} + z_i \left(\frac{\partial c_i}{\partial R} \frac{\partial \theta}{\partial R} + c_i \frac{\partial^2 \theta}{\partial R^2} + c_i \frac{2}{R} \frac{\partial \theta}{\partial R} \right) \right) \quad (2.17)$$

$$\frac{\partial^2 \theta}{\partial R^2} + \frac{2}{R} \frac{\partial \theta}{\partial R} = -R_e^2 \sum_i z_i c_i \quad (2.18)$$

where the dimensionless variable R_e is defined:

$$R_e = r_e \sqrt{\frac{F^2 C_A^*}{RT \epsilon_s \epsilon_0}} \quad (2.19)$$

and may be considered to represent the electrode size in dimensionless coordinates in respect to the Debye length of the solution.

2.3.3 Boundary conditions

The NPP equations are solved subject to ten boundary conditions: one for each species, plus potential, at each of the two boundaries $R = 1$ and $R \rightarrow \infty$. At $R = 1$, Butler-Volmer kinetics are applied, relating the flux of A normal to the electrode to the surface concentrations, $c_{i,0}$, of A and B in the form:

$$\left. \frac{\partial c_A}{\partial R} \right|_{R=1} = K^0 \left(\exp(-\alpha(\theta_{\text{app}} - \theta(R=1))) c_{A,0} - \exp((n - \alpha)(\theta_{\text{app}} - \theta(R=1))) c_{B,0} \right) \quad (2.20)$$

The dimensionless heterogeneous rate constant is defined:

$$K^0 = \frac{k^0 r_e}{D_A} \quad (2.21)$$

with k^0 being the dimensional heterogeneous rate constant. α is the transfer coefficient, and θ_{app} is the dimensionless applied potential:

$$\theta_{\text{app}} = \frac{F}{RT} (E - E_f^\theta) \quad (2.22)$$

where E_f^θ is the formal potential of the A^z/B^{z-n} couple. For the cases in which chronoamperometry is simulated the potential is maintained constant. Whereas, if a cyclic voltammetry experiment is simulated θ_{app} is varied linearly in τ through a triangular waveform, at a dimensionless scan rate σ :

$$\sigma = \left| \frac{\partial \theta_{\text{app}}}{\partial \tau} \right| = \frac{F}{RT} \frac{r_e^2}{D} v \quad (2.23)$$

where v is the dimensional scan rate, $\equiv |\partial E / \partial t|$.

From conservation of mass:

$$\frac{D_B}{D_A} \frac{\partial c_B}{\partial R} \Big|_{R=1} = - \frac{\partial c_A}{\partial R} \Big|_{R=1} \quad (2.24)$$

and assuming M and X to be inert and insoluble in the electrode:

$$\frac{\partial c_M}{\partial R} \Big|_{R=1} = \frac{\partial c_X}{\partial R} \Big|_{R=1} = 0 \quad (2.25)$$

The boundary condition for potential at the electrode surface assumes that the double layer is negligible in extent compared to the diffusion layer, such that the charge on the electrode is fully compensated at $R \approx 1$. Then the enclosed charge is vanishing at this point, and so, from Gauss's law, the electric field is zero:

$$\frac{\partial \theta}{\partial R} \Big|_{R=1} = 0 \quad (2.26)$$

The $R \rightarrow \infty$ boundary is represented by limiting the space considering a finite value which greatly exceeds the thickness of the diffusion layer for a diffusion-only system, being $R_{\max} = 6\sqrt{(D_{\max}/D_A)\tau_{\max}}$ where $D_{\max}$ is the largest diffusion coefficient in the system. The concentrations of A, B, M and X are set to their bulk values at this boundary:

$$c_A = 1 \quad (2.27)$$

$$c_B = 0 \quad (2.28)$$

$$c_M = c_{\text{sup}} \quad (2.29)$$

$$c_X = 1 + c_{\text{sup}} \quad (2.30)$$

Finally, the potential is constrained such that a reference potential of $\theta = 0$ occurs at $R \rightarrow \infty$, which on the assumption of electroneutrality outside the simulation space yields the expression:

$$\theta(R = R_{\max}) + R_{\max} \frac{\partial \theta}{\partial R} \Big|_{R=R_{\max}} = 0 \quad (2.31)$$

Surface flux at the hemisphere, J , is recorded for simulated voltammetric output as:

$$J = n \left. \frac{\partial c_A}{\partial R} \right|_{R=1} \quad (2.32)$$

such that the corresponding dimensional current, i , is:

$$i = 2\pi F C_A^* D_A r_e J \quad (2.33)$$

This theoretical formulation consistently used throughout the present thesis, some variations are presented for boundary conditions where amalgams or more complex mechanistic paths are studied. For the case of amalgams the electrochemical reaction is presented as:



The species B is insoluble in solution but soluble in the mercury electrode where its flux is controlled by diffusion. Therefore the boundary conditions are modified yielding in,

Species / Potential	$R = 0$	$R = R_e$	$R_{\max} = 6\sqrt{(D_{\max}/D_A)\tau_{\max}}$
$B_{(Hg)}^0$	$J_{B_{(Hg)}^0} = 0$	$J_{B_{(Hg)}^0} = J_{A_{(aq)}^z}$	—
$A_{(aq)}^z$	—	Butler-Volmer	$C_{A_{(aq)}^z} = C^*$
M^+	—	$J_{M^+} = 0$	$C_{M^+} = c_{\text{sup}}$
X^-	—	$J_{X^-} = 0$	$C_{X^-} = c^* + C_{\text{sup}}$
θ	—	$\frac{\partial \theta}{\partial R} = 0$	$\theta + R \frac{\partial \theta}{\partial R} = 0$

Table 2.1: Boundary conditions for the NPP equations for amalgams.

In order to solve the equations presented, simulations are used. The simulations are based on the Newton-Raphson algorithm and discretized by Crank-Nicholson.

2.3.4 Numerical Methods

Newton-Raphson method

The non-linear system of NPP equations described in previous section are solved using the matrix form of the Newton-Raphson method. In this method, a vector $\mathbf{x}$ contains all the unknown variables to be found, labelled $x_0, x_1 \dots x_n$. The system of equations to be solved is in the form $\mathbf{F}(\mathbf{x}) = 0$, where the vector $\mathbf{F}(\mathbf{x})$ contains the equations $f_0(\mathbf{x}), f_1(\mathbf{x}) \dots f_n(\mathbf{x})$. A vector $\mathbf{u}$ is introduced where $\mathbf{u} = \mathbf{u}^{z+1} - \mathbf{u}^z$, which represents the difference between successive iterations of Newton's method. The iterative formula is then given by:

$$\mathbf{J}\mathbf{u} = -\mathbf{F} \quad (2.35)$$

where $\mathbf{J}$ is the following matrix:

$$\mathbf{J} = \begin{bmatrix} \frac{\partial f_0}{\partial x_0} & \frac{\partial f_0}{\partial x_1} & \dots & \frac{\partial f_0}{\partial x_n} \\ \frac{\partial f_1}{\partial x_0} & \frac{\partial f_1}{\partial x_1} & \dots & \frac{\partial f_1}{\partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_n}{\partial x_0} & \frac{\partial f_n}{\partial x_1} & \dots & \frac{\partial f_n}{\partial x_n} \end{bmatrix} \quad (2.36)$$

The procedure is iterated until the termination criterion $|\mathbf{x}^{z+1} - \mathbf{x}^z| < \varepsilon$ is met for all unknowns, where ε is chosen to be a suitably small number.

2.3.5 NPP equations

The NPP equations described in previous section are discretised over an expanding grid containing n grid points. The vectors $\mathbf{x}$ and $\mathbf{F}$ for the non-linear NPP equations are given by Equation 2.37, where the label j refers to the point on the spatial grid, and the label $k + 1$ indicates that the unknowns are

for the next time step.

$$\mathbf{x} = \begin{bmatrix} c_{A,0}^{k+1} \\ c_{B,0}^{k+1} \\ \theta_0^{k+1} \\ c_{M^+,0}^{k+1} \\ c_{X^-,0}^{k+1} \\ \vdots \\ c_{A,j}^{k+1} \\ c_{B,j}^{k+1} \\ \theta_j^{k+1} \\ c_{M^+,j}^{k+1} \\ c_{X^-,j}^{k+1} \\ \vdots \\ c_{A,n}^{k+1} \\ c_{B,n}^{k+1} \\ \theta_n^{k+1} \\ c_{M^+,n}^{k+1} \\ c_{X^-,n}^{k+1} \end{bmatrix} \quad \mathbf{F} = \begin{bmatrix} f_{A,0}(\mathbf{x}) \\ f_{B,0}(\mathbf{x}) \\ f_{\theta,0}(\mathbf{x}) \\ f_{M^+,0}(\mathbf{x}) \\ f_{X^-,0}(\mathbf{x}) \\ \vdots \\ f_{A,j}(\mathbf{x}) \\ f_{B,j}(\mathbf{x}) \\ f_{\theta,j}(\mathbf{x}) \\ f_{M^+,j}(\mathbf{x}) \\ f_{X^-,j}(\mathbf{x}) \\ \vdots \\ f_{A,n}(\mathbf{x}) \\ f_{B,n}(\mathbf{x}) \\ f_{\theta,n}(\mathbf{x}) \\ f_{M^+,n}(\mathbf{x}) \\ f_{X^-,n}(\mathbf{x}) \end{bmatrix} \quad (2.37)$$

The equations $f_{A,j}$, $f_{B,j}$, $f_{M^+,j}$ and $f_{X^-,j}$ are the discretised mass transport equations for $0 < j < n$.

For example, $f_{M^+,j}(\mathbf{x})$ is the discretised version of the following equation:

$$-\frac{\partial c_{M^+}}{\partial \tau} + \left(\frac{\partial^2 c_{M^+}}{\partial R^2} + \frac{2}{R} \frac{\partial c_{M^+}}{\partial R} + c_{M^+} \left(\frac{\partial^2 \theta}{\partial R^2} + \frac{2}{R} \frac{\partial \theta}{\partial R} \right) + c_{M^+} \frac{\partial c_{M^+}}{\partial R} \frac{\partial \theta}{\partial R} \right) = 0 \quad (2.38)$$

The equation $f_{\theta,j}(\mathbf{x})$ is the discretised version of the following form of the Poisson equation:

$$\frac{\partial^2 \theta}{\partial R^2} + \frac{2}{R} \frac{\partial c_{M^+}}{\partial R} + c_{M^+} - c_{X^-} + z c_A + (z+1) c_B = 0 \quad (2.39)$$

The following discretisations are used:

$$\frac{\partial c}{\partial \tau} \approx \frac{c_j^{k+1} - c_j^k}{\Delta \tau} \quad (2.40)$$

$$\frac{\partial^2 c}{\partial R^2} + \frac{2}{R} \frac{\partial c}{\partial R} \approx \frac{c_{j+1} - c_j}{0.5\Delta^+R(\Delta^+R + \Delta^-R)} - \frac{c_j - c_{j-1}}{0.5\Delta^-R(\Delta^+R + \Delta^-R)} \quad (2.41)$$

$$\frac{\partial^2 \theta}{\partial R^2} + \frac{2}{R} \frac{\partial \theta}{\partial R} \approx \frac{\theta_{j+1} - \theta_j}{0.5\Delta^+R(\Delta^+R + \Delta^-R)} - \frac{\theta_j - \theta_{j-1}}{0.5\Delta^-R(\Delta^+R + \Delta^-R)} \quad (2.42)$$

$$\frac{\partial \theta}{\partial R} \approx \frac{\theta_{j+1} - \theta_{j-1}}{\Delta^+R + \Delta^-R} \quad (2.43)$$

where Δ^+R refers to the spacing between grid points j and $j + 1$, and Δ^-R refers to the spacing between grid points j and $j - 1$. The labels k and $k + 1$ have been removed from Equations 2.41-2.43 for clarity. The Cranck-Nicholson discretisation of time is used, which is expected to be more accurate than a fully implicit scheme.²²

The equations $f_{A,0}$, $f_{B,0}$, $f_{\theta,0}$, $f_{M^+,0}$ and $f_{X^-,0}$ are the discretised forms of the boundary conditions at the electrode surface. For example:

$$f_{M^+,0}(x) = \frac{c_{M^+,1} - c_{M^+,0}}{\Delta R} + c_{M^+,0} \frac{\theta_1 - \theta_0}{\Delta R} = 0 \quad (2.44)$$

The equations $f_{A,n}$, $f_{B,n}$, $f_{\theta,n}$, $f_{M^+,n}$ and $f_{X^-,n}$ are the boundary conditions at $y = 1$ For example:

$$f_{M^+,n}(x) = c_{M^+,n} - c_{\text{sup}} = 0 \quad (2.45)$$

The matrix $\mathbf{J}$ is found by differentiating equations $\mathbf{F}(x)$ as described in Equation 2.36. Matrix $\mathbf{J}$ has non-zero elements only on its central 15 diagonal lines. The matrix equation 2.35 can therefore be solved using a generalised form of the Thomas algorithm.

2.3.6 The assumption of a negligible electrical double layer

The main assumption present in the theory of developed in this thesis is that the electrical double layer (EDL) is negligibly small and does not influence the rate of electron transfer. A previous study by Streeter et al. first developed the Nernst-Planck-Poisson model and is the basis of the treatment in this thesis.²³ Simulations obtained by the Nernst-Planck-Poisson model were compared with different models as the electroneutrality model and another model which simulated the electrical double layer. In Streeters work it was found that results obtained for the simulation of weakly supported chronoamperometry the NPP and full EDL model are equivalent except at short times in the order of 10^{-5} s or less or for electrodes of nano-dimensions.

Therefore, that study validates the assumption of a negligible electrical double layer as is used throughout this thesis. The work in this thesis aims to present an experimental validation of the Nernst-Planck-Poisson model and to give a theoretical interpretation of the features occurring when insufficient concentrations of supporting electrolyte are present in solution, encouraging the reader to use such approach as a complementary electrochemical methodology for cases in which conclusions cannot to be drawn from experiment with high concentrations of supporting electrolyte. It is further shown that by deliverately using conditions were migration occurs additional mechanistic information can be obtained.

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Chapter 3

Chronoamperometry at various concentrations of supporting electrolyte of the reduction of non-charged electroactive species

It is conventional when conducting an electrochemical experiment to add supporting electrolyte¹⁻⁴ in order to confine the differences of potential to a narrow region close to the electrode and to avoid potential losses along the solution.¹ In the present chapter, the potential step chronoamperometry of a reduction of a neutrally electroactive charged species at different concentrations of supporting electrolyte C_{sup} is examined either experimentally and then compared with the corresponding theoretical predictions. In particular, a potential step is applied to a solution of ferrocene (Fc) in acetonitrile containing different concentrations of tetrabutylammonium perchlorate, at different applied potentials in order to observe the effects on the chronoamperometric response arising from the resulting oxidation:



This chapter represent a quantitative treatment of potential loss in solution, in which neutral electroactive species are present in solution at various concentrations of supporting electrolyte; from high supported diffusion only voltammetry, to the understanding of potential losses in solution.

3.1 Theoretical model and numerical simulation

An appropriate theoretical model of a partially supported electrolysis experiment was presented in our previous chapter,⁵ avoiding the common assumption of electroneutrality often made in transient and steady state problems of this type.⁶⁻¹¹ Typically it was shown that a potential step chronoamperometry experiment can be modeled using the Nernst-Planck-Poisson (NPP) equations to generate concentration profiles of each species and the electric potential profile in solution. The electrode is

hemispherical in shape with radius r_e , so the relevant equations are formulated in terms of the radial coordinate, r . The electric potential, ϕ , is allowed to vary near the electrode surface, but it tends towards a value of zero as r tends towards infinity.

The following reaction mechanism is modeled in which a neutral species is oxidized to give a singly charged cation:



Both species A and B^+ are soluble, but only species A is present in bulk solution with concentration C^* . The charged species M^+ and X^- represent the dissolved supporting electrolyte, and both are present in bulk solution with concentration C_{sup} . A Butler-Volmer expression describes the rate of the electron transfer:

$$J = k^0 [B^+]_{r=r_e} \exp\left(\frac{-\alpha F}{RT} (E - E_f^\circ - \phi_e)\right) - k^0 [A]_{r=r_e} \exp\left(\frac{\beta F}{RT} (E - E_f^\circ - \phi_e)\right) \quad (3.3)$$

where J is the flux density of the electroactive species at the electrode, k^0 is a heterogeneous rate constant, α and β are charge transfer coefficients, E is the cell potential, E_f° is the formal cell potential, and ϕ_e is the potential at the point in solution immediately adjacent to the electrode surface (measured relative to the potential $\phi = 0$ in bulk solution).

The flux of a charged species, i , in solution is given by the Nernst-Planck expression, which contains terms of both diffusion and migration:

$$J_i = -D_i \frac{\partial C_i}{\partial r} - z_i D_i C_i \frac{F}{RT} \frac{\partial \phi}{\partial r} \quad (3.4)$$

where D_i is a diffusion coefficient of i , C_i is the local concentration of i , and z is the number of units charge on the migrating species. The time-dependence of each species is therefore given by the following mass transport equation:

$$\frac{\partial C_i}{\partial t} = D_i \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} + z_i \frac{F}{RT} \left(C_i \frac{\partial^2 \phi}{\partial r^2} + C_i \frac{2}{r} \frac{\partial \phi}{\partial r} + \frac{\partial C_i}{\partial r} \frac{\partial \phi}{\partial r} \right) \right) \quad (3.5)$$

At all times the electric field in solution must satisfy the Poisson equation:

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} = -\frac{\rho}{\epsilon_r \epsilon_0} \quad (3.6)$$

where ρ is the local charge density, ϵ_r is the dielectric constant of the medium and ϵ_0 is the permittivity of space. The charge density can be expressed in terms of the local concentrations of the charged species in solution:

$$\rho = F \sum_i z_i C_i \quad (3.7)$$

The concentration profiles of the various species in solution and the potential profile throughout solution can be found by using numerical methods to simultaneously solve Equations 3.5 and 3.6. This system of equations is collectively known as the Nernst-Planck-Poisson equations.

Table 3.1: Boundary conditions for the NPP equations.

Species / Potential	$r = r_e$	$r = r_e + 6\sqrt{Dt}$
A	Butler-Volmer	$C_A = C^*$
B^-	$J_A = -J_{B^-}$	$C_{B^-} = 0$
M^+	$J_{M^+} = 0$	$C_{M^+} = C_{\text{sup}}$
X^-	$J_{X^-} = 0$	$C_{X^-} = C_{\text{sup}}$
ϕ	$\frac{\partial \phi}{\partial r} = 0$	$\phi + r \frac{\partial \phi}{\partial r} = 0$

Table 3.1 shows the necessary boundary conditions for solving the NPP equations. The boundary conditions are applied at the electrode surface ($r = r_e$), and at a distance $6\sqrt{Dt}$ from the electrode surface, beyond which the electron transfer reaction has no effect on the solution concentrations.⁴ The boundary condition for ϕ at $r = r_e$ states that there is no electric field in solution at the electrode surface. In our previous paper, we modeled electron transfers using alternative boundary conditions that took account of the potential gradient at the electrode surface due to the electric double layer.⁵ However, it was shown that the condition in Table 3.1 is sufficient when modelling an electrode with a radius greater than $10 \mu\text{m}$ at times greater than 10^{-4} s. The model assumes that ϕ tends towards zero as r tends towards infinity. In our previous papers this condition was set explicitly by setting $\phi = 0$ in this limit,^{5, 12} but this approach required the simulation space to extend to infinity, far beyond the extent of the depletion layer thickness. However, since in the present paper we have a finite simulation space, we note that the electric field in the region $r_e + 6\sqrt{Dt} < r < \infty$ satisfies the following relationship,

which comes from the Poisson equation, noting that the solution is electroneutral in this region:

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} = 0 \quad (3.8)$$

Partially solving this differential equation subject to the condition $\phi = 0$ as $r \rightarrow \infty$ leads to the boundary condition in Table 3.1 at $r = r_e + 6\sqrt{Dt}$.

The NPP equations and the corresponding boundary conditions were discretized using the Crank-Nicolson finite difference method.¹³ The discretized equations were non-linear, so were solved using the iterative Newton-Raphson method. At each time step the flux of the electroactive species through the electrode surface was calculated from the concentration and potential profiles. The flux is related to the current, i , by the following expression:

$$I = 2\pi F r_e^2 J \quad (3.9)$$

The simulation programme was tested for convergence by ensuring that an increase in the number of spatial or temporal nodes lead to a negligible change in the simulated current. The local resistance of the medium is calculated via Ohm's law ($V = IR$).

3.2 Experimental

3.2.1 Chemicals

All solutions were made with acetonitrile solvent (MeCN, HPLC grade, Fisher Scientific), using ferrocene (>98%, Aldrich) as the electroactive species and tetra-n-butylammonium perchlorate (TBAP, $\geq 99\%$, Fluka) as supporting electrolyte. Electrode materials were obtained from Goodfellow Metals, Cambridge, UK with a purity $\geq 99\%$, and AgNO_3 ($\geq 99\%$) from Aldrich. All the chemicals were used without any further purification.

3.2.2 Electrochemical apparatus

A three electrode cell was used. The working electrode was made in-house by melting the end of a gold wire (of a diameter of $25\mu\text{m}$) in order to form a spherical bead. The wire was placed in a glass capillary and was sealed with wax in order to leave a hemispherical electrode. The electrode

was measured using an optical microscope to have a radius of $3.0 \pm 0.05 \times 10^{-2}$ cm. Three different solutions were used, each containing 3mM of ferrocene but with varying concentrations of supporting electrolyte (100, 1 and 0.1 mM of TBAP). The solution therefore had support ratios (C_{sup}) of 33.3, 0.333 and 0.033 respectively. Hereafter the solutions are identified by their support ratios.

The Ag/Ag⁺ reference electrode was made following the method of Wain et al.,¹⁴ in which a silver wire (Goodfellow) is immersed in solution of 20 mM AgNO₃ and 100mM of TBAP in MeCN, and placed in a glass tube with a porous frit. A bright platinum wire was used as a counter electrode.

All the electrochemical procedures were carried out using a μ Autolab type III (Eco Chemie, Utrecht, Netherlands).

3.3 Results and Discussion

Cyclic voltammetry (CV) was first recorded in the solution of $C_{sup} = 33.3$ (100mM TBAP) at a scan rate of 25 mV s⁻¹ to obtain a fully reversible response, and E_f° was obtained from the mid point of the forward and reverse peak potentials. A value of 97.6 mV vs. Ag/Ag⁺ was measured.

The chronoamperograms were next recorded by applying a potential step from open circuit to various potentials between 200 to 700 mV vs. Ag/Ag⁺. In preliminary work it was found that some minor electrode fouling occasionally occurred; to avoid this, a cleaning regime was used consisting of three cycles of potential steps of duration of 0.1 s between 0.0 V and -2.0 V, followed by rinsing in pure MeCN and replacement of the solution under investigation.

First, a chronoamperogram was recorded for the solution of $C_{sup} = 33.3$ by applying a potential step from open circuit to +500 mV vs. Ag/Ag⁺. The resulting transient is shown in Figure 3.1 A in the usual $I-t$ form and in Figure 3.1 D plotted as $\log(I)$ vs. $\log(t)$. Figure 3.1 D shows a linear region with a gradient of -0.5, which is as expected from the Cottrell¹⁵ equation (eq. 3.10) and describes the chronoamperometric response of a macroelectrode under diffusion-only (fully supported) conditions.

$$I = nFAC_i \sqrt{\frac{D_i}{\pi t}} \quad (3.10)$$

where I is the current, A is the electrode area, C_i is the bulk concentration of the electroactive species and D_i is its diffusion coefficient.

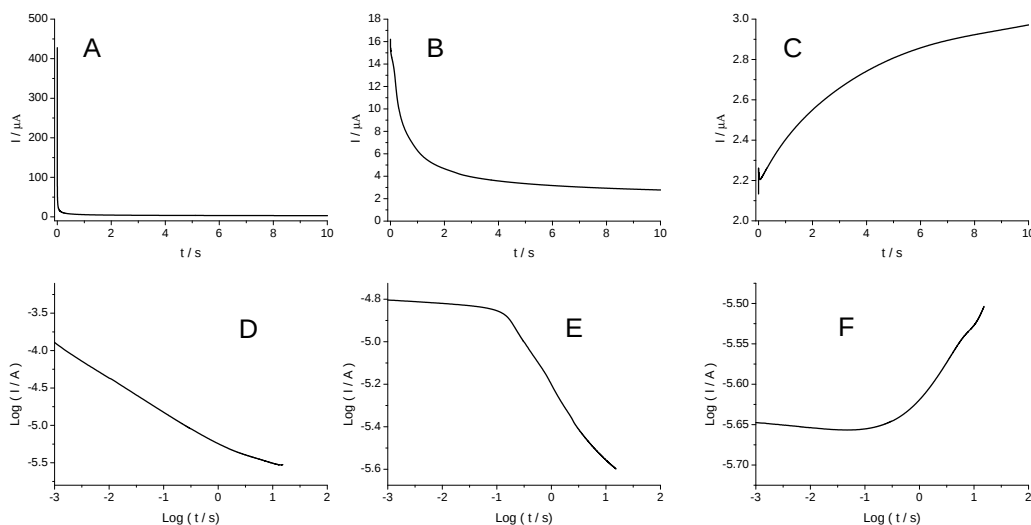


Figure 3.1: Experimental transients of the potential steps in I vs. t (A,B,C) and in $\log(I)$ vs. $\log(t)$ scale (D,E,F). The corresponding support ratios are: for A,D) $C_{sup} = 33.3$; B,E) $C_{sup} = 0.33$ and C,F) $C_{sup} = 0.033$. All transients were recorded with an applied potential of 500mV vs. Ag/Ag^+

Analogous experiments (potentials stepped to +500 mV vs. Ag/Ag^+) were conducted on the less supported solutions ($C_{sup} = 0.333$ and $C_{sup} = 0.033$), and it is clear that the results do not show Cottrellian behaviour at short times (Figure. 3.1 B and C), due to the lack of supporting electrolyte in the solution. Under high support ratios ($C_{sup} > 30$), the creation of charged ferrocenium cations at the electrode surface causes redistribution of the supporting electrolyte near the interface to maintain electroneutrality. When the support ratio is lowered, the fewer inert ions are less effective at preserving electroneutrality, and so a local electric field develops. The reduced availability of supporting electrolyte also leads to a marked reduction in the conductivity of the medium and increases potential drop within the solution overall, (Figure 3.1 E and F).

The potential step chronoamperometry was simulated using the model described in section 3.1, with appropriate parameters given in Table 3.2. In the absence of literature values the diffusion coefficients of TBA^+ and ClO_4^- were estimated by the Wilke-Chang expression.¹⁷ The comparison of the experiment and the simulation is shown in Figure 3.2, and excellent, quantitative agreement is apparent in all three cases.

We now turn to investigating the effects on the chronoamperometry of changing the concentration of supporting electrolyte. The simulated current responses, applied potentials and solution resistance are shown in Figure 3.3 for different supporting ratios.

Table 3.2: Values used for the numerical simulations

Parameter	Value	Source
k_0	0.99 cm s^{-1}	Clegg et al. ¹⁶
α	0.48	Clegg et al. ¹⁶
E_f^0	0.1 V vs. Ag/Ag ⁺	Section 6.3
D_{Fc}	$2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Clegg et al. ¹⁶
D_{TBA^+}	$1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Section 3.2.2
$D_{\text{ClO}_4^-}$	$3.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Section 3.2.2
r_e	$3.0 \times 10^{-2} \text{ cm}$	Section 3.2.2

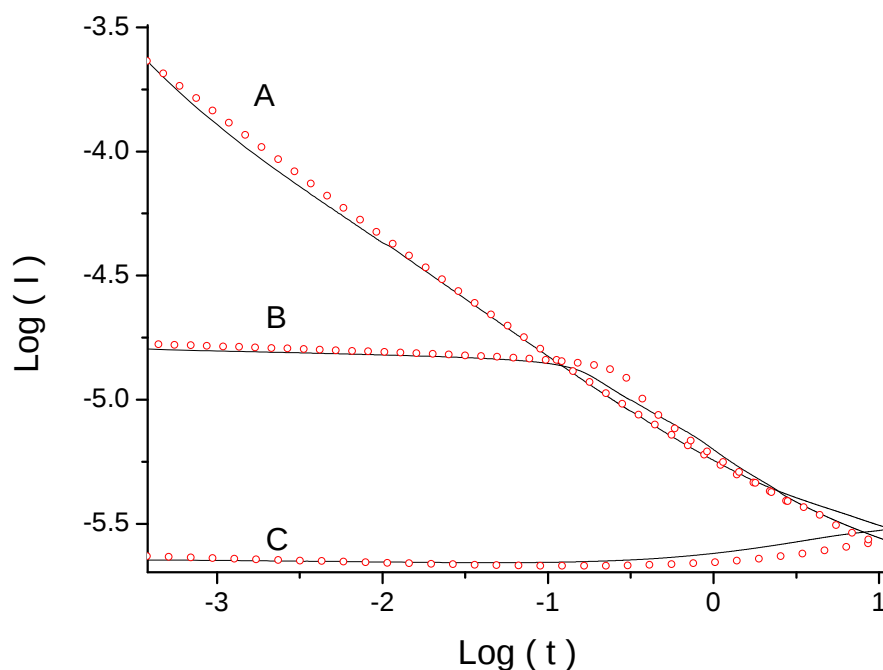


Figure 3.2: Comparison between simulation (circles) and experiment (solid line) for potential steps to +500mV vs. Ag/Ag⁺, A $C_{sup} = 33.3$, B $C_{sup} = 0.333$, and C $C_{sup} = 0.033$.

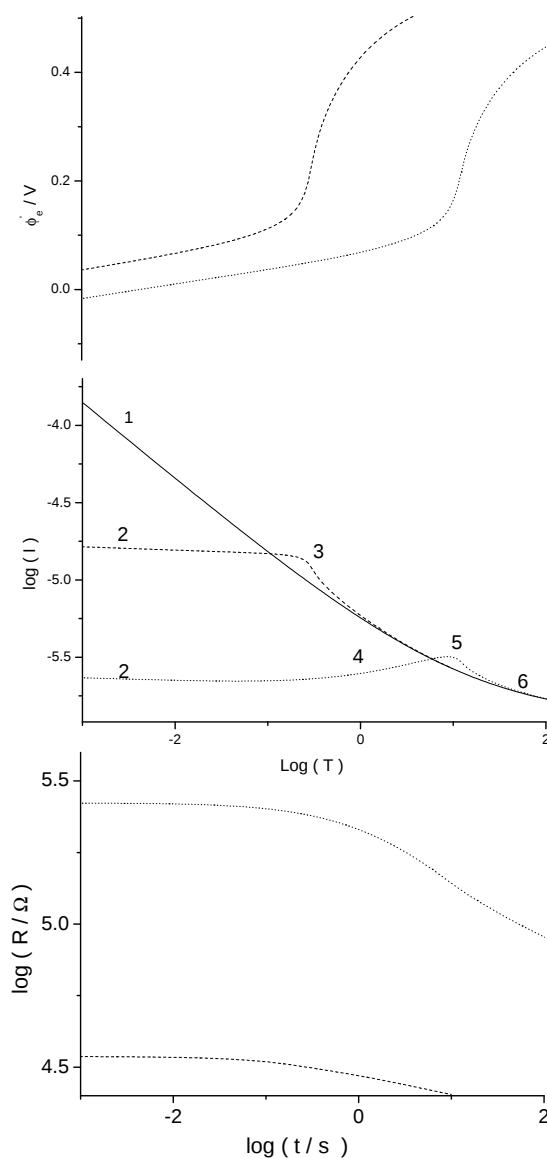


Figure 3.3: Simulated time profiles showing A) the potential in the solution adjacent to the electrode ϕ_e' , B) the current response, and C) the resistance of the medium, for solutions $C_{sup} = 33.3$ (—), $C_{sup} = 0.333$ (---), and $C_{sup} = 0.033$ (···). The numerical labels indicate regions of interest showing the effects : 1) Cottrellian flux, 2) potential drop controlled, 3) starting point of diffusion controlled regime, 4) decreasing of the potential drop, 5) purely diffusional behaviour.

As we have seen, a macroelectrode chronoamperometric response adopts Cottrellian (i.e. diffusion-only) behaviour when the relative concentration of supporting electrolyte is high (Figure 3.3 line 1), but that this breaks down when the concentration of supporting electrolyte falls to values approaching or lower than that of the electroactive species itself. In this latter case, there are fewer ions in the solution to disperse the charge created by the reaction at the electrode. Potential loss in solution therefore becomes dominant, and so at short times ($t \sim 10^{-3}$ s) the potential in solution adjacent to the electrode surface (ϕ_e)⁵ is controlled mainly by the potential loss through the solution. Simulations in Figure 3.5 show that varying the electron transfer kinetics has no significant effect on timescales longer than 10^{-5} s for a potential step to +600 mV in either $C_{sup}=0.333$ or $C_{sup}=0.033$.

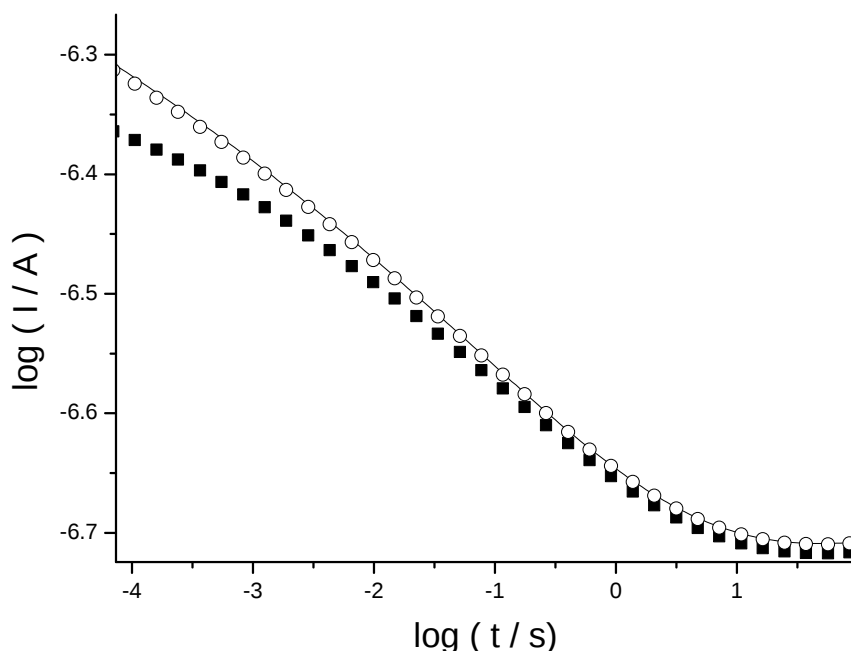


Figure 3.4: Sensitivity to electron transfer kinetics at an overpotential of -20 mV in $C_{sup} = 0.033$. Values of k^0 in cm s^{-1} are 1 (—), 0.1 ($\circ$), and 0.01 ($\blacksquare$).

Figure 3.4 shows that even at very low overpotentials (in this case -20 mV) in $C_{sup}=0.033$, there is no significant difference in the transient response for k^0 between 0.01 and 1 cm s^{-1} . The resulting current-time behaviour is an interplay between the interfacial potential and the resistance of the medium (Figure 3.3, region 2 in A),B) and C)). There is therefore no realistic possibility of detecting fast kinetics at a macroelectrode by lowering the supporting electrolyte ratio, and electrode size would

need to be reduced by at least a factor of 10 to begin to observe kinetic discrimination.

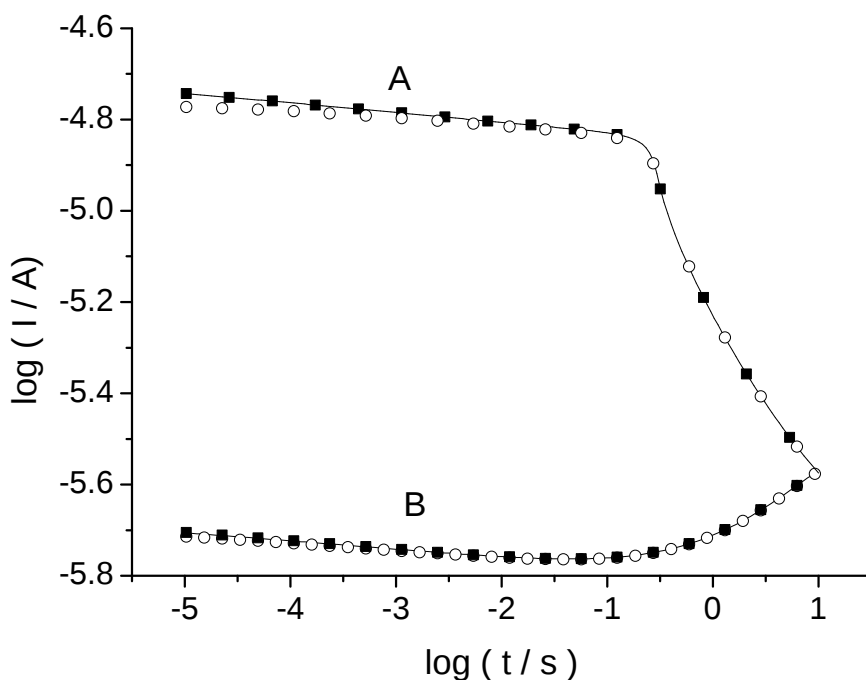


Figure 3.5: Comparison between simulations for potential steps to +600mV vs. Ag/Ag⁺, for A) $C_{sup} = 0.333$, and B) $C_{sup} = 0.033$. Values for k^0 in cm s^{-1} are 10 (■), 1.0 (—), and 0.1 (○)

Immediately after the potential step the cell potential is +0.5 V with respect to the reference electrode. The diffuse double layer cannot form and respond immediately to this change in potential, but there is now a potential gradient that extends far into solution. The potential profiles in Figure 3.3,A) show that after the potential step, the value of ϕ'_e at the place in which the reaction takes places is less than E_f° (where ϕ'_e is the same property as ϕ_e except that it is measured relative to the reference electrode rather than bulk solution), so there is very little potential driving force for the electron transfer. After some time, (approximately 0.1 and 3 s for $C_{sup} = 0.333$ and 0.033 respectively), mass transport of the charged species has led to an excess of ClO_4^- and a depletion of TBA^+ ions near the electrode. This has distorted the electric field so that it is largely constrained to the region close to the electrode, although there is still a significant potential gradient at larger distances, such that migration will contribute to the mass transport of the charged species. The value of ϕ'_e is now greater than E_f° , so there is significant oxidation of ferrocene at the electrode. This creates a depletion layer of the electroactive species extending into solution, whilst the electroinactive species TBA^+ will have

migrated away from the electrode. The growing depletion layer and its resulting concentration gradient drives diffusional mass transport, which rapidly becomes the dominant factor in determining the current-time response. Hence by point 3 in Figure 3.3,B) the current transient begins to adopt a diffusional character and tends to Cottrellian behaviour for longer times (point 5 in the same figure).

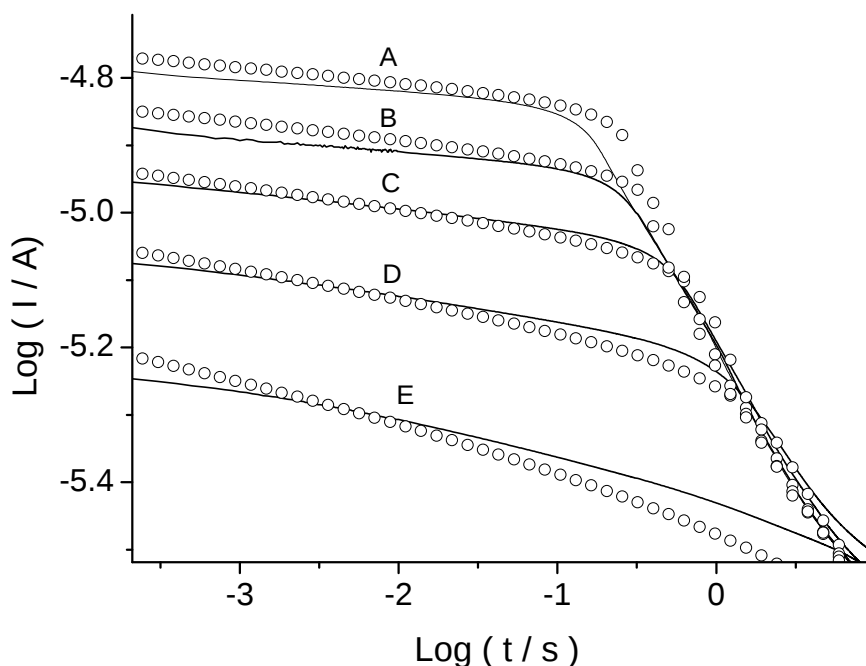


Figure 3.6: Experimental (solid line) and simulated (circles) chronoamperograms for $C_{sup} = 0.333$, varying the applied potential from 600, 500, 400, 300 and 200 mV vs. Ag/Ag⁺, labeled A, B, C, D, E respectively.

The changeover from potential drop limiting behaviour and diffusion-limiting behaviour can be observed in Figure 3.6, which shows both experimental and simulation data for the chronoamperometric responses for a variety of applied potentials for a solution containing a support ratio of 0.33. It can be seen that the changeover point (marked by the sharp change in gradient of the plot) moves to shorter times as the applied over potential increases. This is as expected since when the current is higher the depletion zone grows faster, driving diffusional mass transport earlier and reaching the point of diffusion control in less time than where a lower potential is applied.

. Finally, Figure 3.7 shows how the cyclic voltammetric response is affected by the potential drop in the solution. The potential drop causes a delay in the voltammetric response, making it appear increasingly more irreversible as the concentration of supporting electrolyte drops. As we have seen

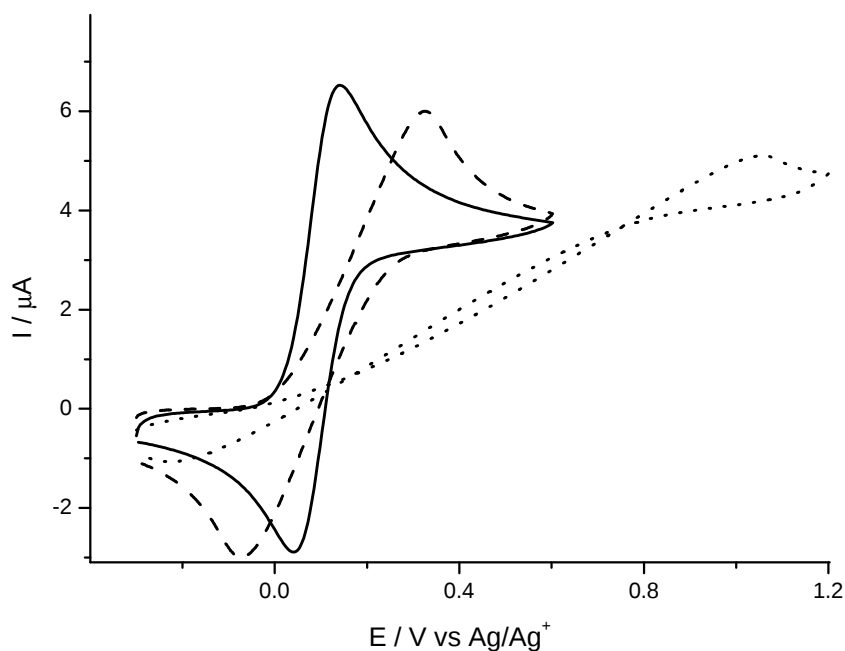


Figure 3.7: Cyclic Voltammetry at different ratios of supporting electrolyte, $C_{sup} = 33.3$ (Solid line), $C_{sup} = 0.333$ (Dashed line) and $C_{sup} = 0.033$ (Dotted line). Voltage scan rate used was 200mV s^{-1}

previously in the chronoamperometry (Figure 3.3 C), the potential drop in the solution is not constant at all times, moreover is decreasing as the ions migrate closer to the electrode to neutralize the electric field created in the solution. This effect can be seen in Figure 3.7 where there is overlapping of the current in the potential drop controlled region for the experiment with the lowest supporting ratio.

3.4 Conclusions

It has been demonstrated that the model presented in this thesis using the Nernst-Planck-Poisson equations without electroneutrality could be applied to real electrochemical systems of interest either under dynamic conditions or at steady state. The model has been highly successful in quantitatively predicting and explaining interesting features of experiments in poorly and fully supported media.

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Chapter 4

Chronoamperometry of reduction of charged electroactive species at various concentrations of supporting electrolyte

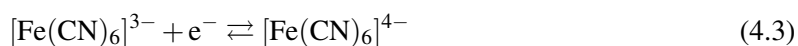
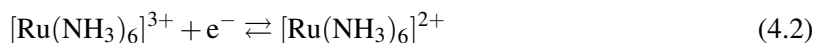
In an electrochemical reaction at the electrode-solution interface, charge is exchanged between the electrode and the electroactive species in solution; the loss/gain of charge from the electrode in solution is rapidly compensated by the movement of charged species within solution in a way that tends to dissipate the electric field. A common practice is to add large quantities of charged species (supporting electrolyte) to the solvent to better disperse the charge created by the electrochemical reaction, and by doing so, avoid the creation of an electric field in solution that would cause voltammetric distortions.

When an experiment lacks sufficient supporting electrolyte, the charged species present are not able to fully disperse the charge created by the electrochemical reaction. This causes a potential drop in the solution, and transport by migration, resulting in distortions to the observed voltammetry and deviations from the behaviour calculated for diffusion-only conditions. Quantitative voltammetry has been almost exclusively restricted to ‘supported’ conditions although this creates an ‘artificial’ medium in many cases. The interest for studying systems with low electrolytic support lies in the features and applications of electrochemistry under these conditions; for example to avoid complexation,¹ to study weak and strong acids,^{2,3} Ion paring,⁴ biological systems, and for non-aqueous electrochemistry.⁵ In addition, any study of electrochemical processes at the nanoscale requires a detailed understanding of coupled diffusion and migration.^{6,7}

Previous studies have investigated some of the features of insufficient supporting electrolyte with the explicit assumption of electroneutrality, which is a reasonable approach under steady state conditions,^{8–12} but lacks the necessary precision to study dynamic conditions such as apply in chronoamperometry or cyclic voltammetry.

In the previous chapter transient chronoamperograms for the reduction of a neutrally charged specie were presented, in the present chapter we present the influence and contribution of migration

of charged electroactive couple. Recently, experimental studies have achieved direct experimental evidence of migration.¹⁴ In the present work we consider the impact of weak or zero support on a wide range of electrochemical systems, focusing exclusively on redox couples involving the gain of one electron, but examining a wide range of charges and comparing the experimental cases of cobaltocenium/cobaltocene in acetonitrile, hexaammineruthenium (III/II) in water, and hexacyanoferrate (III/II) in water, as shown below.



We seek to provide a general understanding of the features induced by the absence of supporting electrolyte in solution by comparing and contrasting the differently charged electroactive species in order to derive new physical insights into the effects of coupled diffusion-migration as a function of species charge. It is anticipated that the mass transport to the electrode is increased by ‘attractive’ migration when a positive charged electroactive species is reduced. Conversely, when a negatively charged species is reduced, the migration is ‘repulsive’ and the mass transport to the electrode is expected to decrease. Using the Poisson equation removes the constraint of electroneutrality, and so we are able to more accurately assess the manner in which the charge generated by the electrolysis is dispersed in solution. We find that contrary to the traditional point of view, deviations from electroneutrality are maintained at experimentally significant length and time scales.

4.1 Theoretical model

In a recent study, Streeter et al.¹³ applied the Nernst-Planck-Poisson system of equations to weakly supported voltammetry to simulate transient conditions and showed that there is no need to simulate the double layer to obtain reliable simulations under transient conditions for single potential step chronoamperometry, provided that the electrode is larger than nanoscale.⁷ For the present chapter a

similar simulation procedure is used as the one presented in the previous chapters.

The following mechanism is modeled:



in which A and B are the electroactive species in solution, z is the charge of the initially present electroactive species and n is the number of electrons transferred. For this particular chapter, $n = \pm 1$, and the reaction is supported by a concentration C_{sup} of a monovalent inert species M^+X^- . It should be noted that A and B are the same molecule, but are labeled differently for clarity of notation in the following sections.

The flux of the species in solution is modeled using the Nernst-Planck equation

$$\mathbf{J}_i = -D_i \left(\nabla C_i + \frac{z_i F}{RT} C_i \nabla \phi \right) \quad (4.5)$$

where for species i , $\mathbf{J}_i$ is the flux vector, D_i is the diffusion coefficient, C_i is concentration, z_i is the species charge, ϕ is potential, F is the Faraday constant, R is the gas constant and T is the absolute temperature. The first term describes the contribution of diffusion to the flux and the second corresponds to the migration induced by electrostatic forces. The migration influences all the charged species, so the simulation has to consider not just the electroactive species, but also the supporting electrolyte species.

To calculate the electric field in solution, the Poisson equation is solved simultaneously with the Nernst-Planck equation:

$$\nabla^2 \phi = -\frac{F}{\epsilon_s \epsilon_0} \sum_i z_i C_i \quad (4.6)$$

where ϵ_s is the dielectric constant of the solvent and ϵ_0 is the permittivity of free space.

The flux of a species as a function of time is then calculated by the continuity equation

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{J}_i \quad (4.7)$$

The heterogeneous reaction rate at the electrode is controlled by the Butler-Volmer expression.

$$\left. \frac{\partial C_A}{\partial r} \right|_{r=r_e} = k^0 \left(\exp \left(\frac{-\alpha F}{RT} (E - E_f^0 - \Delta\phi_{PD}) \right) C_{A,0} - \exp \left(\frac{(1-\alpha)F}{RT} (E - E_f^0 - \Delta\phi_{PD}) \right) C_{B,0} \right) \quad (4.8)$$

where $C_{i,0}$ is the concentration of the species i at PET(plane of electron transfer), E_f^0 is the formal potential of the couple, k^0 is the standard electrochemical rate constant, and α is the transfer coefficient. The other appropriate boundary conditions for the solution of these equations are as in Table 1.

4.2 Experimental

All aqueous solutions were made with ultra pure water with resistivity $> 18.2 \text{ M}\Omega \text{ cm}$ at 298 K, and non-aqueous solutions were prepared with acetonitrile (MeCN, HPLC grade, Fisher Scientific).

Hexaammineruthenium(III) chloride ($> 98\%$, Aldrich), cobaltocenium hexafluorophosphate ($> 98\%$, Strem Chemicals), potassium hexacyanoferrate(III) ($> 98\%$, Aldrich), potassium nitrate ($> 99\%$, Aldrich) and tetra-butylammonium hexafluorophosphate (TBAP; $> 99\%$, Fluka) were used as purchased and without any further purification.

For this part, two different Pt planar working electrodes (WEs) of radii $r_e = 0.2 \text{ cm}$ and $r_e = 0.05 \text{ cm}$ were used (areas of 0.126 cm^2 and 0.00785 cm^2 respectively). Two reference electrodes were used, depending on the solvent under study: a saturated calomel electrode for water and a Ag/Ag^+ electrode for MeCN (prepared in agreement with the procedure of Wain et al.¹⁵). A platinum wire of large surface area was used as a counter electrode. A $\mu\text{Autolab}$ type III (EcoChemie, Utrecht, Netherlands) potentiostat was used throughout.

All solutions were thoroughly degassed with N_2 (BOC, High Purity Oxygen free) before starting each experiment and performed under thermostatic control at $298 \pm 1 \text{ K}$ using a water bath.

4.3 Results and Discussion

4.3.1 Theoretical results

Single potential step chronoamperometry was simulated using the theoretical model described in previous chapters: simulations were performed in which the working electrode is stepped from open

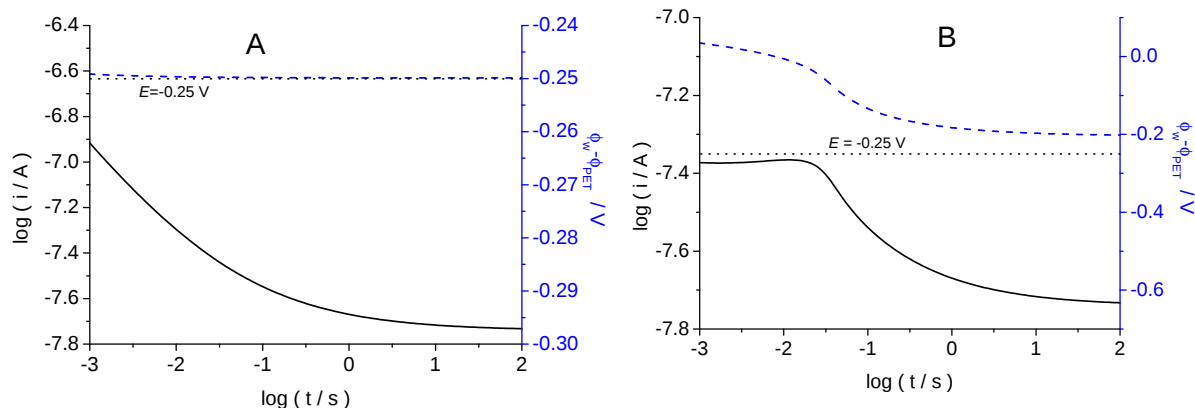


Figure 4.1: Simulated potential step chronoamperograms for a neutral electroactive species. In (A), there is a high support ratio $c_{\text{sup}} = 200$, and in (B) a low support ratio $c_{\text{sup}} = 0.1$. In both cases, $\Delta\phi_{\text{PD}}$, the potential difference arising between the reference and working electrodes (dashed line), and E , that applied, vs. the reference electrode, at the working electrode (dotted line), are shown. The current-time response to the potential step is shown as a solid line.

circuit to a potential, E_1 , at which electron transfer occurs rapidly, under two different concentrations of supporting electrolyte (Figure 4.1).

The first system chosen for study was the single electron reduction of an electroactive neutral species with a formal potential set at $E_f^0 = 0$ V, and fast kinetics set as $k^0 = 1 \text{ cm s}^{-1}$.



This case was selected initially on the basis of it being the simplest to understand; more complicated cases will be examined in due course.

The additional parameters used for simulating the chronoamperometry are given in Table 4.1, together with a concentration of 600 mM supporting electrolyte, and an overpotential $E_1 - E_f^0$ of 250 mV. Figure 4.1 A shows the resulting current time response, which obeys the Cottrell equation¹⁶ (which is an analytical solution for the purely diffusional flux to an electrode under fast kinetics), so proving the purely diffusional behaviour of this simulation with respect to the electroactive species. The potential drop through the solution is very small compared to the applied overpotential, which is therefore approximately constant. There is negligible distortion to the concentration profiles of the supporting species compared to their bulk concentration. This is because high concentrations of supporting electrolyte confer the solution with high charge mobility compared to the charge exchanged at the in-

interface. Therefore the exchanged charge is easily dispersed in the solution and the potential is almost constant throughout it.

Parameter	Value
C_A	3mM
k^0	1 cm s^{-1}
D_A	$1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
D_B	$1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
D_{M^+}	$1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
D_{X^-}	$1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
r_e	$10 \times 10^{-4} \text{ cm}$

Table 4.1: Values used for the numerical simulation

Figure 4.1 B shows another chronoamperogram, simulated as above, but with the supporting electrolyte concentration decreased to 0.3 mM. The solution does not possess such high levels of charged species, and when charge is exchanged between the electrode and the solution all the charged species are significantly attracted/repelled due to migration, modifying their concentrations and creating a potential drop through the solution. This potential drop is considerable and affects the rate of electron transfer. As time passes, the positively charged supporting species (i.e. those with opposite sign to the charge generated by the reaction) accumulates near to the electrode, reducing the local resistivity of the solution and increasing the potential difference experienced by the species at the PET. In turn this increases the observed rate of electron transfer, until mass transport (diffusion and migration) becomes rate limiting due to the depletion of electroactive species at the electrode surface. At this point the potential drop decreases considerably, due to the decrease of the flux of electroactive species to the electrode.

Figure 4.2 shows concentration profiles computed for the chronoamperogram in Figure 4.1 B. At a time of 10^{-3} s (t_a) the potential difference at the electrode interface ($\phi_{\text{PET}} - \phi_w$) is smaller than E_f^0 due to the potential drop in solution ($\Delta\phi_{\text{PD}}$). The electroactive species are in equilibrium at the interface, since kinetics are fast, but are equilibrated at a low interfacial potential difference compared to that applied (Figure 4.2, t_a), with a surface reactant concentration of 2.3 mM and product concentration of 0.5 mM. As the solution becomes negatively charged due to the reaction, the migrating

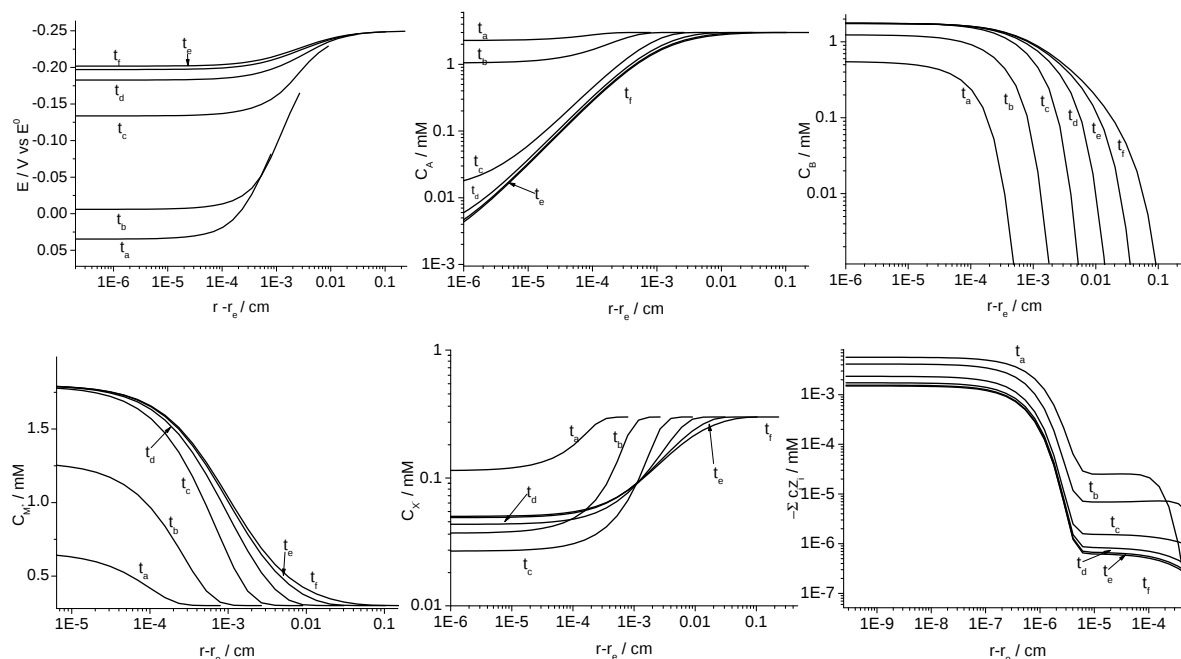


Figure 4.2: Simulated profiles for the chronoamperograms in figure 2B at different times ($t_a = 10^{-3}$ s, $t_b = 10^{-2}$ s, $t_c = 10^{-1}$ s, $t_d = 1$ s, $t_e = 10$ s). (A) shows the variation of potential with distance from the electrode, and the other plots are concentration profiles of reactant (B), product (C), positive supporting species (D), negative supporting species (E), and uncompensated charge concentration (F).

positive ions concentrate near to the electrode, and the concentration of negative ions is reduced near to the electrode. As the reaction proceeds the local charge mobility in solution near the electrode increases because of the increased concentration of charged species (both electrolytically generated and supporting species). The potential difference at the interface increases due to reduced potential drop and the equilibrium between product/reactant then lies more to the product side, until the mass transport (diffusion and migration) due to the depletion layer becomes rate-limiting. At this point the potential drop through the solution lowers considerably. Then the negative ions disperse back to near to the electrode but the concentration of positive ions remains high (more than 8 times the bulk concentration) in order to disperse the charge exchanged at the interface.

Figure 4.2 F shows the differences of the charge in solution with distance from the electrode, illustrating that the principle of electroneutrality is not followed. At short times following the potential step, the magnitude of the uncompensated charge in solution is about one tenth of the concentration of supporting electrolyte, and although previous studies⁸⁻¹¹ have used this electroneutrality approximation it is clear that it is not obeyed, and that even at relatively long times (t_e , 100 s) there is not

exact electroneutrality within a distance of 10^{-3} cm from the electrode interface (Figure 4.2).

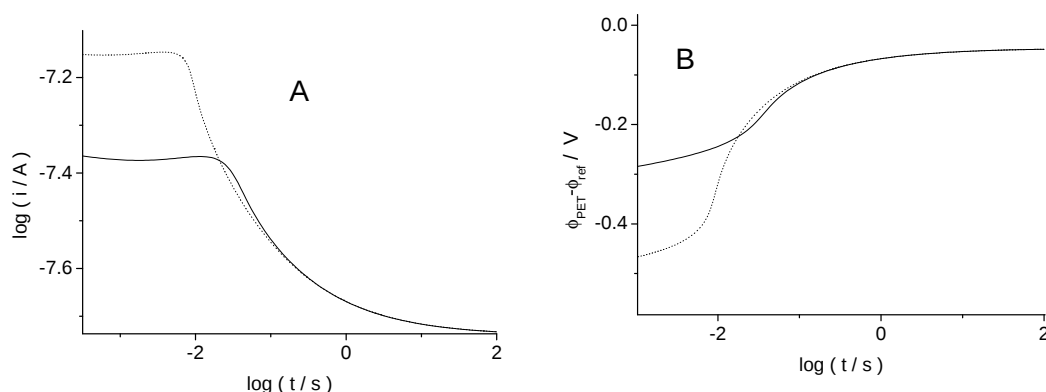


Figure 4.3: Simulated potential steps using the parameters in Table 4.1 with overpotentials of 200 mV (solid line) and 300 mV (dotted line). (A) shows the current transients, and (B) the potential drop vs. time.

As previously explained, the potential drop through the solution decreases the actual potential difference at the interface, which also is a function on the overpotential applied to the system. The real applied potential ($\phi_w - \phi_{PET}$) reflects a balance between the current driven and the potential loss. The higher the potential applied between the electrode and the reference, the higher the potential applied at the interface, and therefore higher currents are expected causing greater potential drop through the solution (Figure 4.3).

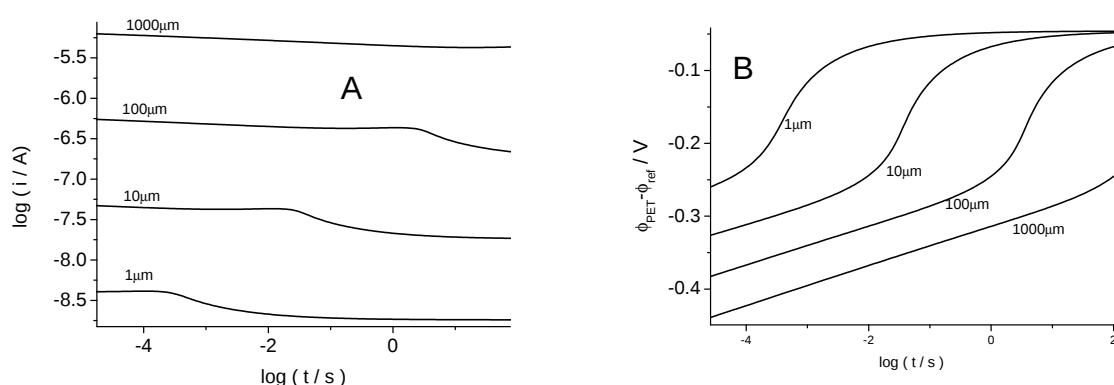


Figure 4.4: Simulated potential step responses with varying electrode size (radius stated on the figure). (A) shows the current-time transient, and (B) the potential drop vs. time

It has been widely observed since the development of the microelectrode (see for example Mon-

tenegro⁸ and references therein) that the potential drop is highly dependent on the electrode size.^{18,19} Smaller electrodes are better able to disperse the charge in solution than large electrodes, and therefore their potential drop is smaller and the temporal region controlled by this potential drop is shorter. Figure 4.4 B shows the variation of the potential drop with time, and it is clear that at small electrodes the potential drop decreases at a faster rate than for larger electrodes.

In Figure 4.4 A, in the region ($t < 10^{-3.5}$ s) where the potential drop is the controlling factor ($E_f^0 > \phi_w - \phi_{PET}$), the current response is sensitive to the electrode kinetics. Where the kinetics are fast the potential drop has only to decrease a little to make a large change in charge transfer rate (and hence the observed current) whereas if the kinetics are slow a large change in potential drop gives only a very small difference in the rate of charge transfer. Consequently, one could observe kinetic effects, depending on the dispersion of the uncompensated charge (figure 4.5). Using a small electrode the charge created by the reaction is dispersed faster and the effect on the chronoamperometry due to kinetics is observable even at high values of k^0 , whereas in larger electrodes these effects are negligible due to the slow rate of dissipation of charge.

Due to the charge transferred at the electrode surface, electrically charged species will migrate to distort the charge. The migration will be present in all systems, but if large amounts of supporting species are present compared to the quantity of electroactive species, the migration of the electroactive species can be small enough to consider that its transport approaches the purely diffusional limit. In a system with a low concentration of supporting electrolyte, however, the added species are less able to distort the charge distribution and so the migration of the electroactive species will be comparable to its rate of diffusion. To explore this, the following part presents a study on differently charged electroactive species to obtain a general understanding of migration and potential drop under transient conditions. Chronoamperograms for different reductions are presented in Figure 4.6, each one with a differently charged electroactive species ($z=+3,+2,+1,0,-1,-2$, A to F respectively), simulated according to the parameters in Table 4.1, and with no extra supporting electrolyte except for Case D, where a supporting electrolyte concentration of 0.3 mM is input into the simulation, as the species is neutral.

Whilst the following considers the case of electrochemical reduction, the results can be easily interpreted for oxidations because the key factor is the absolute charges on the reactant and product. For example, the reduction process that decreases the charge on the reactant from 2 to 1 gives numerically exactly the same current-time behaviour, but with opposite sign, than the oxidation that increases the

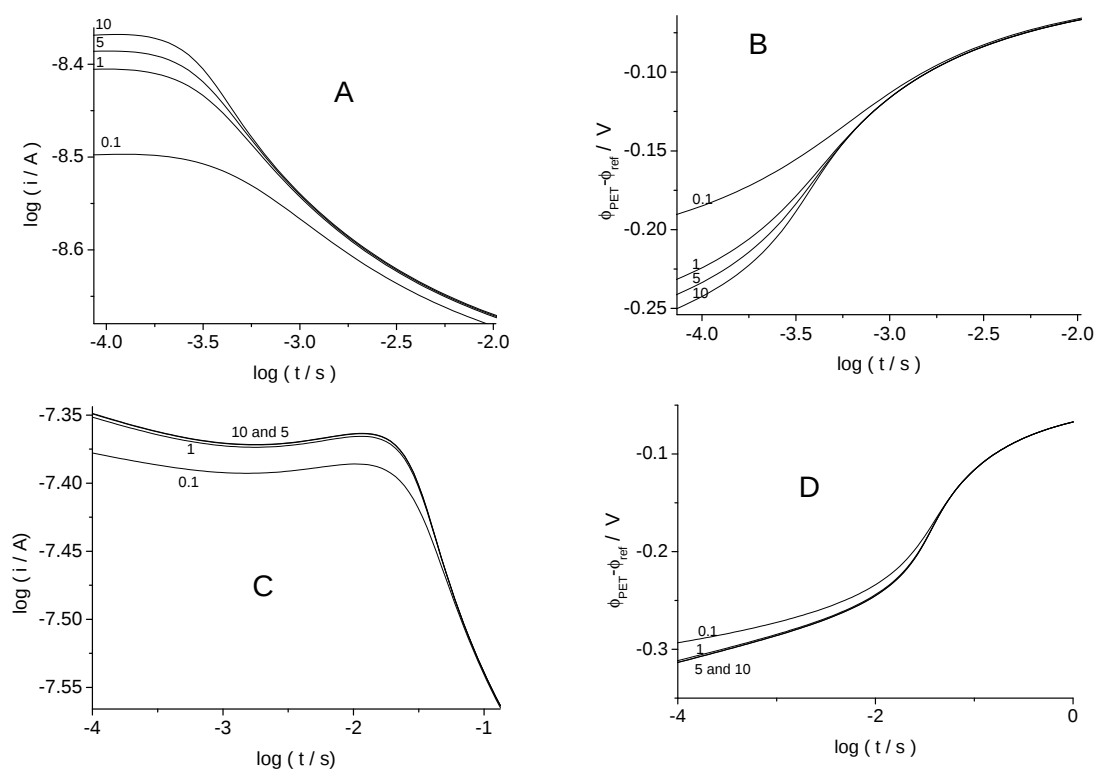


Figure 4.5: The influence of kinetics on weakly supported chronoamperometry for two different electrode radii $1\mu\text{m}$ (A and B) and $10\mu\text{m}$ (C and D), varying k^0 between 0.1 , 1, 5 and 10 cm s^{-1} as stated in the image. (A) and (C) show current-time transients and (B) and (D) show potential drop vs. time.

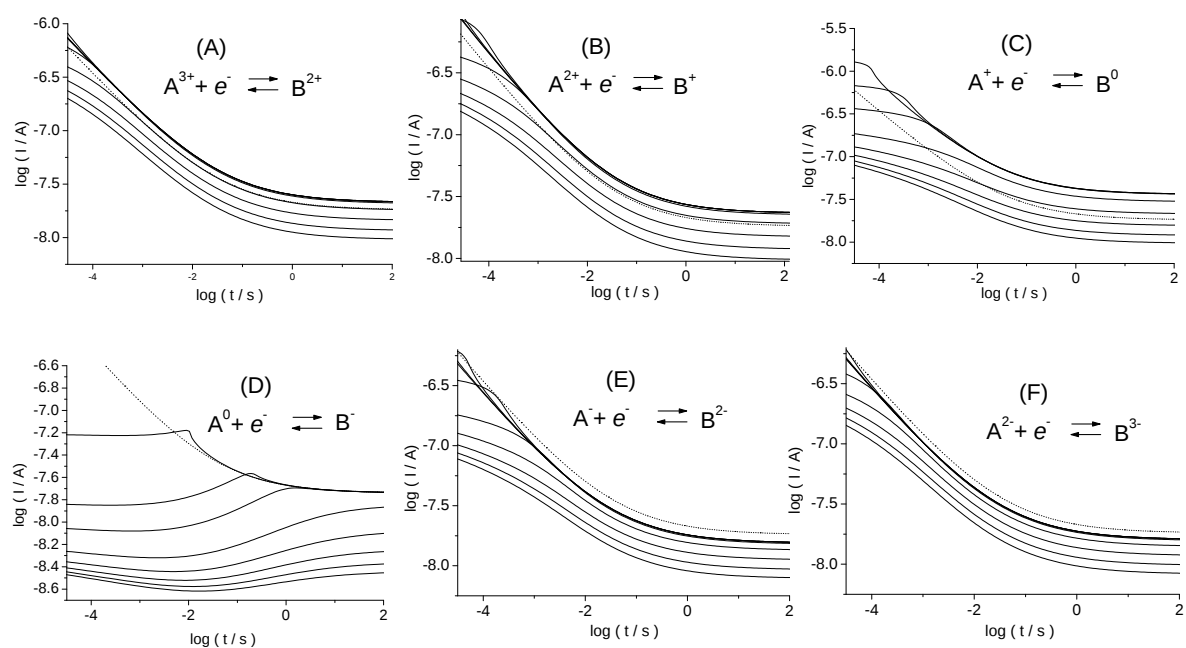


Figure 4.6: Potential steps for differently charged electroactive species over a range of applied overpotentials, E_1 , of 0, 0.01, 0.025, 0.05, 0.1, 0.5, 1 and 2 V, compared with fully supported chronoamperometry (dotted line).

charge carried by another reactant from -2 to -1, and if the diffusion coefficients of all species are all equal, the electrostatic attraction and migration rates of all the species will be the same.

In the reduction of a positively charged electroactive species or the oxidation of a negatively charged electroactive species (Figure 4.6 A, B and C) it is observed that the current is higher (solid lines) than for purely diffusional mass transport (dotted lines). Since the electroactive species has positive charge and the solution is accumulating negative charge (due to the reaction), the electroactive species is attracted by migration to the electrode, which increases its incident flux and hence the current.

In the case of a neutral electroactive species either being oxidized or reduced, its mass transport to the electrode remains purely diffusional as a neutral electroactive species cannot be attracted or repelled by migration (Figure 4.6 D). This case exhibits a much more extensive potential drop effect, as it cannot be self-supported, and the concentration of added supporting ions in solution is much less than the concentration of counter ions in the other cases. Certain unusual features of this extended potential drop regime for very weakly supported chronoamperometry, including minima in the observed Faradaic current, in the previous chapter.

In the reduction of a negatively charged electroactive species or a oxidation of a positively charged electroactive species (Figure 4.6 E and F), the charge of the electroactive species has the same sign as the charge accumulated in solution. Therefore, repulsive migration will decrease the mass transport of the electroactive species to the electrode surface and the current is correspondingly decreased.

The steady state currents from the previous simulations are compared in Figure 4.7 with the values obtained by Oldham¹¹ with a good agreement between the NPP model and the electroneutral model at the limiting overpotential values.

Figure 4.7 shows that cases with less supporting electrolyte (less self-supporting electrolyte) have greater mass transport due to migration. For example, a electroactive species with charge of +3 under self-supported conditions (with 3 singly charged counter ions), increases its mass transport to the electrode by 17%, but for the singly charged species with just a single counter ion, the mass transport is increased by a factor of 200%.

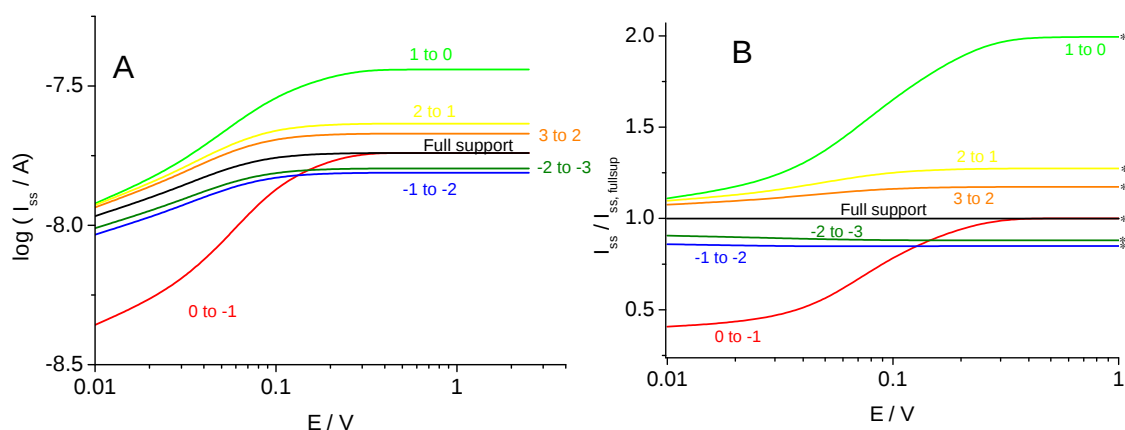


Figure 4.7: Steady state currents at different applied overpotentials for different electroactive species, and normalized (to full support currents) steady state currents. The limiting values are compared (*) with the previous study by Oldham¹¹ (see main text).

4.3.2 Experimental results and discussion

	Hexaammineruthenium(III/II)	Cobaltocenium/cobaltocene	Hexacyanoferrate(III)/(II)
Solvent	Water	Acetonitrile	Water
E_f^0	-0.20 V vs. SCE ^(20,21)	-1.2 V vs. Ag/Ag ⁺ ⁽²³⁾	0.22 V vs. SCE
k^0	0.7 cm s ⁻¹ ^(20,21)	1 cm s ⁻¹ ⁽²²⁾	0.6 cm s ⁻¹
D_A	0.85×10^{-5} cm ² s ⁻¹ ^(20,21)	2.3×10^{-5} cm ² s ⁻¹ ⁽²³⁾	0.6×10^{-5} cm ² s ⁻¹ ^(20,21)
D_B	0.85×10^{-5} cm ² s ⁻¹ ^(20,21)	2.3×10^{-5} cm ² s ⁻¹ ⁽²³⁾	0.6×10^{-5} cm ² s ⁻¹ ^(20,21)
D_{M^+}	1.8×10^{-5} cm ² s ⁻¹ ⁽²⁴⁾	3.0×10^{-5} cm ² s ⁻¹ *	1.8×10^{-5} cm ² s ⁻¹ ⁽²⁴⁾
D_{X^-}	1.8×10^{-5} cm ² s ⁻¹ ⁽²⁴⁾	2.1×10^{-5} cm ² s ⁻¹ *	1.8×10^{-5} cm ² s ⁻¹ ⁽²⁴⁾

Table 4.2: Values used for the comparison between experiment and theory. * Values estimated by Wilke-Chang Method

In order to corroborate the theory, experiments were performed for different processes using standard electrochemical reagents known to display fast electron transfer, namely hexaammineruthenium(III) chloride, potassium hexacyanoferrate(III) and cobaltocenium hexafluorophosphate. Single potential step chronoamperometry was performed by stepping from open circuit to a potential, E_1 , at which electron transfer occurs rapidly, and the current-time response was compared with simulated chronoamperograms produced according to the model previously described. Diffusion coefficients

for the electroactive species were established by chronoamperometry, using the Cottrell equation, and by cyclic voltammetry at varying scan rate, using a Randles-Ševčík plot, both under fully supported conditions. In all of the simulations, it was approximated that the diffusion coefficients for the electroactive species at full support and those in the weakly supported solutions were equivalent; that is, that the effect of viscosity on the diffusion coefficients is negligible.

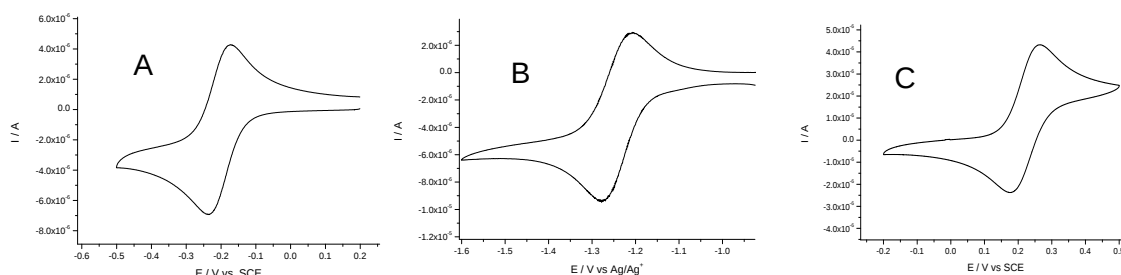


Figure 4.8: Cyclic voltammetry at a scan rate of 100 mVs^{-1} at a planar platinum electrode with $r_e=0.5 \text{ cm}$ of: (A) 3mM hexaammineruthenium(III) chloride and 600mM of potassium nitrate; (B) 3mM cobaltocenium hexafluorophosphate and 600 mM of tetrabutylammonium hexafluorophosphate; and (C) 3mM potassium hexacyanoferrate(III) and 600 mM of potassium nitrate.

Hexaammineruthenium(III/II)

First, cyclic voltammetry was performed using a platinum electrode in an aqueous solution containing 3 mM of hexaammineruthenium(III) chloride and 600 mM of potassium nitrate (i.e. fully supported conditions). A reversible cyclic voltammogram was obtained at a scan rate of 100 mV s^{-1} with a reversible peak-to-peak separation of ca 60 mV (Figure 4.8), which enabled a formal potential, E_f^0 , of -0.20 V (vs SCE) to be determined which was found to be in agreement with literature values.^{20,21} The diffusion coefficient was calculated by a Randles-Ševčík plot using cyclic voltammograms with scan rates of 100, 200, 500 and 1000 mV s^{-1} , and a value of $8.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ obtained.

Next, chronoamperometry was performed in this solution using both sizes of platinum electrode, by stepping the potential from open circuit to -350 mV vs SCE (i.e. an overpotential of ca 150 mV). The recorded chronoamperogram is shown in Figure 4.9 (in a logarithmic scale), and shows a typical diffusion-only response with a logarithmic gradient of -0.5 in accordance with the Cottrell equation. A value for the diffusion coefficient was determined from this plot to be $8.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, again in good agreement with literature values.^{20,21}

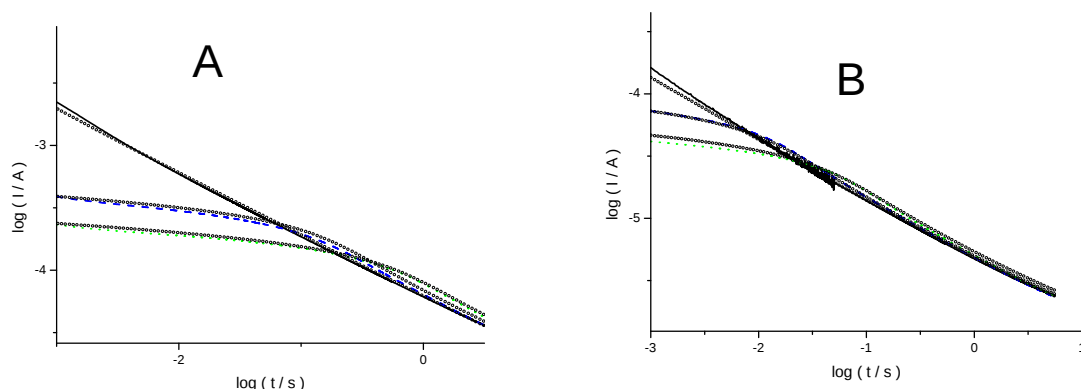


Figure 4.9: Comparison between experiment (lines) and simulation (circles) for the hexaammineruthenium(III/II) couple, with applied potentials of -0.350 V vs SCE and different concentrations of supporting electrolyte: 600mM (line), 30mM (dashed line) and self-supported (dotted). Comparison of different electrode radius: (A) 0.2 cm and (B) 0.05 cm

Analogous chronoamperograms were recorded for solutions containing the same concentration of hexaammineruthenium(III) chloride but less supporting electrolyte (concentrations of 0 and 9 mM). Figure 4.9 also shows these data for both electrodes. Using the computational model described above, simulations were run using the experimental values for diffusion coefficient and formal potential, and other literature values listed in Table 4.2. These simulations were found to be in very good agreement with the experimental chronoamperograms, as indicated by the open circles in Figure 4.9. The transients recorded under highest support (600 mM) show purely diffusional behaviour, whereas the weakly supported (30 mM) and self-supported transients exhibit at short time (10^{-2} s) a potential drop controlled region and at longer times ($t > 0.1$ s) a mass transport controlled region where current is enhanced by a factor of 1.12 by migration, as this is a reduction of a positively charged species(+3 to +2).

Cobaltocenium/cobaltocene

Using the same methodology as described for the case of the reduction of hexaammineruthenium(III) chloride, cyclic voltammetry was performed in a solution containing 3 mM of cobaltocenium hexafluorophosphate and 600 mM of supporting electrolyte (TBAP) in acetonitrile. As before, a reversible cyclic voltammogram recorded at a scan rate of 100 mV s^{-1} is shown in Figure 4.8 with a peak-to-peak separation of 60 mV, which enabled a formal potential of -1.20 V (vs Ag/Ag^+) to be determined. The diffusion coefficient calculated by a Randles-Ševčík for cyclic voltammograms with scan rates

of 100, 200, 500 and 1000 mV s^{-1} was $2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

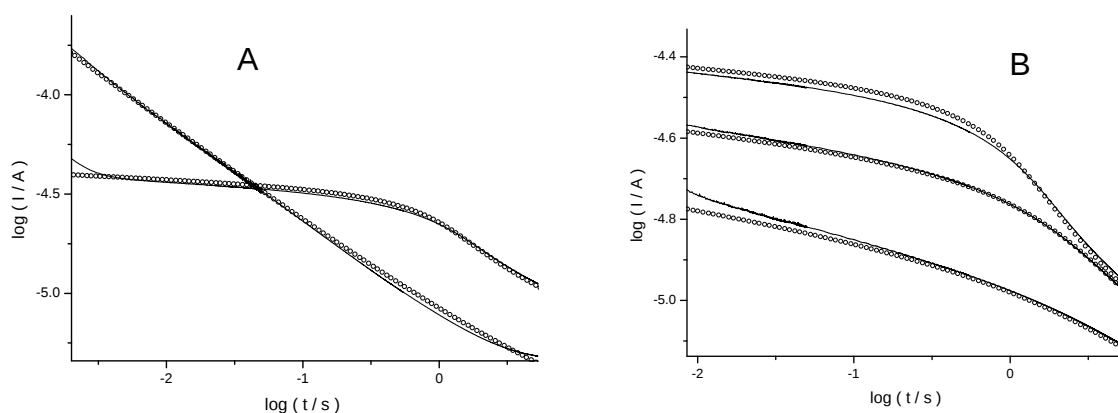


Figure 4.10: Comparison between experiment (line) and simulation (circles) for the cobaltoce-nium/cobaltocene couple. (A) Different concentrations of supporting electrolyte 600mM and self-support; and (B) different applied potentials (-1.30, -1.40 and -1.50 V vs Ag/Ag⁺), without added supporting electrolyte

Then, single potential step chronoamperometry was carried out, stepping from open circuit to a potential of -1.50 V(vs Ag/Ag⁺) (Figure 4.10 A). In the highest supported case (600 mM), a fully diffusional, Cottrellian-type response was obtained, which yielded a diffusion coefficient of $2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Both formal potential and diffusion coefficient were in good agreement with the literature.²²

Similar chronoamperometric experiments were then carried out with zero added supporting electrolyte, and also for potential steps to the potentials -1.30 V, -1.40 V and -1.50 V (vs Ag/Ag⁺) (Figure 4.10 B). As before, the experimental results were compared with simulations undertaken using the parameter values listed in Table 4.2, assuming the diffusion coefficients to be independent of the supporting electrolyte concentration. Figure 4.10 shows the excellent agreement between experiment and simulation, and the dependence of the current response in the potential drop region and applied overpotential.

In the self-supported chronoamperogram the mass transport is enhanced as cobaltocenium is positively charged and the reaction is a reduction. As cobaltocenium has just one counter ion, higher migration rates than for hexaammineruthenium(III) are expected. It was found that under self-support conditions the steady-state current is enhanced by a factor of 2.80. This is larger than the factor of 2.0 in the theoretical results, because the diffusion of the hexafluorophosphate anion is slower than

the diffusion of the cobaltocenium cation(table 4.2).

Hexacyanoferrate(III)/(II)

Finally, the reduction of potassium hexacyanoferrate(III) was investigated. In fully supported solution containing 3 mM potassium hexacyanoferrate(III) and 600 mM of potassium nitrate, a reversible cyclic voltammogram was observed (Figure 4.8) which gave a formal potential of the redox couple to be +0.22V (vs SCE). The diffusion coefficient was calculated by a Randles-Ševčík plot using cyclic voltammograms with scan rates of 100, 500 and 1000 mV s^{-1} , and a value of $6.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was obtained.

Chronoamperometry in this solution, stepping from open circuit to +0.52 V (vs SCE), gave a diffusional response for the high support case, enabling a value for the diffusion coefficient of $6.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ to be determined. As before, formal potentials and diffusion coefficients agree well with literature.^{20,21}

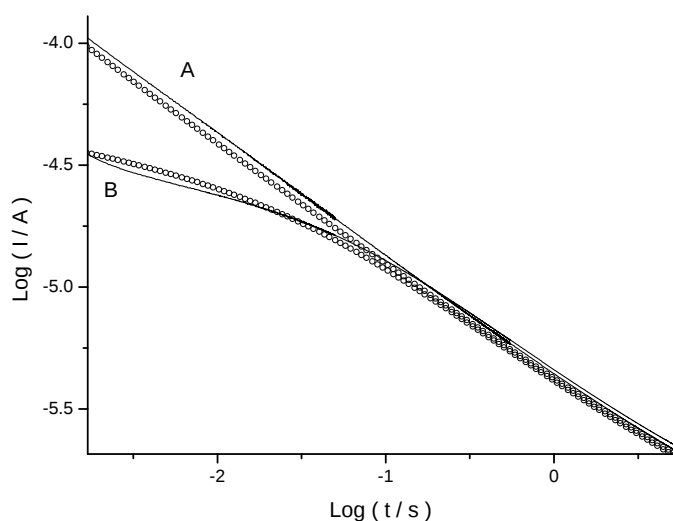


Figure 4.11: Comparison between experiment (line) and simulation (circles) for the hexacyanoferrate(III/II) couple, at an applied potential of +0.24 V vs SCE and different concentrations of supporting electrolyte: (A) 600mM of supporting electrolyte; and (B) self-supported.

A chronoamperogram was recorded for the self-supported case (zero supporting electrolyte), and simulations conducted as described before. Figure 4.11 again shows that good agreement is observed between theory and experiment, and as this is the case of a reduction of a negatively charged elec-

troactive species, the migration decreases the mass transport to the electrode (Figure 4.11).

Comparison

From the experimental observations described above, the strongest migrational influence is seen in the cobatocenium (+/0) system, in which the flux to the electrode is enhanced by migration by a factor of ca 2.8 in self-supported long time transient conditions. For hexaamineruthenium (3+/2+), under self-support, an enhancement of long time transient flux of ca 1.12 is presented compared to the purely diffusional case. The contrast between the two cases arises from the stoichiometry, since there is just one anion per ion of cobaltocenium, whereas for hexaammineruthenium(III) there are three. In the case of hexacyanoferrate(III) reduction, theory predicts a 'repulsive' steady state migration effect of ca 0.98, so that the experimental chronoamperograms for self- and full support essentially overlap. It should be noted although the overall effect of migration under transient conditions is common with that at steady state, a true steady state has not yet been attained and so the ratios presented differ from those calculated theoretically.¹¹ It is expected that at infinite time and in the absence of convective effects, the experimental transients would tend towards those limiting values.

The migration effects observed under self-supported conditions for a single electron transfer depend most strongly on the number of counter ions associated with the electroactive species, since the extent of migration of the electroactive species reflects its proportion among all the charged species present in solution.

4.4 Conclusions

The NPP system of equations enables us to simulate with good agreement redox systems under different quantities of supporting electrolyte (support ratios of 0.1 to 200) for an electrode of size significantly greater than the nanoscale. The NPP model used here avoids the traditional approximation of electroneutrality.

The present study indicates that weakly supported chronoamperometry with micro-electrodes could be used for electroanalytical research for obtaining kinetic parameters in self-supporting systems (Figure 4.5). This model has shown that the commonly used assumption of electroneutrality is weak since even at even at long time scales (up to 100 s) the solution is not electroneutral in a region up to 10^{-3} cm from the electrode (Figure 4.2).

We have demonstrated that the NPP equations combined with carefully selected boundary conditions are able to simulate different redox couples involving single step electron transfer, different species and concentrations of supporting electrolyte either in the steady state regime or under transient conditions. Mass transport (diffusion and migration) as predicted by the NPP model compared well with experiment. It is shown how the charge of the electroactive species affects its mass transport to the electrode when only small amounts of supporting electrolyte are added to the solution. The mass transport to the electrode is enhanced due to ‘attractive’ migration, when low amounts of supporting electrolyte are used for a reduction of a positively charged species or a oxidation of a negatively charged electroactive species (Figures 4.6 A,B and C). Conversely, when a positively charged electroactive species is oxidized or a negatively charged electroactive species is reduced, the mass transport to the electrode is reduced as the contribution of migration is ‘repulsive’ (Figures 4.6 E and F). In the case of a neutral species under low supporting electrolyte conditions, its mass transport to the electrode will remain purely diffusional as neutral species do not migrate (Figures 4.6 D).

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Chapter 5

Chronoamperometry of deposition and stripping of an amalgam; dependence of supporting electrolyte with deposition time

Previous chapters presented a comparison between theoretical interpretation and comparison with experiment for voltammetry under weakly support for species in which the oxidized and reduced form are soluble in solution. The present chapter deals with electrochemical experiments in which a metal is deposited in a mercury hemisphere and then ‘stripped back’ into the solution. As the rate of stripping will depends upon the concentration in the amalgam it is expected that when the concentration of the metal in the amalgam is similar to that of the supporting electrolyte in solution the stripping process cannot be considered well supported. So for experiments in which the deposition time is short the stripping is likely to be well supported and diffusion controlled. Whereas, for the cases in which longer deposition times are used, divergences from diffusion controlled processes might be found .

The thallium-mercury amalgam has been the subject of many experimental studies in electrochemistry, mostly with a view to measuring the diffusion coefficient of thallium in the amalgam and aqueous phases.^{9–17} In particular, in recently published work it was measured the chronoamperometric current was measured at a 12.5 μm radius mercury drop in thallium nitrate solution,¹⁸ and the work presented here follows the same experimental procedure. The hemispherical mercury drop was first created by electrodeposition on a platinum microdisc electrode. The mercury was then subjected to two successive potential steps in the Tl(I) solution, as shown schematically in Figure 5.1. The first step was to a reducing potential for a time period t_a , which introduced Tl(0) into the amalgam phase; the second step was to an oxidative potential for a time period $t_b - t_a$, which effected the stripping of thallium back into solution.

The thallium content of the amalgam can be controlled by varying the length of time that the reductive potential is applied. When the amalgam droplet is rich in thallium, the subsequent stripping

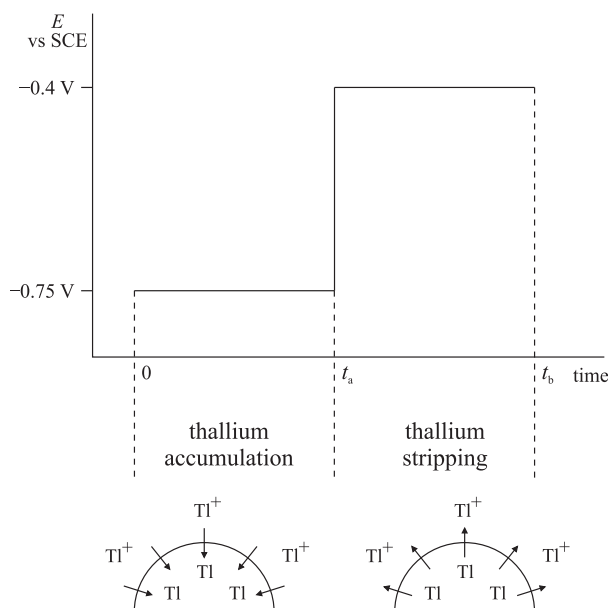


Figure 5.1: Schematic diagram of the experiment showing the two potential steps: first for the accumulation of thallium in the amalgam for time t_a , second for the stripping of thallium of duration $t_b - t_a$.

potential will release Tl(I) cations back into solution in large quantities, leading to very high local concentrations in the solution near the electrode. If the local concentration of thallium approaches or even exceeds the concentration of the background electrolyte then the experiment can no longer be described as supported. The extent to which the experiment is supported can therefore be varied, by changing the length of time that the first (reductive) potential is applied.

In this chapter potential step chronoamperometry is explored under conditions that cannot be described as fully supported. A 50 fold excess of supporting electrolyte is used and the thallium accumulation times are so long that the concentrations of Tl^+ that are released in the stripping phase cannot be supported. In section 5.1 an appropriate model is described for the experimental system, which is based on previous theoretical work on partially supported chronoamperometry.⁷ In section 5.3 the experimentally measured current is compared with theoretical simulations. Cyclic voltammetry experiments under fully supported conditions were used to confirm the values of the physical parameters that are used in the theoretical model, most importantly the rate constant and formal electrode potential of the electron transfer.

5.1 Theoretical model and numerical simulation

A number of different chemical species feature in the experiment. Thallium is found in the aqueous phase in the form of the cation Tl(I) and in the amalgam phase as the neutral species Tl(0) . The supporting electrolyte consists of electrochemically inert cations and anions, which are denoted M^+ and X^- , respectively. The bulk solution concentration of Tl(I) is written C_{Tl}^* and the concentration of additionally added supporting electrolyte is written C_{sup} . In the model, X^- is also the counter anion of the dissolved thallium salt; the bulk concentration of species X^- is therefore equal to $C^* + C_{\text{sup}}$. It is noted that a different counter anion is used in the real experiment (see section 5.2.2), but the inclusion of a second inert anion to the model is expected to make negligible difference to the simulated currents because $C_{\text{sup}} \gg C^*$. The local concentrations of thallium in the aqueous and amalgam phases are written as $C_{\text{Tl(aq)}}$ and $C_{\text{Tl(amal)}}$, respectively, and its diffusion coefficients are written $D_{\text{Tl(aq)}}$ and $D_{\text{Tl(amal)}}$, respectively. For the inert cation and anion in the solution phase, the local concentrations are written C_{M^+} and C_{X^-} , respectively, and the diffusion coefficients are D_{M^+} and D_{X^-} , respectively.

The mercury droplet is assumed to be hemispherical in shape with a constant radius r_e . When the negative potential is applied, Tl(I) from the aqueous phase is reduced to Tl(0) at the mercury-solution interface. The Tl(0) immediately enters the amalgam phase, where it freely diffuses through the droplet. When the more positive potential is applied to the mercury drop, the accumulated Tl(0) is stripped from the amalgam phase back into the aqueous phase as Tl(I) , with the electron transfer occurring at the mercury drop surface. The Butler-Volmer expression was used to describe the rate of this electron transfer:

$$J = k^0 \exp\left(\frac{-\alpha F}{RT} \Delta\phi\right) C_{\text{Tl(aq)}} - k^0 \exp\left(\frac{(1-\alpha)F}{RT} \Delta\phi\right) C_{\text{Tl(amal)}} \quad (5.1)$$

where J is the flux of thallium into the amalgam phase, k^0 is a heterogeneous rate constant, α is a charge transfer coefficient, and the concentrations refer to the values at the amalgam-aqueous boundary. The value $\Delta\phi$ represents the potential driving force of the electron transfer; this value will be discussed in the subsequent sections.

5.1.1 Fully supported cyclic voltammetry

A relatively simple theoretical model may be used to describe a fully supported experiment, since mass transport of the electroactive species is entirely due to diffusion and the ohmic potential drop through solution is negligible. This simple model is used to simulate the cyclic voltammetry experiments in an excess of supporting electrolyte. The same model to simulate the mercury droplet in a potential step chronoamperometry experiment and is described elsewhere.¹⁸

The diffusion of each species within their respective phases is described by Fick's second law of diffusion. Within the mercury hemisphere this expression is written in terms of the radial coordinate r , but in the solution phase it is more convenient to use the transformed coordinate y :

$$y = 1 - \frac{r_e}{r} \quad (5.2)$$

The coordinate y scales between the values 0 and 1, corresponding to the hemisphere's surface and an infinite distance from the electrode, respectively. The mass transport equations to be solved by numerical simulation are as follows:

$$\text{amalgam phase:} \quad \frac{\partial C_{\text{Tl(amal)}}}{\partial t} = D_{\text{Tl(amal)}} \left(\frac{\partial^2 C_{\text{Tl(amal)}}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{\text{Tl(amal)}}}{\partial r} \right) \quad (5.3)$$

$$\text{aqueous phase:} \quad \frac{\partial C_{\text{Tl(aq)}}}{\partial t} = D_{\text{Tl(aq)}} \frac{(1-y)^4}{r_e^2} \frac{\partial^2 C_{\text{Tl(aq)}}}{\partial y^2} \quad (5.4)$$

The boundary conditions for the two thallium species are given in the top two rows of Table 5.1. Equation 5.1 is used as the Butler-Volmer boundary condition at the site of the electron transfer. There is no ohmic potential drop for this fully supported system, so the potential driving force for the electron transfer, $\Delta\phi$, is directly related to the applied electrode potential, E :

$$\Delta\phi = E - E_f^\circ \quad (5.5)$$

where E_f° is the formal electrode potential. In the simulated cyclic voltammetry experiment, the applied electrode potential is varied at a constant scan rate, v , from the oxidising potential E_1 , to the reducing potential E_2 , and then back to E_1 .

Species / Potential	$r = 0$	$r = r_e / y = 0$	$y = 1$
Tl(0)	$J_{\text{Tl(amal)}} = 0$	$J_{\text{Tl(amal)}} = J_{\text{Tl(aq)}}$	—
Tl ⁺	—	Butler-Volmer	$C_{\text{Tl(aq)}} = C^*$
M ⁺	—	$J_{\text{M}^+} = 0$	$C_{\text{M}^+} = C_{\text{sup}}$
X ⁻	—	$J_{\text{X}^-} = 0$	$C_{\text{X}^-} = C^* + C_{\text{sup}}$
ϕ	—	$\frac{\partial \phi}{\partial y} = 0$	$\phi = 0$

Table 5.1: Boundary conditions for the NPP equations.

5.1.2 Partially supported chronoamperometry

The potential step experiment cannot be described as supported if the local concentration of thallium approaches or even exceeds the concentration of the background electrolyte. The release of large quantities of Tl(I) into the solution phase during the stripping procedure creates a region that is locally charged. With insufficient supporting electrolyte to compensate for this charge an electric field is generated that extends into solution away from the electrode. A more complex model is needed to simulate electron transfer experiments in weakly supported media, to account for this electrical potential gradient. Migration effects will contribute to the mass transport of the charged species in this electric field, and electron transfer kinetics will be retarded because the potential driving force across the amalgam-solution interface is no longer equal to the potential difference between the bulk phases.

An appropriate theoretical model of a partially supported electrolysis experiment was presented in a previous paper.⁷ It was shown that the Nernst-Planck-Poisson (NPP) equations can be solved to generate concentration profiles of each species and the potential field in the solution. The paper was an extension of other researchers' work, who solved the NPP equations for similar systems but only under steady state conditions.^{19–22} The numerical approach avoided use of the electroneutrality approximation, which has previously been used for both steady state^{23–25} and transient^{26–28} problems. The electron transfer experiment that it has been previously modelled assumed that the reactant and the product of the electron transfer were soluble in solution. Here it is adapted that model to account for the accumulation of Tl(0) in the mercury droplet.

It is necessary to model all three of the charged species Tl⁺, M⁺ and X⁻ in solution, and the uncharged species Tl(0) in the amalgam phase. It is also necessary to model the potential in solution, ϕ , which is defined as having a value of zero in bulk solution. Deviations from this value of zero near the electrode are referred to as ohmic potential drop. The flux of a charged species, i , in solution is

given by the Nernst-Planck expression:

$$J_i = D_i \left(\frac{\partial C_i}{\partial r} + z_i C_i \frac{F}{RT} \frac{\partial \phi}{\partial r} \right) \quad (5.6)$$

where z is the charge of the species. The first term in parentheses of Equation 5.6 is the diffusional contribution, and the second term is the migrational contribution to the flux. The mass transport of $Tl(0)$ in the amalgam is still given by Equation 5.3, but the equivalent expressions for the charged species in solution are more complicated:

$$\frac{\partial C_i}{\partial t} = D_i \frac{(1-y)^4}{r_e^2} \left(\frac{\partial^2 C_i}{\partial y^2} + z_i \frac{F}{RT} \left(C_i \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial C_i}{\partial y} \frac{\partial \phi}{\partial y} \right) \right) \quad (5.7)$$

where the equation has been written in terms of the transformed coordinate y . At all times, the electric field in solution must satisfy the Poisson equation:

$$\frac{(1-y)^4}{r_e^2} \frac{\partial^2 \phi}{\partial y^2} = - \frac{\rho}{\epsilon_r \epsilon_0} \quad (5.8)$$

where ρ is the local charge density, ϵ_r is the dielectric constant of the medium and ϵ_0 is the permittivity of space. The Poisson equation states that there will be ohmic potential drop between two electrodes when the parts of the solution develop an overall charge. The charge density can be expressed in terms of the local concentrations of the charged species in solution:

$$\rho = F \sum_i z_i C_i \quad (5.9)$$

The concentration profiles of the various species and the potential profile throughout solution can be found by using numerical methods to simultaneously solve Equations 5.3, 5.7 and 5.8. This system of equations is collectively known as the Nernst-Planck-Poisson equations.

Table 5.1 shows the boundary conditions for all four species and for the potential in solution. Equation 5.1 is used as the Butler-Volmer boundary condition at the site of the electron transfer. The potential driving force, $\Delta\phi$, depends on the applied electrode potential and also on the ohmic potential drop through the solution:

$$\Delta\phi = E - E_f^\circ - \phi_e \quad (5.10)$$

where ϕ_e is the potential at the point in solution immediately adjacent to the mercury droplet surface. A double potential step chronoamperometry experiment is simulated by setting the potential E to a reductive value, E_1 , for times $0 < t \leq t_a$, and then immediately changing it to an oxidative value, E_2 , for times $t_a < t \leq t_b$.

The boundary condition given in Table 5.1 for ϕ at $y = 0$ states that there is no electric field in solution at the phase boundary. Strictly speaking, the electric field at an electrode-solution interface depends on the structure of the electrical double layer. The justification of this boundary condition is that the electrical double layer is negligibly narrow compared to a diffusion layer thickness on the used experimental timescales. Streeter et al. modelled electron transfers using more complete descriptions of the electrical double layer and the potential gradient at the electrode surface;⁷ however, these calculations were computationally expensive and had much longer CPU simulation times. Simulations using the more complicated boundary conditions are not shown in this work, but it was found that the simulated current was not changed compared to using the boundary condition in Table 5.1 on the timescale of interest for this work. This is consistent with previous findings that the boundary condition of no electric field was accurate and appropriate for an electrode with a radius greater than $10 \mu\text{m}$ at times greater than 10^{-4} s .⁷

5.1.3 Numerical simulation

The partial differential equations describing the theoretical model and the corresponding boundary conditions were discretised using the Crank-Nicolson finite difference method.^{29,30} The discretised equations for the fully supported model described in section 5.1.1 are linear, and may be solved using the Thomas algorithm.³¹ The NPP equations for the weakly supported system described in section 5.1.2 are non-linear, so were solved using the iterative Newton-Raphson method. At each time step the flux of thallium into the amalgam phase was calculated from the simulated concentration and potential profiles. The flux is related to the measured current, i , by the following expression:

$$i = 2\pi F r_e^2 J \quad (5.11)$$

The simulation programme was tested for convergence by varying the size of the time steps and the spatial increments. It was confirmed that a five fold increase in the total number of spatial or temporal nodes lead to a change in the simulated current of less than 0.1% over the timescale that was used for

analysis of the experiment.

5.2 Experimental

The experimental procedures described here were recently used in previous work on the thallium-mercury amalgam.¹⁸

All the solutions were prepared with ultra-pure water with a resistivity not less than 18.2 $M\Omega$ (at 25 °C) and degassed for 30 minutes with N_2 (BOC, high purity oxygen free) before starting each experiment. The chemicals used were $Hg_2(NO_3)_2$ (>97%, Aldrich), KNO_3 (99+%, Aldrich), $TlNO_3$ (99.999%, Aldrich) and KF (99%, Aldrich), and were used without further purification.

5.2.1 Electrodes and electrochemical apparatus

A platinum microelectrode was used, upon which the mercury was electro-deposited. This working electrode was fabricated in-house by sealing a 25 μm diameter Pt wire (Goodfellow, Cambridge, UK) into a pyrex glass capillary. The working electrode was polished before each deposition of mercury using diamond spray of particle sizes of 3, 1 and 0.1 microns (Kemet, Maidstone, UK). A silver wire was used as a pseudo-reference electrode during the Hg deposition and a saturated calomel electrode (SCE) was the reference electrode for the thallium deposition-stripping experiment. A platinum wire was used as a counter electrode. An AutoLab Type III potentiostat (Eco Chemie, Netherlands) was used for all electrochemical procedures.

5.2.2 Thallium deposition-stripping chronoamperometry

The electrodeposited mercury hemisphere was first washed in ultra-pure water. The electrode was then placed in a solution of 2 mM $TlNO_3$, with 0.1 M KF supporting electrolyte and two successive potential steps were applied.¹⁷ A potential step to -0.75 V vs SCE was applied to effect thallium accumulation in the Hg hemisphere, and was immediately followed by a potential step to -0.4 V vs SCE for the stripping of thallium. The time of the thallium accumulation potential was varied between 0.1 s and 100 s, and the stripping potential was applied for 0.4 s. The length of time of the Tl stripping step exceeds the time that is required for the full elimination of Tl in the amalgam by at least a factor of 5.¹⁸ Here “full elimination” is taken to be when >99.9% has been eliminated, measured by the amount of charge passed. Due to the speed of the elimination process it was necessary to record

each data point at an acquisition time of 0.05 ms, which was the minimum time step possible for the potentiostat used.

Previous studies into the Tl/Hg system have shown the amalgam has several distinct phases at ambient temperatures and pressures depending on its composition. At 40.5% (molar percentage) of Tl, the amalgam becomes solid,^{8,33–35} and at 28.6% of Tl a phase composition of Tl_2Hg_5 has also been reported with solidification of 14.3 °C.⁸ To ensure a fully liquid hemisphere, care was taken to ensure that the amalgam contained <25% of Tl.

5.2.3 Cyclic Voltammetry

Cyclic voltammograms were recorded using the mercury hemisphere in 0.02 mM TlNO_3 and 0.1 M KF. Note that this is a 5000 fold excess of supporting electrolyte. The low concentration of thallium in the solution was to limit the rate of thallium accumulation in the mercury droplet, and therefore to ensure the system was fully supported during the stripping part of the voltammogram. The cyclic voltammograms were recorded at scan rates of 250, 500 and 1000 mV s^{-1} . Numerical simulations confirm that the supporting electrolyte concentration is always in great excess of the local Tl(I) concentrations at these scan rates.

5.3 Results and discussion

5.3.1 Potential step chronoamperometry

The stripping of thallium from a hemispherical mercury drop was studied via the double potential step chronoamperometry experiment described in section 5.2.2. The aqueous solution concentrations were as given in section 5.2.2, which correspond to a bulk solution support ratio of 50. A cathodic current was recorded during the first potential step, corresponding to the reduction of Tl(I) and the accumulation of Tl(0) in the amalgam phase. Figure 5.2a shows the transient current recorded for the first 0.1 s of an accumulation step.

Immediately after the second potential step, an anodic current was recorded, corresponding to the stripping of thallium from the amalgam phase. The current measured depended on the length of time that the preceding reductive potential had been applied. Figures 5.2b–d show the chronoamperometry for thallium stripping after accumulation times of 0.1, 10, and 100 s. After an accumulation time

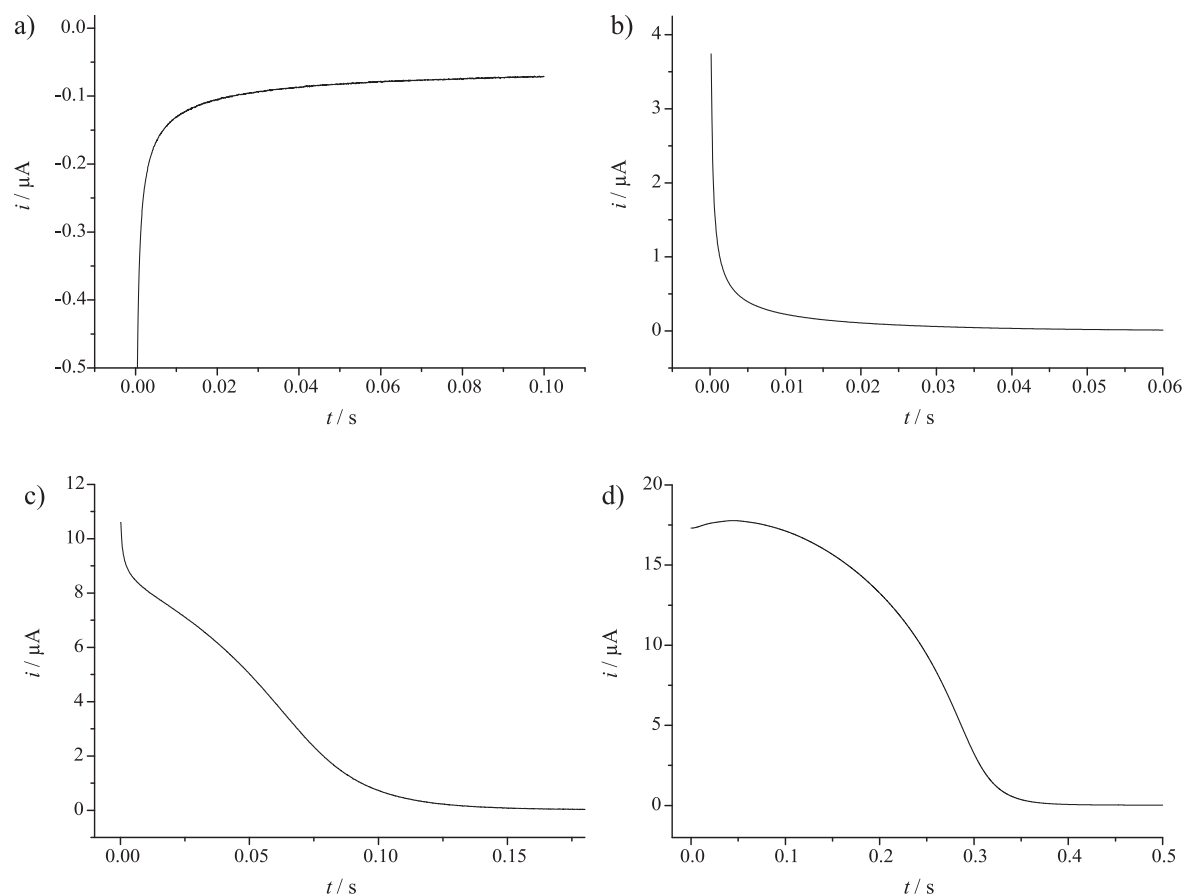


Figure 5.2: Chronoamperometry recorded in the double potential step experiment. Part a shows thallium accumulation; parts b–d show thallium stripping. Accumulation times are b) 0.1 s, c) 10 s, d) 100 s.

of 0.1 s, the stripping current is largest immediately after the potential step, and then decreases with time until all thallium has been stripped from the amalgam. The shape of this curve is qualitatively in agreement with a previous study of this system for short accumulation times.¹⁸ The continual decrease in current is due to the slowing of the diffusional flux within the mercury drop as $Tl(0)$ is depleted.

After longer thallium accumulation times, the stripping current does not decay to zero in such a smooth manner, but shows distortions in the curve shape shortly after the potential step is applied. For an accumulation time of 100 s, this distortion is so great that the current goes through a maximum at around 0.045 s before decaying to zero. This unusual current behaviour has been observed previously for this system, especially for high concentrations of $Tl(0)$ in the amalgam.¹⁷ It was speculated that at these high concentrations poorly soluble species on the electrode were inhibiting the process of oxidation at longer times, but the short-time behaviour was not fully explained. It is proposed that the short timescale observations can be attributed to the current deviations caused by ohmic potential drop.

When $Tl(I)$ cations are stripped from the amalgam, the solution near the phase boundary develops an overall positive charge. Associated with this charge is an electric field, which is described by the Poisson equation, and means that the electric potential of the solution near the electrode is more positive than in bulk solution. This is the phenomenon that is often referred to as ohmic potential drop, and its effect is to decrease the potential driving force at the site of the electron transfer. When the amount of thallium in the amalgam is not too high (short accumulation times), the majority of the excess charge in solution can be negated by separation of the supporting electrolyte. The inert anions migrate in the electric field towards the positively charged region, and the inert cations migrate away. When the amalgam is loaded with large amounts of thallium (long accumulation times), the charge that is deposited in solution is so high that ohmic drop significantly inhibits the electron transfer. The supporting electrolyte is slow to separate sufficiently to negate the charge, but as it does, the ohmic potential drop is slowly removed and the current increases. The peak in current and the subsequent current decay occurs when the electron transfer is sufficiently fast that mass transport of thallium to the mercury surface becomes the rate limiting process.

This argument for the shape of the recorded current can be strengthened by simulating the experiment using the model described in section 5.1.2. However, this model requires values for the

rate constant and formal electrode potential for the electron transfer, which are currently unknown. Turning to cyclic voltammetry under fully supported conditions in order to deduce these values.

5.3.2 Cyclic voltammetry

Cyclic voltammograms were recorded at three different scan rates using the experimental conditions described in section 5.2.3. The aqueous concentrations of TlNO_3 and KF were 0.02 mM and 100 mM, respectively, giving a bulk solution support ratio of 5000. In each case, a fairly steady cathodic current was observed on the reductive scan, corresponding to the accumulation of Tl(0) in the amalgam, and a sharp anodic peak on the return scan, corresponding to thallium stripping. This is qualitatively in agreement with previous studies of this system.¹⁷

Parameter	Value	Justification
$D_{\text{Tl(amal)}}$	$1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Limon-Petersen et al. ¹⁸
$D_{\text{Tl(aq)}}$	$2.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Limon-Petersen et al. ¹⁸
D_{M^+}	$1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Sevryugin et al., ⁴⁰ Shaposhnik ⁴¹
D_{X^-}	$1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Sevryugin et al., ⁴⁰ Turq et al. ⁴²
k^0	0.07 cm s^{-1}	Section 5.3.2
α	0.5	Section 5.3.2
$E^{0'}$	-0.43 V vs SCE	Section 5.3.2

Table 5.2: Values used for numerical simulation of thallium stripping.

The model described in section 5.1.1 was used to numerically simulate the cyclic voltammetry experiment. The diffusion coefficients of thallium in the two different phases were known from previous studies of the system,¹⁸ and their values are shown in Table 5.2. The rate constant and formal electrode potential were varied systematically to achieve the best fit between experimental and simulated data. The following values were found to give the best fit in terms of the peak size and peak position for both the forward and reverse scans and across the full range of scan rates: $k^0 = 0.07 \text{ cm s}^{-1}$, $E^{0'} = -0.435 \text{ V vs SCE}$, $\alpha = 0.5$. Figure 5.3 shows a comparison of the experimental and simulated currents for a scan rate of 500 mV s^{-1} . Similarly good fits were achieved for the other scan rates.

It is noted that the literature contains many other reported values for the rate constant of the reduction of Tl(I) at mercury. These values are typically larger than the one reported here, and often greater than 1 cm s^{-1} .^{36–39}

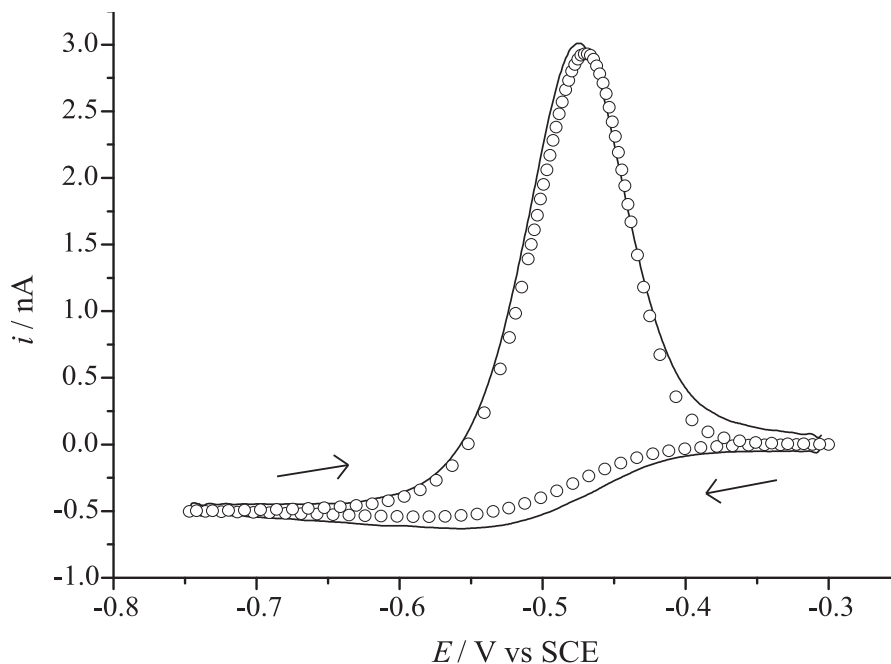


Figure 5.3: Cyclic voltammetry of TlNO_3 at a mercury hemisphere. The solid line is experimental data and the circles are simulated currents. The arrows show the direction of the potential sweep. Scan rate, $\nu = 500 \text{ mV s}^{-1}$.

5.3.3 Simulated chronoamperometry

The potential step chronoamperometry reported in section 5.3.1 was simulated using the model described in section 5.1.2 for partially supported systems. Table 5.2 lists each physical parameter used for the simulations, and cites previous studies which justify the values used. The values D_{M^+} and D_{X^-} are the literature diffusion coefficients of K^+ and F^- , respectively. The value for $E^{0'}$ differs by 5 mV from the value suggested by the fully supported cyclic voltammetry experiment; however, this small shift in potential is within experimental error. The simulated current-time behaviour was particularly sensitive to the value of $E^{0'}$ used, and it was found that this shift of 5 mV gave a much better fit with the experiment.

The first requirement of the theoretical model is that it accurately simulates the accumulation of thallium in the mercury drop before the stripping procedure begins. Integration of the current-time curve for the first potential step gives a measure the total thallium accumulation. Table 5.3 presents a comparison of these values for simulation and experiment in terms of the molar percentage of thallium in the amalgam, and there is reasonable agreement between the two sets of data.

Figure 5.4 shows a comparison of experimental and simulated stripping currents after a range of

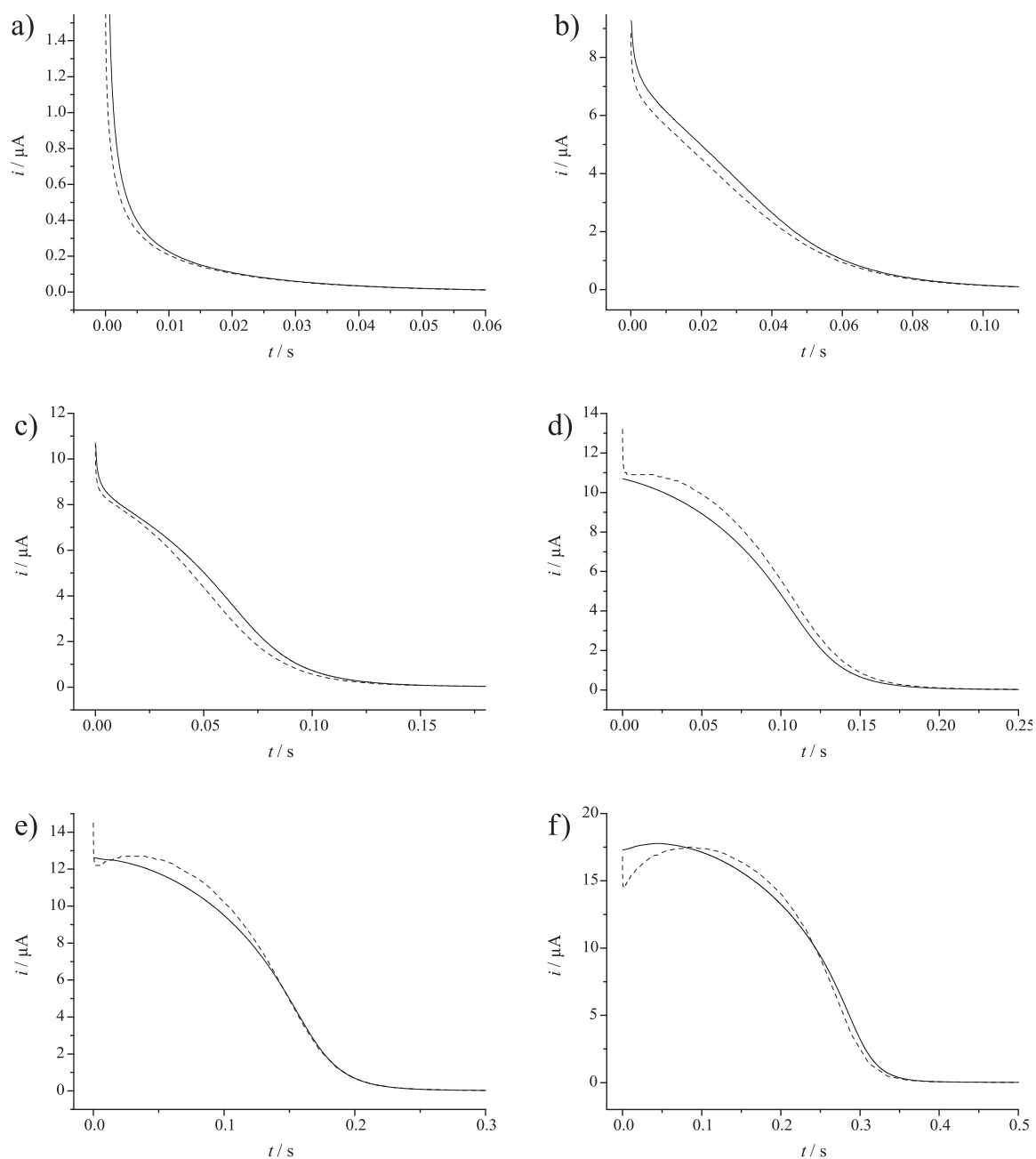


Figure 5.4: Comparison of simulated and experimental chronoamperometry for the stripping of thallium from the amalgam. The solid line is experimental and the broken line is simulated data. Accumulation times are a) 0.1 s, b) 5 s, c) 10 s, d) 25 s, e) 40 s, f) 100 s.

Accumulation Time / s	Thallium content of amalgam	
	Experiment	Simulation
0.1	0.035%	0.030%
5	0.969%	0.883%
10	1.96%	1.71%
25	4.39%	4.14%
40	7.58%	6.91%
100	17.6%	15.9%

Table 5.3: The molar content of thallium in the amalgam drop at the end of the accumulation period.

thallium accumulation times. The theoretical model is clearly successful in a number of respects. Firstly, the magnitude of the current is correctly predicted, including the observation of larger currents for longer accumulation times. Secondly, there is agreement in the timescale of the transient response; both data sets show that longer times are required to complete the stripping process when there is more thallium in the drop. Finally, the distorted shape of the curve at short times is replicated in the simulated data, with the greatest deviations from supported behaviour occurring with longer accumulation times. At the longest accumulation times, the theoretical model even predicts the maximum in current before the process becomes diffusion controlled.

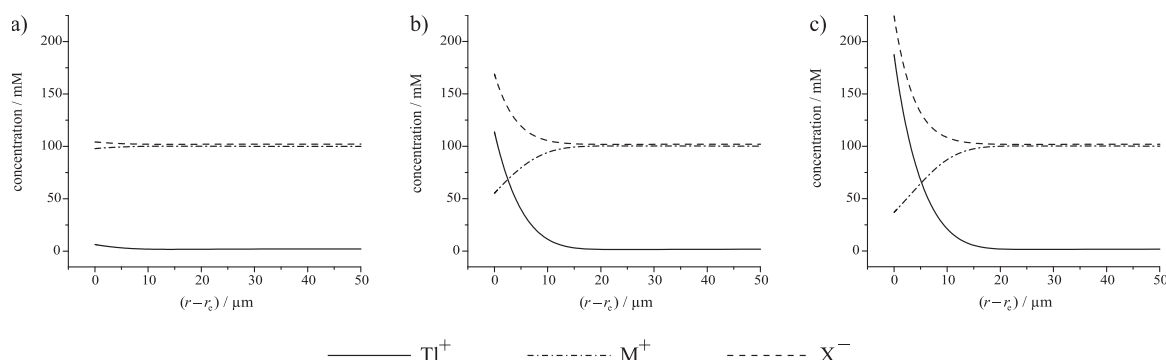


Figure 5.5: Simulated concentration profiles in solution at the amalgam surface for Tl^+ and the inert species, M^+ and X^- . Accumulation times are a) 0.1 s, b) 10 s, c) 100s. The profiles are taken 0.01 s after the stripping potential is applied.

It is informative to look at the simulated concentration profiles of the various species in solution during the stripping process. Figure 5.5 shows the concentrations of Tl(I) , the inert cation and the inert anion extending away from the mercury hemisphere. These profiles are all taken 0.01 s after the stripping potential step, which is approximately the time of the current distortions in the simulated chronoamperometry. Each part of the figure corresponds to a different thallium accumulation time, and therefore a different concentration of Tl(0) within the amalgam. The simulations predict that

longer accumulation times lead to significantly more thallium being released into solution during the first 0.01 s of the stripping potential. The separation of the supporting electrolyte to negate the charge in solution can be seen. After a 0.1 s accumulation step, the concentration of the inert salt is still greatly in excess of the concentration of Tl(I) in solution, and the system is therefore fully supported. The same cannot be said after a 100 s accumulation period; excessive rearrangement of the electrolyte is required, and the electron transfer cannot be fully supported.

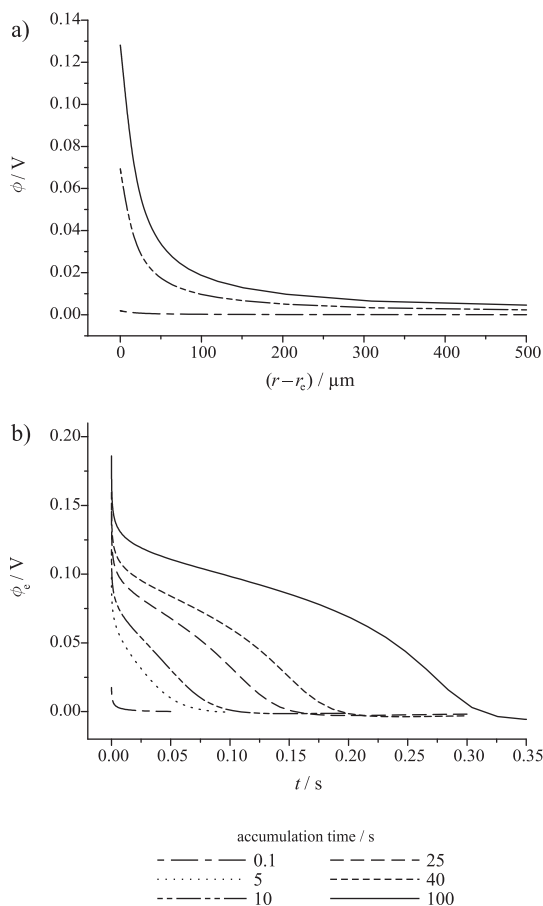


Figure 5.6: The electrical potential in solution during the stripping phase: a) profile through solution after 0.01 s, b) potential at the amalgam surface as a function of time. Each curve corresponds to a different thallium accumulation period.

The numerical simulations can also be used to show the magnitude of the ohmic potential drop during the experiment. The parameter ϕ was introduced in section 5.1.2 to represent the local electric potential in aqueous solution relative to the potential of bulk solution. Ohmic potential drop is represented by a positive values of ϕ during the stripping phase of the potential step experiment, and acts to inhibit the electron transfer. Figure 5.6a shows the potential through solution for each of the concen-

tration profiles that were presented in Figure 5.5, taken after 0.01 s of the applied stripping potential. The greatest ohmic drop is seen at the electrode after 100 s of thallium accumulation, demonstrating the inadequacy of the supporting electrolyte under these conditions. The ohmic drop at the electrode is negligible after a 0.1 s accumulation time. Figure 5.6b shows the value of the potential at the site of the electron transfer, ϕ_e , as a function of time for the stripping of thallium for each of the experimentally studied accumulation periods. In each case, the ohmic potential drop relaxes to zero after a certain period of time, as rearrangement of the supporting electrolyte negates the excess of charge.

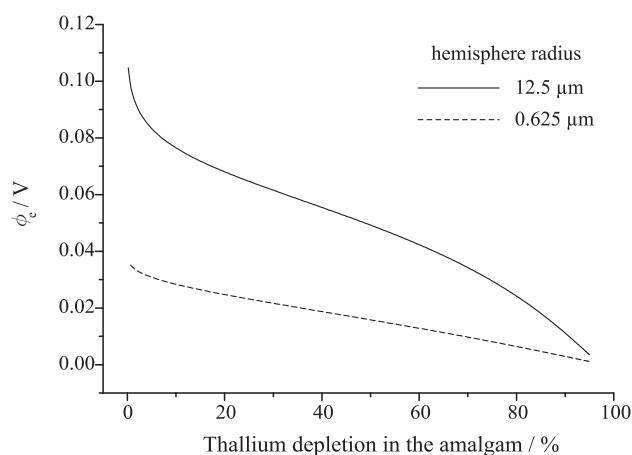


Figure 5.7: The simulated ohmic potential drop during the stripping procedure at different sized hemispheres. Accumulation times are 10 s and 25.3 ms for the 12.5 μm and 0.625 μm hemispheres, respectively. The abscissa is the percentage of thallium depletion in the amalgam, i.e. 50% means that half of the thallium that was present at end of the accumulation period has been stripped.

Given the importance of ohmic potential drop on the measured current, it is interesting to consider how the experiment would differ if the size of the working electrode was decreased, with all other parameters remaining the same. The first difference to appreciate is that a smaller mercury drop will accumulate thallium on a much faster timescale. This can be demonstrated by numerical simulations, comparing the 12.5 μm radius hemisphere described previously to one with a 0.625 μm radius. A 10 s accumulation time at the 12.5 μm hemisphere was found to give an amalgam that was 1.71% thallium (Table 5.3), whereas the same percentage thallium content at the 0.625 μm was achieved in only 25.3 ms. Having established the conditions required to generate equivalent amalgams, the stripping procedure was also simulated for these two differently sized drops. Again, the processes occurred on different timescales, with the stripping reaching its completion at approximately 150 ms for the larger hemisphere, and 1.2 ms for the smaller one. Figure 5.7 shows a comparison of the ohmic potential drop at the electrode over the duration of the stripping procedure. Comparing the

two amalgams after an equivalent fraction of the thallium has been stripped, there is considerably less ohmic potential drop at the smaller electrode. Decreasing the size of the mercury electrode therefore provides a way of negating the ohmic potential drop when studying the stripping of amalgams with a high concentration of thallium.

5.4 Conclusions

It has been demonstrated that presented theoretical model for partially supported electrolysis based on the Nernst-Planck-Poisson system of equation can be applied to real electrochemical systems of interest. The model has been highly successful in terms of predicting unusual chronoamperometric features that would not be observed in a fully supported system.

It was noted in section 5.3.1 that the unusual behaviour of the thallium amalgam in a potential step experiment was previously attributed at least in part to poorly soluble species on the electrode.¹⁷ The work presented here demonstrates that ohmic potential drop can account for the unusual chronoamperometric behaviour at short times.

Is recommended that for the understanding and simulation of stripping chronoamperograms a model considering potential drop and migration is considered as clear divergences from diffusion only limits are observed when the concentration of deposited metal are higher than 5% of the concentration of supporting electrolyte in solution.

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Chapter 6

Cyclic Voltammetry at weakly supported conditions

The power of voltammetry for the measurement of kinetic and thermodynamic redox data and for understanding the mechanisms of reactions involving electron transfer is widely recognized¹ and utilized. That said, experiments are conventionally restricted to solvents containing large amounts of electrolyte, either naturally or else through the deliberate addition of ‘supporting’ or ‘background’ electrolyte. The purpose of this is to ensure that the potential drop between the electrode and the solution occurs over a sufficiently short distance to be compatible with electron transfer via tunneling. Consequently the electric field associated with the potential drop is confined to a narrow interfacial region and is very close to zero in bulk solution. Hence, transporting ions to or from the electrode occurs only by diffusion; migration does not participate.

It is the case that the addition of supporting electrolyte can introduce problems to an experiment. In particular, the altered ionic strength can change the values of the kinetic and thermodynamic properties sought. Also, complexation of the redox species of interest with the added electrolyte can occur, while for the case of many non polar solvents it is impossible to dissolve the required levels of supporting electrolyte needed for rigorous elimination of migrational effects. The theoretical results obtained by the model are compared with experimental results for the cobaltocenium/cobaltocene couple in acetonitrile, the agreement is presented corroborating the theoretical approach.

6.1 Theoretical model

6.1.1 Establishment of the model

We have a solution containing a cationic electroactive species A^z , which is capable of undergoing electron transfer to form a species B :



The solution is additionally supported by a concentration C_{sup} of a monovalent inert salt MX, which is presumed to be completely dissociated. An extra equivalent of X^- is initially present as the counter-ion of the electroactive species.

The continuum Nernst-Planck equation is used to describe the flux of any species i at any point in solution. Assuming convection to be negligible, this equation has a contribution from diffusion and from migration:

$$\mathbf{J}_i = -D_i \left(\nabla C_i + \frac{z_i F}{RT} C_i \nabla \phi \right) \quad (6.2)$$

where for species i , $\mathbf{J}_i$ is the flux vector, D_i is the diffusion coefficient, C_i is concentration, z_i is the species charge, ϕ is potential, F is the Faraday constant, R is the gas constant and T is temperature. Conservation of mass then requires that the space-time evolution of the concentration of i obeys:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{J}_i \quad (6.3)$$

6.1.2 Dimensionless coordinates

Having established the Poisson equation as most appropriate, we may hence write, in a hemispherically symmetric space surrounding the electrode and extending into bulk solution, with spatial coordinate r , for $i = A^+, B^0, M^+, X^-$:

$$\frac{\partial C_i}{\partial t} = D_i \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} + \frac{z_i F}{RT} \left(\frac{\partial C_i}{\partial r} \frac{\partial \phi}{\partial r} + C_i \frac{\partial^2 \phi}{\partial r^2} + C_i \frac{2}{r} \frac{\partial \phi}{\partial r} \right) \right) \quad (6.4)$$

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} = -\frac{F}{\epsilon_s \epsilon_0} \sum_i z_i C_i \quad (6.5)$$

A range of conventional normalisations are introduced to simplify these equations and reduce the number of independent variables in the system such that the most general possible conclusions may be drawn:

$$c_i = \frac{C_i}{C_A^*} \quad (6.6)$$

$$\theta = \frac{F \phi}{RT} \quad (6.7)$$

$$R = \frac{r}{r_e} \quad (6.8)$$

$$\tau = \frac{D_A}{r_e^2} t \quad (6.9)$$

where C_A^* is the bulk concentration of species A and r_e is the electrode radius.

The resulting set of dimensionless Nernst-Planck-Poisson (NPP) equations are then:

$$\frac{\partial c_i}{\partial \tau} = \frac{D_i}{D_A} \left(\frac{\partial^2 c_i}{\partial R^2} + \frac{2}{R} \frac{\partial c_i}{\partial R} + z_i \left(\frac{\partial c_i}{\partial R} \frac{\partial \theta}{\partial R} + c_i \frac{\partial^2 \theta}{\partial R^2} + c_i \frac{2}{R} \frac{\partial \theta}{\partial R} \right) \right) \quad (6.10)$$

$$\frac{\partial^2 \theta}{\partial R^2} + \frac{2}{R} \frac{\partial \theta}{\partial R} = -R_e^2 \sum_i z_i c_i \quad (6.11)$$

where the dimensionless variable R_e is defined:

$$R_e = r_e \sqrt{\frac{F^2 C_A^*}{RT \epsilon_s \epsilon_0}} \quad (6.12)$$

and may be considered to represent the scale of the electrode relative to the solution Debye length.²

6.1.3 Boundary conditions

The NPP equations are solved subject to ten boundary conditions: one for each species, plus potential, at each of the two boundaries $R = 1$ and $R \rightarrow \infty$. At $R = 1$, Butler-Volmer kinetics are applied, relating the flux of A normal to the electrode to the surface concentrations, $c_{i,0}$, of A and B in the form:

$$\left. \frac{\partial c_A}{\partial R} \right|_{R=1} = K^0 \left(\exp(-\alpha(\theta_{\text{app}} - \theta(R=1))) c_{A,0} - \exp((1-\alpha)(\theta_{\text{app}} - \theta(R=1))) c_{B,0} \right) \quad (6.13)$$

The dimensionless heterogeneous rate constant is defined:

$$K^0 = \frac{k^0 r_e}{D_A} \quad (6.14)$$

with k^0 being the dimensional heterogeneous rate constant. α is the transfer coefficient, and θ_{app} is the dimensionless applied potential:

$$\theta_{\text{app}} = \frac{F}{RT} (E - E_f^\theta) \quad (6.15)$$

where E_f^θ is the formal potential of the A^+/B couple. For a cyclic voltammetry experiment θ_{app} is varied linearly in τ through a triangular waveform, at a dimensionless scan rate σ :

$$\sigma = \left| \frac{\partial \theta_{\text{app}}}{\partial \tau} \right| = \frac{F}{RT} \frac{r_e^2}{D} v \quad (6.16)$$

where v is the dimensional scan rate, $\equiv |\partial E / \partial t|$.

From conservation of mass:

$$\frac{D_B}{D_A} \frac{\partial c_B}{\partial R} \bigg|_{R=1} = - \frac{\partial c_A}{\partial R} \bigg|_{R=1} \quad (6.17)$$

and assuming M and X to be inert and insoluble in the electrode:

$$\frac{\partial c_M}{\partial R} \bigg|_{R=1} = \frac{\partial c_X}{\partial R} \bigg|_{R=1} = 0 \quad (6.18)$$

The boundary condition for potential at the electrode surface assumes that the double layer is negligible in extent compared to the diffusion layer, such that the charge on the electrode is fully compensated at $R \approx 1$. Then the enclosed charge is vanishing at this point, and so, from Gauss's law, the electric field is zero:

$$\frac{\partial \theta}{\partial R} \bigg|_{R=1} = 0 \quad (6.19)$$

This zero-field approximation has shown wide applicability^{3,5,6} and remains valid where the diffusion layer extends beyond a few nanometres.

The $R \rightarrow \infty$ boundary is represented by limiting the simulation space to a finite value which greatly exceeds the thickness of the diffusion layer for a diffusion-only system, being $R_{\text{max}} = 6\sqrt{(D_{\text{max}}/D_A)\tau_{\text{max}}}$ where D_{max} is the largest diffusion coefficient in the system. The concentrations of A, B, M and X are set to their bulk values at this boundary:

$$c_A = 1 \quad (6.20)$$

$$c_B = 0 \quad (6.21)$$

$$c_M = c_{\text{sup}} \quad (6.22)$$

$$c_X = 1 + c_{\text{sup}} \quad (6.23)$$

Finally, the potential is constrained such that a reference potential of $\theta = 0$ occurs at $R \rightarrow \infty$, which on the assumption of electroneutrality outside the simulation space yields the expression:

$$\theta(R = R_{\text{max}}) + R_{\text{max}} \left. \frac{\partial \theta}{\partial R} \right|_{R=R_{\text{max}}} = 0 \quad (6.24)$$

Surface flux at the hemisphere, j , is recorded for simulated voltammetric output as:

$$j = \left. \frac{\partial c_A}{\partial R} \right|_{R=1} \quad (6.25)$$

such that the corresponding dimensional current, i , is:

$$i = 2\pi F C_A^* D_A r_e j \quad (6.26)$$

6.1.4 Numerical methods

The NPP equations are solved using a finite difference method. An expanding grid is used corresponding to previous work,² with a region of extremely dense regular grid spacing close to the electrode that expands proportionally to R further from the electrode. This provides an efficient and accurate simulation. A regular time grid was employed. The equations are discretised by a Crank-Nicolson method and solved by the iterative Newton-Raphson method. All simulations were programmed in C++ and run on a desktop computer (Intel Core2 Quad 2.4 GHz, 2 GB RAM), with running times of 10 minutes per voltammogram being typical.

6.2 Experimental

6.2.1 Chemicals and Equipment

All solutions were made with acetonitrile solvent (MeCN, HPLC grade, Fisher Scientific). Cobaltocenium hexafluorophosphate (>98%, Strem Chemicals) was used as the electroactive species, with tetra-*n*-butylammonium perchlorate (TBAP, $\geq 99\%$, Fluka) as supporting electrolyte. A three electrode cell was used: a 25 micron radius platinum disk or a 25 micron radius mercury hemispherical electrode was used as a working electrode. The latter was prepared by electrodepositing mercury on a platinum disk, and the size was controlled by passing the necessary amount of current to form a hemisphere, using the procedure stated in Bard et al.²¹ and Limon-Petersen et al.²² A commercial ‘No leak’ reference electrode comprising Ag/Ag⁺ in a PEEK barrel fitted with a membrane junction (66-EE009, Cypress electrodes) was used in order to minimize contamination of the solution.

Note that voltammograms were recorded using a PG-STAT12 potentiostat (Autolab, Utrecht, Netherlands) without the ‘ohmic drop correction’ used or theorised in some early studies of weak support,^{18,19} so as to permit a clear comparison of theory and experiment.

All solutions were thoroughly degassed with N₂ before each experiment, and an inert atmosphere was maintained during the experiments.

6.2.2 Experimental procedure

Solutions containing 3mM of cobaltocenium hexafluorophosphate and different concentrations of TBAP (150, 30 and 0 mM) were studied. The cobatocenium-cobaltocene couple was selected for its fast electron kinetics.²³ The solution containing 150 mM of TBAP was used to estimate the diffusion coefficient of the cobaltocenium cation and the corresponding neutral cobaltocene, by performing double potential step chronoamperometry at a 50 micron diameter platinum microdisk electrode. The experimental results were analyzed using the theoretical methodology described by Klymenko et al.²⁴ giving $D_{\text{CoCp}_2^+} = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{CoCp}_2} = 2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The former is in good agreement with previous experimental data;^{23,25} we are unaware of any literature values for the latter.

Using the microhemispherical mercury electrode, cyclic voltammograms were recorded for the different supporting electrolyte concentrations, at scan rates of 0.05, 0.1, 0.2, 0.5 and 1 V s⁻¹, in a potential window between -0.6 and -1.2 V vs Ag/Ag⁺. A cleaning regime was applied before each

recorded cyclic voltammogram. The cleaning procedure consisted in running three cyclic voltammograms in predegassed pure acetonitrile from -0.6 to -3.5 vs Ag wire in order to remove any contamination.

6.3 Results and Discussion

6.3.1 Theoretical Results

Cyclic voltammograms were simulated for a singly positively charged electroactive species A^+ undergoing a single electron reduction, using the NPP simulation method described above and the parameters $\sigma = 10$, $R_e = 3 \times 10^3$, $D_A = D_B = D_{M^+} = D_{X^-}$, $K^0 = 10^4$ and $\alpha = 0.5$, for different concentrations of supporting electrolyte: $c_{\text{sup}} = 100, 10, 1, 0.1, 0.01$ and 0 . The results are presented in figure 6.1A where the voltammetry can be seen to change dramatically from fully supported (where $c_{\text{sup}}=100$) to self-supported, with the magnitudes of the peak currents, the peak separation, and the mass transport limited currents all increasing with decreased support.

As with any electrolytic process, the transfer of electrons to or from the electrode perturbs the electric field immediately adjacent to the electrode. The migrational transport of ions will act to re-establish local electroneutrality, with concomitant changes in the concentration profiles of the various species in this region. For the reduction of a cation as in the voltammetry of cobaltocenium, negative charge is added to solution, so cations are attracted and anions are repelled from the vicinity of the electrode.

In the case of high levels of supporting electrolyte, there are high concentrations of ions available to respond to the perturbed electric field and move accordingly (via migration); the electroactive species, which is detected at the electrode, has such a low concentration relative to the inert electrolyte that it carries an insignificant proportion of the migrational current and so is observed to show purely diffusional behaviour. As the levels of supporting electrolyte fall, so the proportion of migrational current carried by the electroactive species increases until its migration becomes observable in the voltammetry. The currents (peak and limiting) are noted to increase since the cobaltocenium cation experiences a Coulombic attraction in response to its own reduction, and so migration augments mass transport in this case. Peak separation is also seen to increase, due to the lowering of the potential driving force experienced by the electroactive species at the plane of electron transfer (PET, see figure

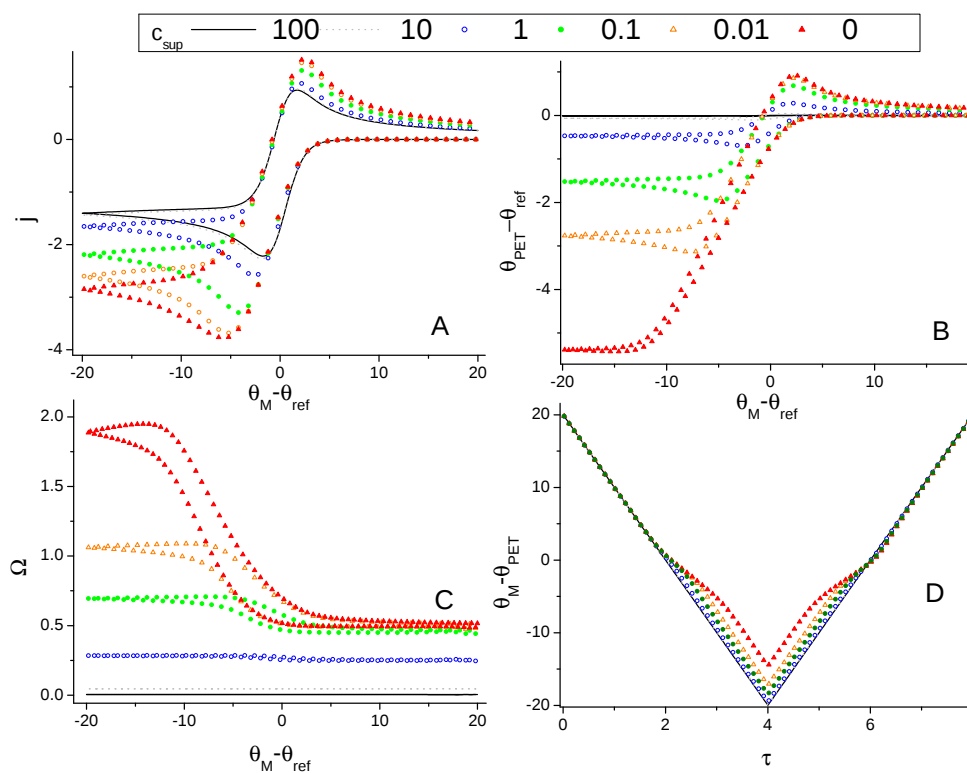


Figure 6.1: Simulations at different concentrations of supporting electrolyte using the parameters $\sigma = 10$, $R_e = 10^3$, $D_A = D_B = D_{M^+} = D_{X^-}$, $K^0 = 10^4$ and $\alpha = 0.5$. A) cyclic voltammetry, B) potential drop in solution vs applied potential, C) inferred resistance of solution vs applied potential, and D) potential at the plane of electron transfer vs dimensionless time.

6.1B) caused by the perturbed electric field (commonly termed ‘ohmic drop’), and the consequently increased overpotential required to achieve a transport-limited current. Note that in the model used the PET corresponds to the layer of solution immediately adjacent to the electrode.

Figure 6.1C illustrates the inferred resistance of the solutions with different concentrations of supporting electrolyte, calculated by Ohm’s Law, ($\Omega = \frac{\theta_{\text{PET}} - \theta_{\text{ref}}}{j}$, potential at the plane of electron transfer, θ_{PET} , minus the potential at the reference electrode, θ_{ref} , is divided by the flux, j). For the highest concentrations, a linear relationship is found as traditionally expected, but it is clear that at lower support levels, the complex dependences of both fluxes and potential drop in solution cause Ohm’s Law to no longer be obeyed in terms of a constant resistance. Hence, in general, the ‘electrical resistance’ of a solution is constant in neither time nor space for all weakly-supported solutions. For this reason, we prefer the terminology ‘potential drop’ rather than ohmic drop.

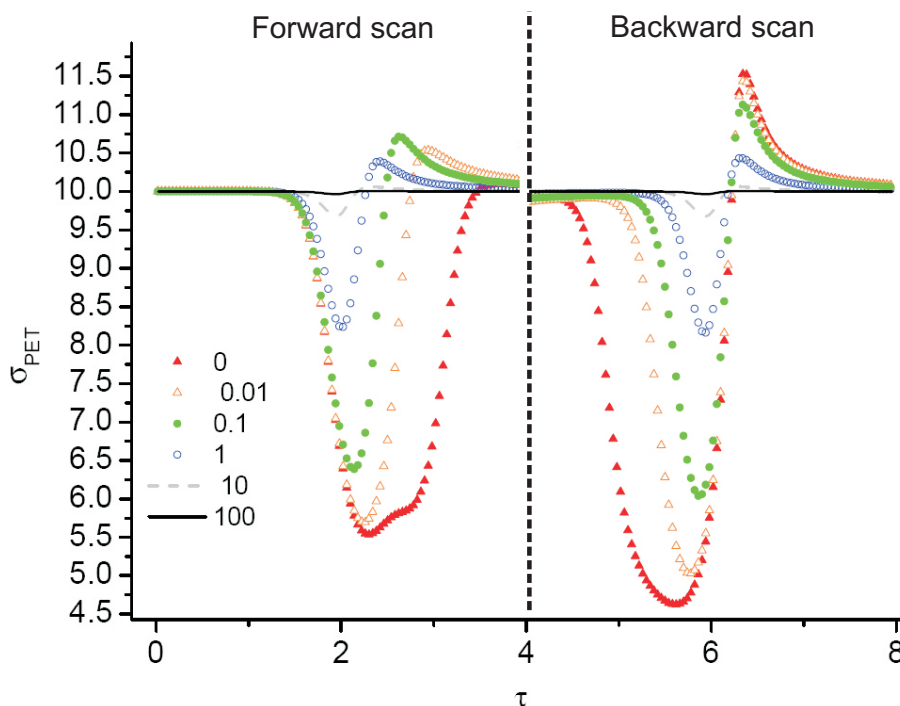


Figure 6.2: Effective scan rate at the plane of electron transfer vs dimensionless time at different concentrations of supporting electrolyte, using the parameters from figure 6.1

Figure 6.1D shows how the lowering of the effective potential difference at the PET for weakly-supported solutions has an effect on the effective voltage scan rate there, such that in the case of zero added supporting electrolyte, there is a clear slowing of the *effective* scan rate close to the peak potentials at the PET, shown in greater detail in figure 6.2 where the dimensionless effective scan rate at the plane of electron transfer (σ_{PET}) is plotted vs. dimensionless time, where σ_{PET} is calculated as;

$$\sigma_{\text{PET}} = \left| \frac{\partial(\theta_{\text{app}} - \theta_{\text{PET}})}{\partial \tau} \right| \quad (6.27)$$

The perceived overpotential acting on the reactant at the surface no longer follows a triangular waveform.

6.3.2 Dependence of peak to peak separation(j_{pf}) and peak height($\Delta\theta_{\text{pp}}$) on c_{sup}

The numerically predicted quantitative variation of the dimensionless observables j_{pf} and $\Delta\theta_{\text{pp}}$ with c_{sup} was studied by producing surfaces in which the change in the observable is plotted in the z -axis against variation in c_{sup} and σ , the dimensionless scan rate. The macro- and microelectrode limits are hence both considered. Figures 6.3 and 6.4 show the variation with c_{sup} for the one-electron oxidation of a neutral species (e.g. ferrocene to ferrocenium).

In Figure 6.3, the recognisable transition with increasing σ from steady-state behaviour to Randles-Ševčík behaviour is observed at high c_{sup} . As c_{sup} decreases, the gradient in the Randles-Ševčík region is reduced from 0.5 and convex deviations from a straight line are noted; this results as the rate of mi-

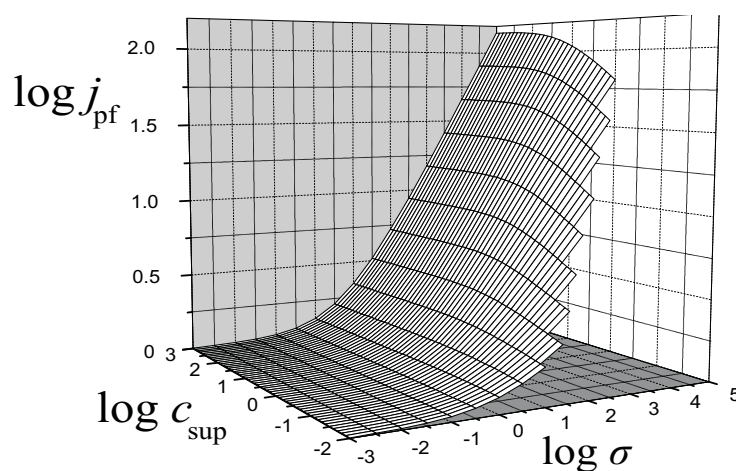


Figure 6.3: $\log j_{\text{pf}}$ vs. $\log \sigma$ and $\log c_{\text{sup}}$ for $A^0 \rightleftharpoons B^+ + e^-$ at a hemispherical electrode with $R_e = 10^5$.

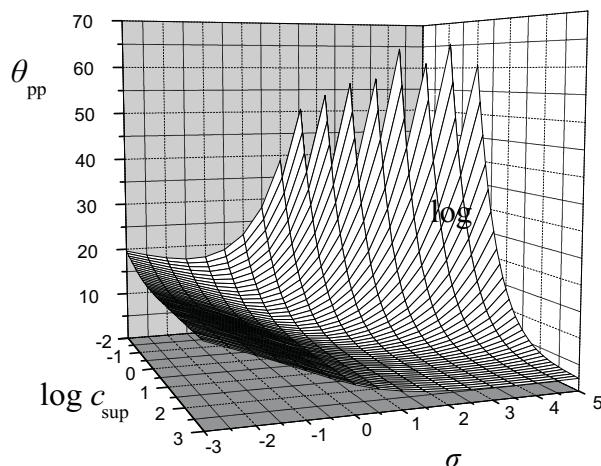


Figure 6.4: $\Delta\theta_{pp}$ vs. $\log \sigma$ and $\log c_{sup}$ for $A^0 \rightleftharpoons B^+ + e^-$ at a hemispherical electrode with $R_e = 10^5$, switching potential $\theta_f = -40$.

gration becomes rate-limiting at high σ and hence some limiting current is approached as $\sigma \rightarrow \infty$. By comparison, peak current is not significantly affected in the low σ regime. We note that the variation of σ does not strictly correspond to a variation in r_e as R_e has been held constant at 10^5 (macroelectrode); it will be demonstrated below, however, that varying R_e has no observable effect on the voltammetry even over the wide range of r_e implied by this range of σ , given that $\sigma \propto r_e^2$. Therefore, the low σ regime may conveniently be treated as equivalent to a microelectrode regime without error, and the conclusion that voltammetry is not strongly affected by c_{sup} at low σ is therefore as expected. We underline that this conclusion cannot hold for nanoelectrodes where the Debye length becomes significant on the scale of the electrode.

Figure 6.4 demonstrates the increased $\Delta\theta_{pp}$ resulting from increased ohmic drop at large electrodes (high σ) in conditions of decreased c_{sup} . Under typical macroelectrode voltammetry conditions of $\sigma > 10^3$, a significant positive deviation from $\Delta E_{pp} \approx 60\text{mV}$ ($\Delta\theta_{pp} \approx 2.3$) is noted below relatively high support ratios, with distinguishable ohmic drop beginning below $10 < c_{sup} < 100$. The extent of the ohmic drop at the lowest support ratios is such that no diffusion-limited peak occurs within the range of the scan, for which the simulated switching potential was $\approx E_f^\ominus + 1.5\text{V}$; consequently, some j_{pf} data values in Figure 6.3 are absent. It is in particular notable that at all scan rates the limit of infinite resistance for a solution with $c_{sup} \rightarrow 0$, and hence no mobile charges, is achieved: infinite peak-to-peak separation would be observed, therefore some simulations in low ionic strength did not reach the peak within the potential window of the simulation, henceforth the discontinuity observed at

the top of the Figure 6.4.

6.3.3 Effect of z_A

Where $z_A \neq 0$, the electroactive species and its counter-ion contribute to compensating solution resistance, and act themselves as supporting electrolyte. Additionally, if its charge is appropriate, the electroactive species can compensate the change in solution charge for its own oxidation or reduction by migrating towards the electrode surface. Where $z_A \neq 0$ and $c_{\text{sup}} \rightarrow 0$, it is likely that migration of the electroactive species and its counter-ion dominate mass transport and are crucial to allowing electron transfer by migrating in order to maintain electroneutrality. Consequently a minimum ‘intrinsic’ support level exists for the case $z_A \neq 0$, being the degree of support provided by the electroactive species itself.

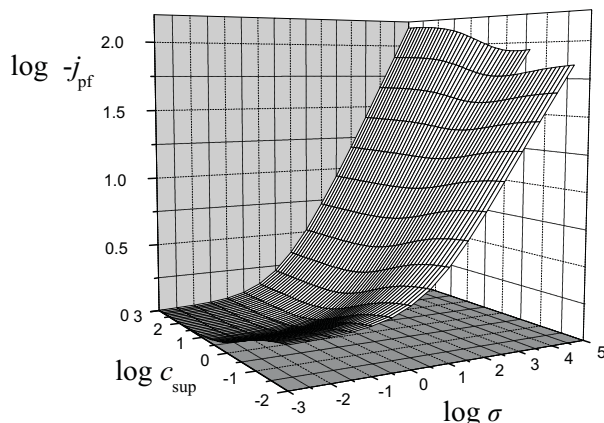


Figure 6.5: $\log -j_{\text{pf}}$ vs. $\log \sigma$ and $\log c_{\text{sup}}$ for $A^+ + e^- \rightleftharpoons B^0$ at a hemispherical electrode with $R_e = 10^5$.

Figures 6.5 and 6.6 show the variation with c_{sup} for the one-electron reduction of a singly-charged species (e.g. cobaltocenium to cobaltocene). Figures 6.7 and 6.8 show the variation with c_{sup} for the one-electron reduction of an ion with $z_A = +3$ (e.g. hexaammineruthenium(III) to hexaammineruthenium(II)). In place of the infinite limit of Figure 6.4, a self-supported limiting maximum $\Delta\theta_{\text{pp}}$ is approached as $c_{\text{sup}} \rightarrow 0$.

Rooney et al. reported “approximately reversible” self-supported macroelectrode voltammetry for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ couple at glassy carbon, Au and Pt electrodes.²⁰ Examination of the published voltammograms suggests $\Delta E_{\text{pp}} \gg 60$ mV is in fact observed, and as noted, at the high concentrations of the electroactive species and low scan rates employed, convection is likely to significantly influence

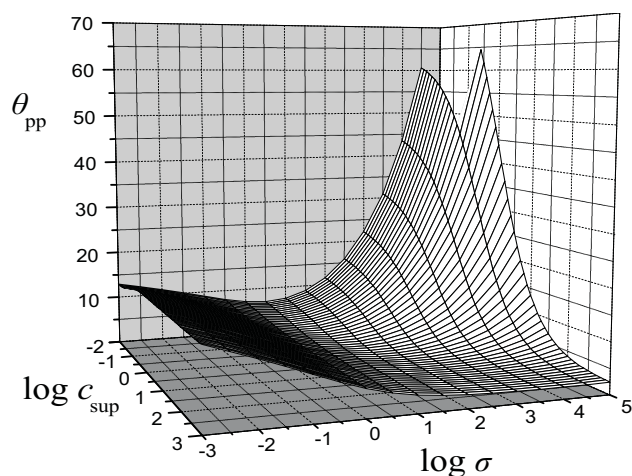


Figure 6.6: $\Delta\theta_{pp}$ vs. $\log \sigma$ and $\log c_{sup}$ for $A^+ + e^- \rightleftharpoons B^0$ at a hemispherical electrode with $R_e = 10^5$, switching potential $\theta_f = -40$.

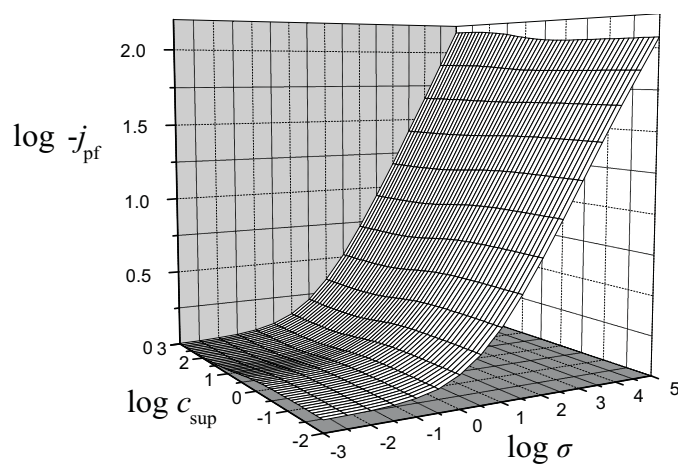


Figure 6.7: $\log -j_{pf}$ vs. $\log \sigma$ and $\log c_{sup}$ for $A^+ + e^- \rightleftharpoons B^0$ at a hemispherical electrode with $R_e = 10^5$, switching potential $\theta_f = -40$.

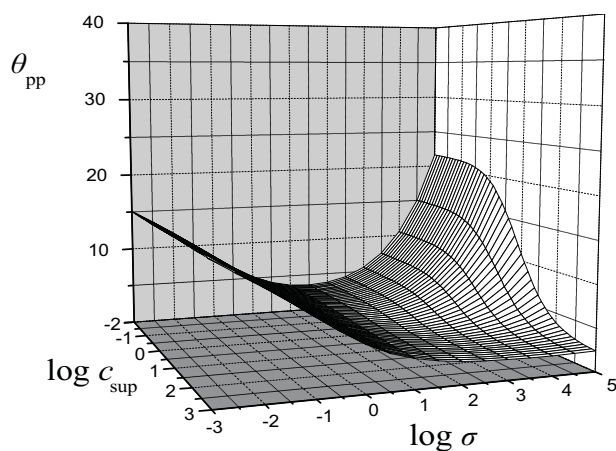


Figure 6.8: $\Delta\theta_{pp}$ vs. $\log \sigma$ and $\log c_{sup}$ for $A^{3+} + e^- \rightleftharpoons B^{2+}$ at a hemispherical electrode with $R_e = 10^5$, switching potential $\theta_f = -40$.

mass transport. Our prediction is that in a self-supported regime, a finite proportion of mobile charges is present at any given concentration of A, and hence the ohmic drop observed in cyclic voltammetry is not a function of the electroactive species concentration, provided there is sufficient ionic strength in solution to render the Debye length much smaller than the diffusion layer. This is confirmed below in the determination that for macroscale voltammetry, R_e , the parameter containing C_A^* , does not affect peak-to-peak separation.

6.3.4 Effect of R_e

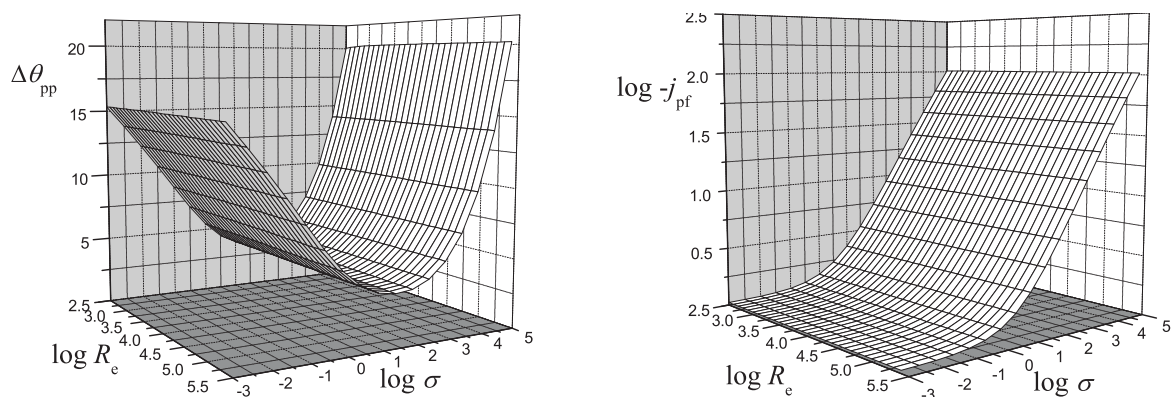


Figure 6.9: $\log j_{pf}$ vs. $\log \sigma$ and $\log R_e$ for $A^0 \rightleftharpoons B^+ + e^-$ at a hemispherical electrode with $c_{sup} = 0.2$.

The dimensionless parameter R_e , which arises in the removal of dimensionality from the Poisson equation, was introduced above as representative of the scale of the electrode compared to the Debye length. Detailed surfaces were produced showing the effect of R_e and σ on j_{pf} and $\Delta\theta_{pp}$ for a one-electron oxidation of a neutral species with $c_{sup} = 5$ and 0.2 (fig. 6.9). In both cases, R_e is shown to have no significant effect on the voltammetry: c_{sup} is sufficient to make the Debye length negligible on the electrode scale, even at low R_e and low σ , such that electroneutrality is maintained until a distance very close to the electrode surface and so perceptible migration effects are negligible, with ohmic drop dominating the effect of c_{sup} on the voltammetry. The gradient in the Randles-Ševčík ‘straight-line region’ is ≈ 0.435 here, with marked convexity at the highest values of σ . A comparison with a similar plot for the one-electron reduction of a species A^+ (supporting information) showed no different results; it is therefore evident that provided R_e is large, its magnitude does not further quantitatively affect the voltammetry.

6.3.5 Effect of D_B/D_A

The effect of the ratio of diffusion coefficients, D_B / D_A , was studied by examination of variations in θ_{pf} and $\Delta\theta_{pp}$. These parameters are affected by D_B only where c_{sup} is very low, and hence the migration of the product species following its creation becomes significant to maintaining charge balance. For the one-electron oxidation of neutral A, increased D_B shifts the peak positions, considered from θ_{pf} , to more negative potentials, as is well established in the diffusion-only case.¹ This effect is enhanced under weakly supported conditions where the diffusion-migration of B becomes more significant to charge balance and hence affects the rate of electrolysis to a greater extent.

6.3.6 Effect of D_M and D_X

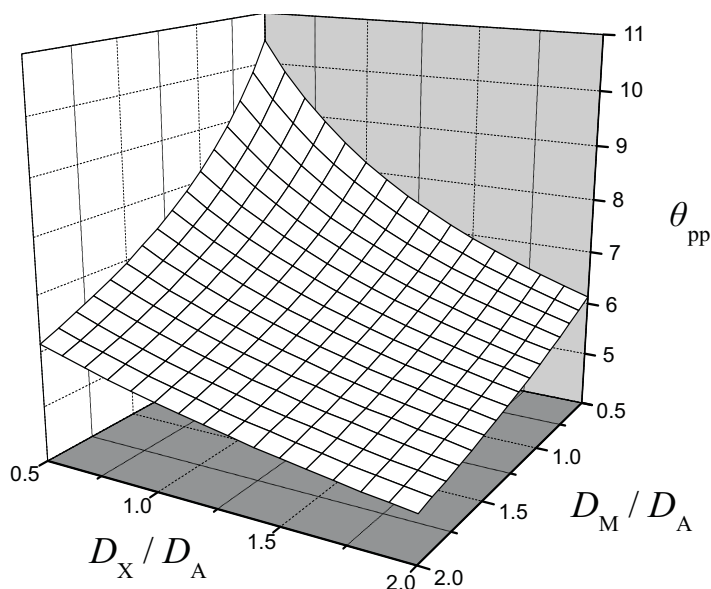


Figure 6.10: $\Delta\theta_{pp}$ vs. D_M/D_A and D_X/D_A for $A^0 \rightleftharpoons B^+ + e^-$ at a hemispherical macroelectrode with $c_{sup} = 10$ (weak support), $\sigma = 10^4$, $R_e = 10^5$, switching potential $\theta_f = 20$.

In cases where one or both of the supporting electrolyte species has a high diffusion coefficient compared to the electroactive species, and so can migrate quickly relative to the rate of electrochemically driven diffusion to the surface, solution resistance is compensated more rapidly and hence the ohmic drop is correspondingly less. A plot of $\Delta\theta_{pp}$ vs. D_M and D_X is shown at Figure 6.10. The symmetry of this plot indicates that the compensation of solution charge is equally well achieved at the electrode surface either by the migration of like charges away from the surface or opposite charges towards it. The importance of a relatively high supporting electrolyte diffusion coefficient to effective

compensation of solution resistance is more deeply .

6.3.7 Experimental Results

In order to corroborate the theoretical treatment and the presented simulated data cyclic voltammograms were run in the solution containing cobaltocenium hexafluorophosphate and different concentrations of supporting electrolyte. Cyclic voltammograms were first run using the hemispherical mercury electrode in a solution containing 3mM cobaltocenium hexafluorophosphate and 150 mM of TBAP at different scan rates of 1000, 500, 200, 100 and 50 mV s^{-1} . The data are presented in figure 6.11 (solid lines) for 1000 to 50 mVs^{-1} and the currents can be seen to increase with scan rate. For a planar electrode a square root dependence of peak current with scan rates is expected.¹ However, for hemispherical electrodes of the size studied the response is intermediate between convergent micro-electrode diffusion and the planar electrode response. This feature also explains the decrease of the peak to peak separation with scan rate.²⁷

Tables and Figures

Parameter	Value
C_A	3mM
$k^0_{(a)}$	10 cm s^{-1}
$D_{\text{CoCp}_2^+}$	$1.8 \pm 0.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} *$
D_{CoCp_2}	$2.3 \pm 0.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
$D_{\text{ClO}_4^- (b)}$	$3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
$D_{\text{TBAP}^+ (b)}$	$2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
r_e	$25 \times 10^{-4} \text{ cm}$

Table 6.1: Values used for the simulations. a) The heterogeneous rate constant was set high enough to maintain electrochemically ‘reversible’ conditions. b) Calculated by the Wilke-Chang Method.³⁰ * A value of $D_{\text{CoCp}_2^+} = 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was used in the simulations with lower supporting electrolyte (see Experimental results).

The cyclic voltammograms of the solution containing 150mM TBAP were simulated with the program DigiSimTM, assuming diffusion-only transport. DigiSimTM has an option for hemispherical diffusion, which was selected. The parameters used for the simulation are stated in table 6.1 and the

simulations are shown in figure 6.11 (open circles). The simulations are found to be in good agreement with the experimental data. In particular the good fit between the experiment and the simulations allows us to infer that the amount of supporting electrolyte was high enough to ensure diffusion-only flux, and that negligible migration of electroactive species occurs. The recorded experimental data were also compared with the NPP simulation model, for the solution containing the highest concentration of supporting electrolyte. Good mutual agreement was obtained between DigiSim, the NPP simulations, and the experimental results. In figure 6.11, the two theoretical curves (DigiSim and NPP simulations) overlap exactly; therefore, for the sake of clarity, just the NPP simulations are presented.

Next, cyclic voltammograms were recorded in a solution containing 3mM cobaltocenium hexafluorophosphate and 30mM TBAP. The experimental data are presented in figure 6.11 by dashed lines. It is observed that a broadening in the peak-to-peak separation occurs, compared to that in the case of higher support concentrations, along with an increase in current. Comparison between simulation and experiment was made using the parameters in table 1, except for the diffusion coefficient of the cobaltocenium cation, which was estimated by means of best fitting to be $D_{\text{CoCp}_2^+} = 1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is close to literature values.²⁸ The small difference in diffusion coefficients of cobaltocenium at different concentrations of supporting electrolyte has been previously studied in detail by Amatore et al.¹¹ Figure 6.11 shows theory (squares) and experiment (dashed lines) to be in good agreement.

Finally, cyclic voltammograms were recorded in a solution containing only 3mM cobaltocenium hexafluorophosphate and no deliberately added supporting electrolyte, although the complete absence of the latter is experimentally rigorously impossible to achieve exactly because of trace impurities in the solution. The experimental results obtained are presented in figure 6.11 (dotted line), and show a larger increase in the peak-to-peak separation compared to the full or partial support cases. The faradaic current is much larger than those observed in the previous cases.

To compare to the experiments, the simulation used the same parameters for diffusion coefficients as presented in the previous case with 30mM supporting electrolyte. The simulated voltammogram had a slightly larger peak current than the experimental result (figure 6.12). Therefore, trace inert ionic impurities were considered in the simulation. The impurities were modeled in terms of an elevated c_{sup} , assuming that the impurities in solution have the same charge and diffusion coefficients as the electroactive species (figure 6.12). A calibration plot was made varying the concentrations of

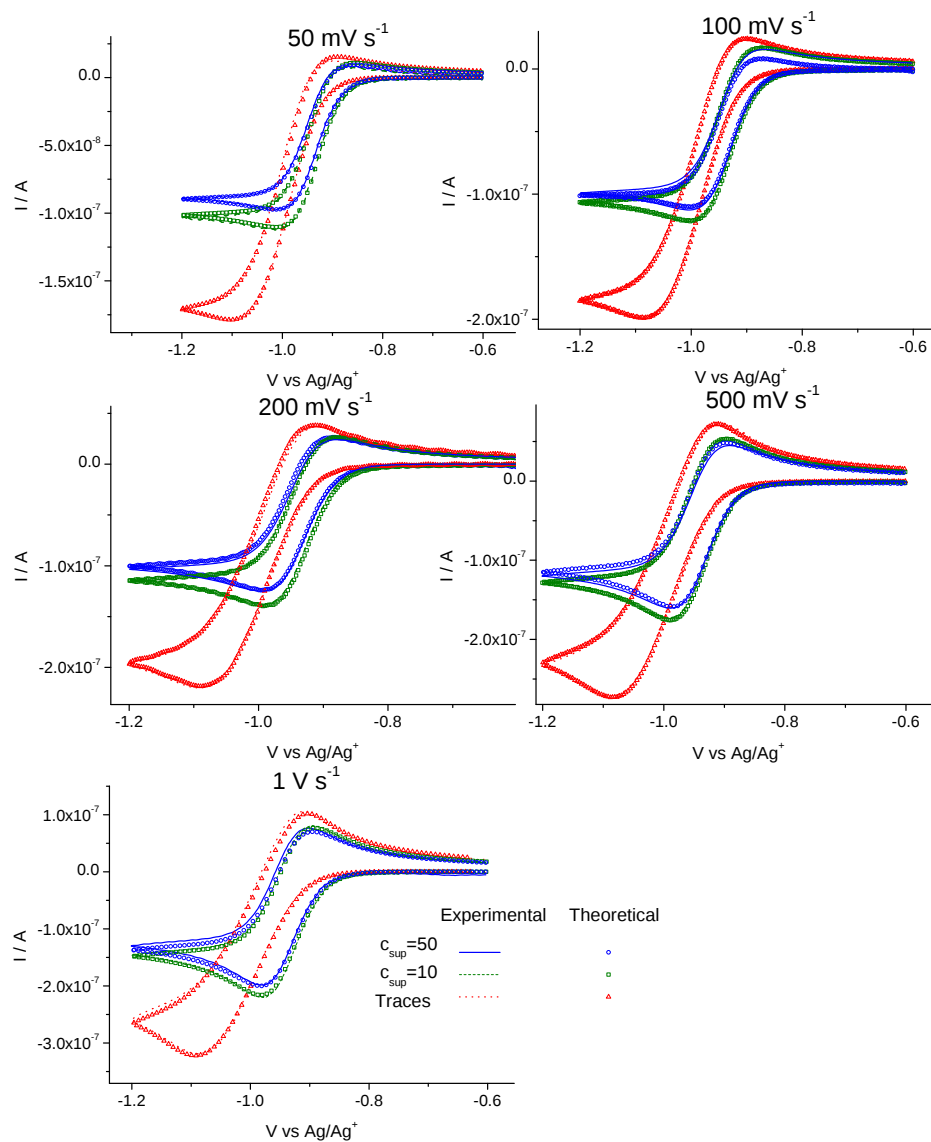


Figure 6.11: Comparison between theory and experiment at different concentrations of supporting electrolyte, for scan rates of 50, 100, 200, 500 and 1000 mV s^{-1} and different concentrations of supporting electrolyte $c_{\text{sup}} = 50$, 10 and traces of ionic impurities (no intentionally added supporting electrolyte).

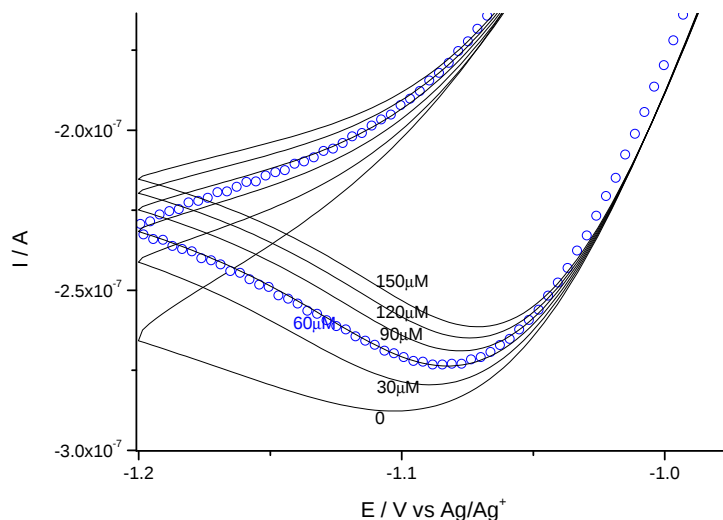


Figure 6.12: Simulation of the self-supported reduction of the 3mM cobaltocenium hexafluorophosphate with different trace levels of monovalent electrolyte MX in the range of 0-150 μM .

trace electrolyte (figure 6); it was found that traces of 60 μM of inert electrolyte gave the best agreement with theory, and this is consistent with the 98% purity stated by the supplier for cobaltocenium hexafluorophosphate, if the remaining 2% is ionic.

It is interesting to note that whilst previous experimental studies²⁹ suggest that a variation in the heterogeneous rate constant (k^0) with the concentration of supporting electrolyte is observable, in the present case such a change was not inferred, and the kinetic parameters remained fast enough not to influence the shape of the cyclic voltammogram. Interestingly we note that an early treatment of reversible cyclic voltammetry, but under the assumption of electroneutrality, did “not considered” the simulation of processes involving the formation of uncharged species (such as CoCp_2 in the present case) since “the concentration of ions” in the depletion layer approaches zero at the electrode surface, “producing very high local resistance”.¹⁸

6.4 Conclusions

The theory of cyclic voltammetry in weakly supported media has been approached using a numerical model invoking a zero-field approximation at the electrode surface. Expected changes in observed voltammetric waveshape with variation of the significant intrinsic parameters of the system were plot-

ted on working surfaces and interpreted appropriately. Comparison was then drawn with experimental cyclic voltammetry for the aqueous $\text{CoCp}_2^{+/0}$ system at mercury hemispherical electrode; by plotting theoretical and experimental data together, the theoretical model was shown to be quantitatively accurate at different scan rates.

The present study proves the usefulness of simulation using the Nernst-Planck-Poisson equations for studying cyclic voltammetry in the absence of intentionally added supporting electrolyte; moreover the agreement between theory and experiment is excellent.

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Chapter 7

Cyclic Voltammetry at weakly supported conditions involving amalgam formation and metal stripping

In the present chapter, we focus on the voltammetric behavior of thallium at mercury microelectrodes. The accumulation (preconcentration) of reduced metals in mercury, followed by their subsequent anodic stripping, is a very popular analytical method of trace analysis.^{1,2} The $\text{Tl}^+/\text{Tl}(\text{Hg})$ couple is a reversible model system that has been widely investigated at mercury drop electrodes,^{3–6} mercury thin-film electrodes^{7,8} and mercury microelectrodes.^{9,10} In a previous chapter⁵¹¹ dealing with the chronoamperometric response of this system, it was shown that even in the presence of fairly large amounts of supporting electrolyte, the potentiostatic stripping of Tl^+ in solution leads to unusual current-time transients. Using the NPP equations in conjunction with the zero-field approximation, it was demonstrated that in such conditions, the system is only partially supported. Here, we extend the combined experimental and theoretical investigations of this system to the study of its potentiodynamic (i.e. cyclic voltammetric) behavior in different supporting conditions. Although the voltammetric features of thallium deposition and stripping are extremely sensitive to many experimental parameters, it will be shown that our model accurately reproduces the experimental results for any supporting electrolyte concentration. As a result, we believe that the NPP model, validated in this work, provides a rigorous basis for the accurate and quantitative modeling of diverse electrode processes which involve mixed diffusion, migration and potential distribution effects. The model, used predictively, thus allows new physical insights on the understanding of the separate roles of each of the factors, for the case reported and more generally.

7.1 Theoretical Model and Numerical Simulations

7.1.1 The model

The voltammetric reduction of a cation A^{z+} into an amalgam of neutral A^0 in a Hg hemisphere and its subsequent anodic stripping are modeled numerically as follows.



The solution is supported by a concentration C_{sup} of a monovalent inert salt MX , which is assumed to be completely dissociated in solution. The concentration of X^- is augmented to include the additional concentration of anions resulting from the A^{z+} salt. The combined diffusional and migrational flux of a species i at any point in solution, neglecting convection, is described by the Nernst-Planck equation:

$$J_i = -D_i \left(\nabla C_i + \frac{z_i F}{RT} C_i \nabla \phi \right) \quad (7.2)$$

where for species i , J_i is the flux vector, D_i the diffusion coefficient, C_i the concentration, z_i the species charge, the electrostatic potential, F the Faraday constant, R the gas constant and T the temperature. The mass continuity equation relates the flux to the time evolution of the concentration of i :

$$\frac{\partial C_i}{\partial t} = -\nabla J_i \quad (7.3)$$

hence

$$\frac{\partial C_i}{\partial t} = D_i \left(\nabla^2 C_i + \frac{z_i F}{RT} (C_i \nabla^2 \phi + \nabla C_i \nabla \phi) \right) \quad (7.4)$$

The electrostatic potential must additionally satisfy the Poisson equation everywhere in solution:

$$\nabla^2 \phi = -\frac{F}{\epsilon_s \epsilon_0} \sum_i z_i C_i \quad (7.5)$$

where ϵ_s is the relative permittivity of the solvent medium and ϵ_0 is the permittivity of free space. Various dimensionless variables are introduced to simplify the equations and to reduce the number of independent variables in the system:

$$c_i = \frac{C_i}{C_a^*}; \quad \theta = \frac{F\phi}{RT}; \quad r = \frac{r}{r_e}; \quad \tau = \frac{D_{\text{sol}}}{r_e^2}; \quad D_i^* = \frac{D_i}{D_{\text{sol}}}$$

where D_{soln} is the diffusion coefficient of A^{z+} in solution, C_A^* is its bulk concentration, and r_e is the Hg drop radius, which is assumed to be constant. The dimensionless Nernst-Planck-Poisson equation set may then be expressed, in a hemispherical space:

$$\frac{\partial C_i}{\partial t} = D_i^* \left(\frac{\partial^2 C_i}{\partial R^2} + \frac{2}{R} \frac{\partial C_i}{\partial R} + z_i \left(c_i \frac{\partial^2 \theta}{\partial R^2} + c_i \frac{2}{R} \frac{\partial \theta}{\partial R} + \frac{\partial c_i}{\partial R} \frac{\partial \theta}{\partial R} \right) \right) \quad (7.6)$$

$$\frac{\partial^2 \theta}{\partial R^2} + \frac{2}{R} \frac{\partial \theta}{\partial R} = R_e^2 \sum_i z_i C_i \quad (7.7)$$

where the dimensionless variable R_e is defined:

$$R_e = r_e \sqrt{\frac{F^2 C_a^*}{RT \epsilon_s \epsilon_0}}$$

and represents the ratio of the electrode radius to the Debye length taken in the absence of supporting electrolyte.

7.1.2 Boundary conditions

Equations 7.6 and 7.7 are solved subject to suitable boundary conditions. Outside the drop, species A^{z+} , M^+ and X^- are present and the electrostatic potential is non-zero, so these four variables have boundaries at $R = 1$ and $R \rightarrow \infty$. Inside the drop only the uncharged species A^0 is present, so A^0 has boundaries at $R = 0$ and $R = 1$, and the potential is not considered in this region since A^0 does not migrate. At $R = 1$, Butler-Volmer kinetics are applied, relating the flux of A^{z+} normal to the electrode to the surface concentrations of A^{z+} and A^0 in the form:

$$\left. \frac{\partial C_{A^{z+}}}{\partial R} \right|_{R=1} = K^0 \left(\exp(-\alpha(\theta_{app} - \theta_0)) c_{A^{z+},1} - \exp(z - \alpha(\theta_{app} - \theta_0)) c_{A^0,1} \right) \quad (7.8)$$

In this equation, α is the electron transfer coefficient, θ_{app} is the dimensionless applied potential, relative to the formal potential E_f^0 :

$$\theta_{app} = \frac{F}{RT} (E - E_f^0) \quad (7.9)$$

K^0 is the dimensionless heterogeneous rate constant defined as:

$$K^0 = \frac{k^0 r_e}{D_{sol}}$$

where k^0 is the heterogeneous rate constant, and θ^0 is given by:

$$\theta_0 = \frac{F\phi_{(R=1)}}{RT}$$

Since we are considering cyclic voltammetry, the applied potential varies linearly in time from its initial value at a dimensionless scan rate σ :

$$\sigma = \frac{\partial \theta_{app}}{\partial \tau}$$

where is the dimensional scan rate. The same scan rate, though with opposite sign, also applies for the reverse sweep. Conservation of mass at the electrode surface additionally requires the equations concerning A^{z+} and A^0 to be coupled at $R = 1$:

$$\left. \frac{\partial c_{A^{z+}}}{\partial R} \right|_{R=1} = \frac{D_{Hg}}{D_{sol}} \left. \frac{\partial c_{A^{z+}}}{\partial R} \right|_{r=1} \quad (7.10)$$

where D_{Hg} is the diffusion coefficient of A^0 in the amalgam. Assuming M^+ and X^- to be inert and insoluble in Hg, we have:

$$\left. \frac{\partial c_{M^+}}{\partial R} \right|_{R=1} = \left. \frac{\partial c_{X^-}}{\partial R} \right|_{R=1} = 0 \quad (7.11)$$

and from symmetry requirements:

$$\left. \frac{\partial c_{A^0}}{\partial R} \right|_{R=0} = 0 \quad (7.12)$$

The boundary condition for the potential at the electrode surface assumes that the double layer is negligible in extent compared to the diffusion layer. Then the outer boundary of the double layer, where the enclosed charge tends to zero and so the electric field (potential gradient) tends to zero as well, may be taken as occurring precisely at the electrode surface:

$$\left. \frac{\partial \theta}{\partial R} \right|_{R=1} = 0 \quad (7.13)$$

This simplifying assumption has been demonstrated by past work¹² to be valid so long as the diffusion layer extends beyond a few nanometres; this condition is met for electrodes of micrometer dimensions or larger, but not for electrodes in the nanometer range. The $R \rightarrow \infty$ boundary is represented by limiting the simulation space to the maximum extent of the diffusion layer for a diffusion-only system,

being $R_{max} = 6\sqrt{\tau_{max}}$,¹³ the requirement of electroneutrality in bulk solution ensures that even in a weakly supported system, this is still an appropriate limiting point for the simulation space. The concentrations of A^{z+} , M^+ and X^- are set to their bulk values at this boundary:

$$c_{A^{z+}} = 1; \quad c_{M^+} = c_{sup}; \quad c_{X^-} = c_{sup} + c_{A^{z+}}z$$

where c_{sup} is the dimensionless support ratio as normalized by the bulk concentration of A^{z+} . Finally, the potential boundary condition in bulk solution is set such that electroneutrality is maintained outside the diffusion layer. The Poisson equation for a uniformly electroneutral medium is:

$$\frac{\partial^2 \theta}{\partial R^2} + \frac{2}{R} \frac{\partial \theta}{\partial R} = 0 \quad (7.14)$$

Solving subject to the condition that $\theta \rightarrow 0$ as $R \rightarrow \infty$ yields the expression:

$$\theta_{(R=R_{max})} + R_{max} \left. \frac{\partial \theta}{\partial R} \right|_{R=R_{max}} = 0 \quad (7.15)$$

which is used as the $R \rightarrow \infty$ boundary condition for potential.

A dimensionless current, j , is recorded simply as:

$$j = -z \left. \frac{\partial c_{A^{z+}}}{\partial R} \right|_{R=1} \quad (7.16)$$

which relates to the dimensional current as:

$$i = 2\pi F C_A^* D_{sol} r_e j \quad (7.17)$$

7.1.3 Numerical Methods

The NPP equations are solved using a fully implicit finite difference method across an irregular grid of points in R . The resulting set of coupled non-linear simultaneous equations is solved using the iterative Newton-Raphson method. The expanding grid corresponds to that used in previous work,³⁸ with a region of extremely dense regular grid spacing close to $R = 0$ and $R = 1$ that expands proportionally to R beyond some characteristic switching point R_s away from these boundaries. A regular time grid was employed, defined by the value PT , a regular number of time steps per unit app. Optimal simulation

parameters were established using detailed convergence studies. All simulations were programmed in C++ and run on a desktop computer (Intel Core2 Quad 2.4 GHz processor, 2 GB of RAM), with a running time of 10 minutes per simulation being typical.

7.2 Experimental

All the solutions were prepared with ultra pure water (Millipore, resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}^{-1}$ at 25°C). Mercury(I) nitrate (Aldrich, $\geq 98\%$), potassium nitrate (Aldrich, ACS Reagent), thallium(I) nitrate (Aldrich, $\geq 99\%$) and nitric acid (Fisher Scientific, 70%) were used without further purification. The experiment were conducted in a thermostated ($T = 298 \text{ K}$) three electrode cell connected to a true linear sweep potentiostat built in-house. Prior to the experiments, the solutions were purged with nitrogen for 20 minutes to remove dissolved oxygen, and a nitrogen blanket was kept over the solutions throughout the measurements. A platinum wire was used as counter electrode, while the reference electrode was a saturated calomel electrode (SCE). The working electrode was a hemispherical mercury drop prepared according to a procedure described in previous publications.^{11,15} Briefly, mercury was electrodeposited on a platinum disk electrode ($45 \mu\text{m}$ radius) from a deaerated solution containing 10 mM mercury(I) nitrate, 0.5 M potassium nitrate and 0.5% nitric acid. A potential of -0.245 V (vs Ag/Ag^+) was applied until the desired amount of charge was passed.

7.3 Results and Discussion

7.3.1 Experimental Results

Due to its large electron transfer rate constant,^{5,6,16,17} the $\text{Tl}^+/\text{Tl}_{(\text{Hg})}$ couple exhibits at the mercury electrode an electrochemically reversible behavior up to fairly high scan rates. In the presence of a very large excess of supporting electrolyte, migration is not expected to contribute to the mass transport of the electroactive species and the current recorded under voltammetric conditions is, therefore, solely controlled by diffusion. However, since Tl^0 is soluble in mercury (up to 43 % w/w at 298 K ¹⁸), both the diffusion of Tl^+ in solution and that of Tl^0 in the mercury hemisphere affect the voltammetric features. Figure 7.1 shows cyclic voltammograms obtained at various scan rates in a 5 mM $\text{TlNO}_3 + 1.5 \text{ M KNO}_3$ solution. The intensity of the peak observed on the forward (negative direction) potential sweep increases significantly with the scan rate, and a shift of the peak potential in the

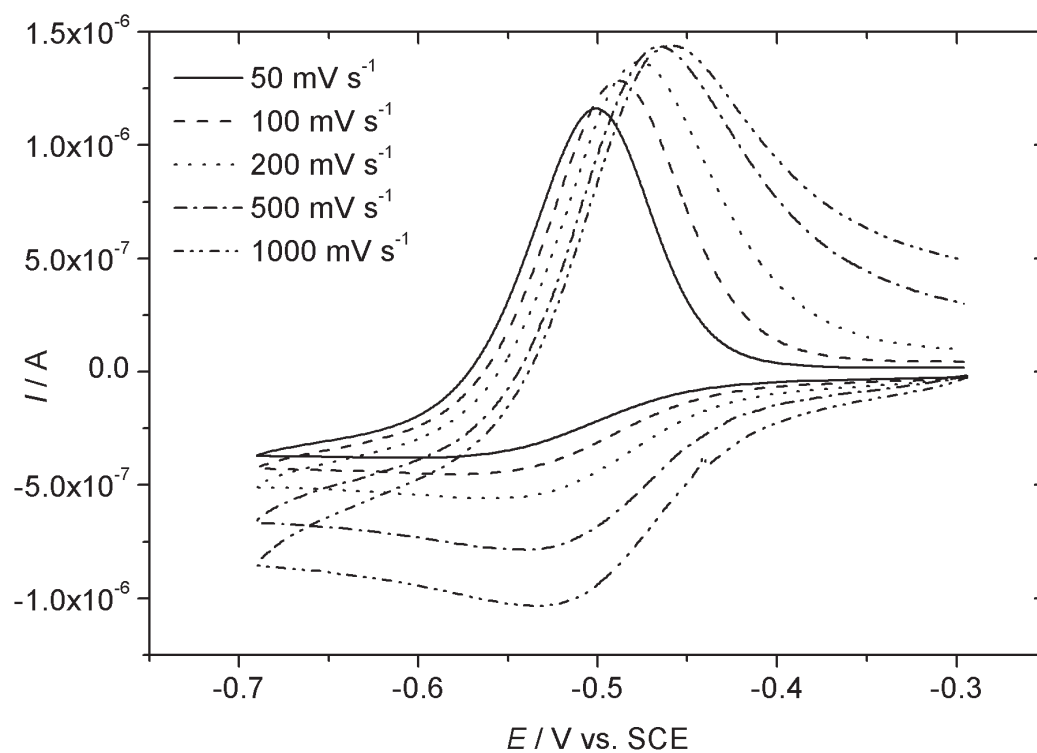


Figure 7.1: Influence of the scan rate on the cyclic voltammograms recorded at a mercury microelectrode in 5 mM TiNO_3 + 1.5 M KNO_3 solutions.

negative direction is observed upon decreasing the scan rate. This rather unusual dependence of the peak position on the scan rate arises from the accumulation of thallium in the mercury hemisphere, so both the concentrations of Tl^+ in solution and of Tl^0 in the amalgam affect the voltammetric response. This point will be explained in more detail below using the theoretical results (Section 4.3). Because the concentration of thallium in mercury is high, a much larger peak is obtained during the reverse (positive direction) potential sweep. The peak position and intensity are now controlled by the concentration profile of thallium within the mercury hemisphere. Increasing the scan rate tends to make the profile steeper, but also decreases the amount of accumulated thallium. As a result, the increase of the anodic peak intensity with the scan rate is less pronounced than that of the cathodic peak, and even seems to level off at the highest scan rates.

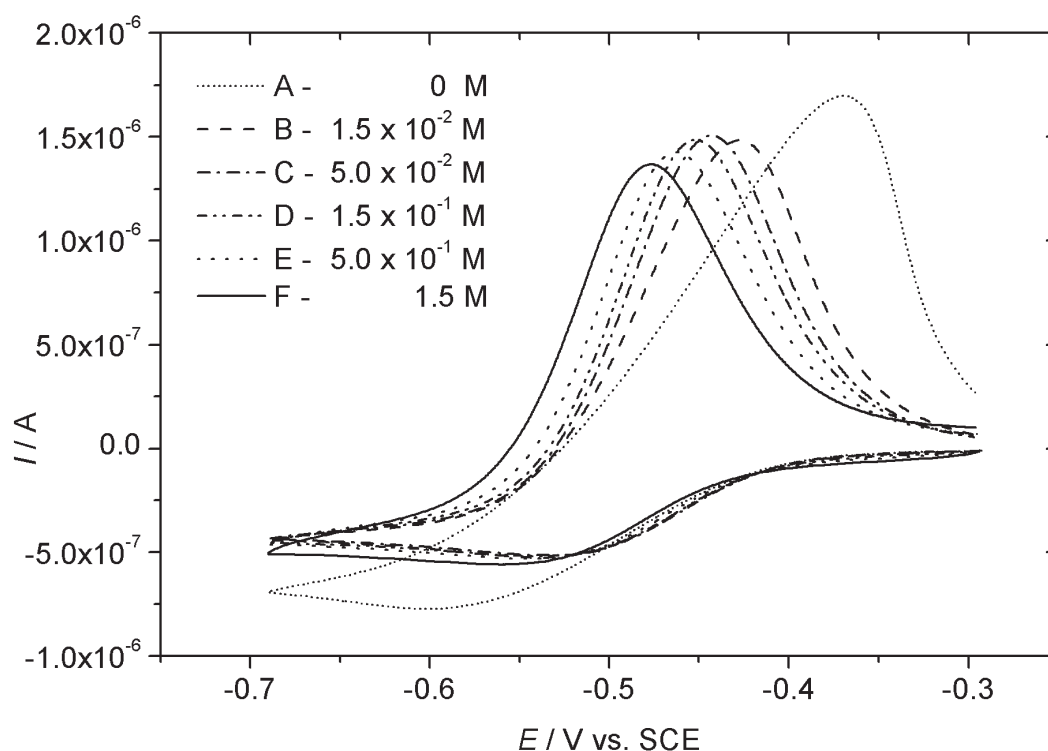


Figure 7.2: Influence of the supporting electrolyte concentration on the cyclic voltammograms recorded at a mercury microelectrode in $5 \text{ mM TlNO}_3 + x \text{ M KNO}_3$ solutions. The values of x are indicated in the image. Scan rate 200 mV s^{-1}

Changing the supporting electrolyte concentration significantly affects the cyclic voltammogram, as shown in Figure 7.2. This figure presents the cyclic voltammograms recorded in 5 mM TlNO_3 solutions in the presence of various concentrations of potassium nitrate, ranging from 0 to 1.5 M. In the absence of supporting electrolyte ('self-supported' conditions), a large enhancement of the reduc-

tion peak is observed due to the contribution of migration to the mass transport of Tl^+ . Addition of supporting electrolyte minimizes the effect of migration, to an extent that depends on the ratio between the electrolyte and electroactive species concentrations. In the presence of 15 mM potassium nitrate, corresponding to a support ratio of 3, the influence of migration on the reduction is almost completely suppressed, in very good agreement with the results of Ciszewska and Osteryoung on the same system (thallium reduction at a mercury microelectrode)¹⁰ It can be seen in Fig. 7.2 that the reduction wave is slightly shifted in the negative direction when the concentration of supporting electrolyte is increased. This displacement is partly due to the effect of the ionic strength on the Tl^+ activity,²³ and hence on the $\text{Tl}^+/\text{Tl}_{\text{Hg}}$ formal potential. It will be shown below that other factors affect the deposition peak position when the supporting electrolyte concentration is varied. The voltammetric features associated with the reoxidation of thallium are very sensitive to the amount of electrolyte. The positive shift of the stripping peak potential observed upon decreasing the electrolyte concentration is too large to arise from the formal potential differences discussed above, and other effects have to be taken into account. In a previous chapter?? dealing with the stripping of thallium from mercury under potentiostatic conditions, we showed that the release of large quantities of positively charged Tl(I) in solution results in a significant potential drop, which in turn affects the driving force of the process. This potential drop was found to be highly dependent on the time, amount of accumulated thallium and supporting electrolyte concentration, leading in some cases to current-time responses largely deviating from purely diffusion-controlled transients. The situation is more complex here, because in cyclic voltammetry the current is recorded under potentiodynamic conditions. It is, therefore, not as easy to extract simple relationships between the experimental parameters (analyte and electrolyte concentrations, scan rate, electrode size) and the analytical output (peak potential and intensity). Similarly, it would be difficult to predict the electrochemical response in a given set of experimental conditions, or to assess quantitatively the extent of effects other than diffusional.

7.3.2 Comparison of theoretical and experimental results

To overcome the problem, a program was written to simulate the electrochemical response obtained in voltammetric experiments. Effects other than diffusional were explicitly included in the program through the implementation of the Nernst-Planck-Poisson equations, and a fast electron transfer kinetics was assumed, which is reasonable in regards of the high value of the electron transfer

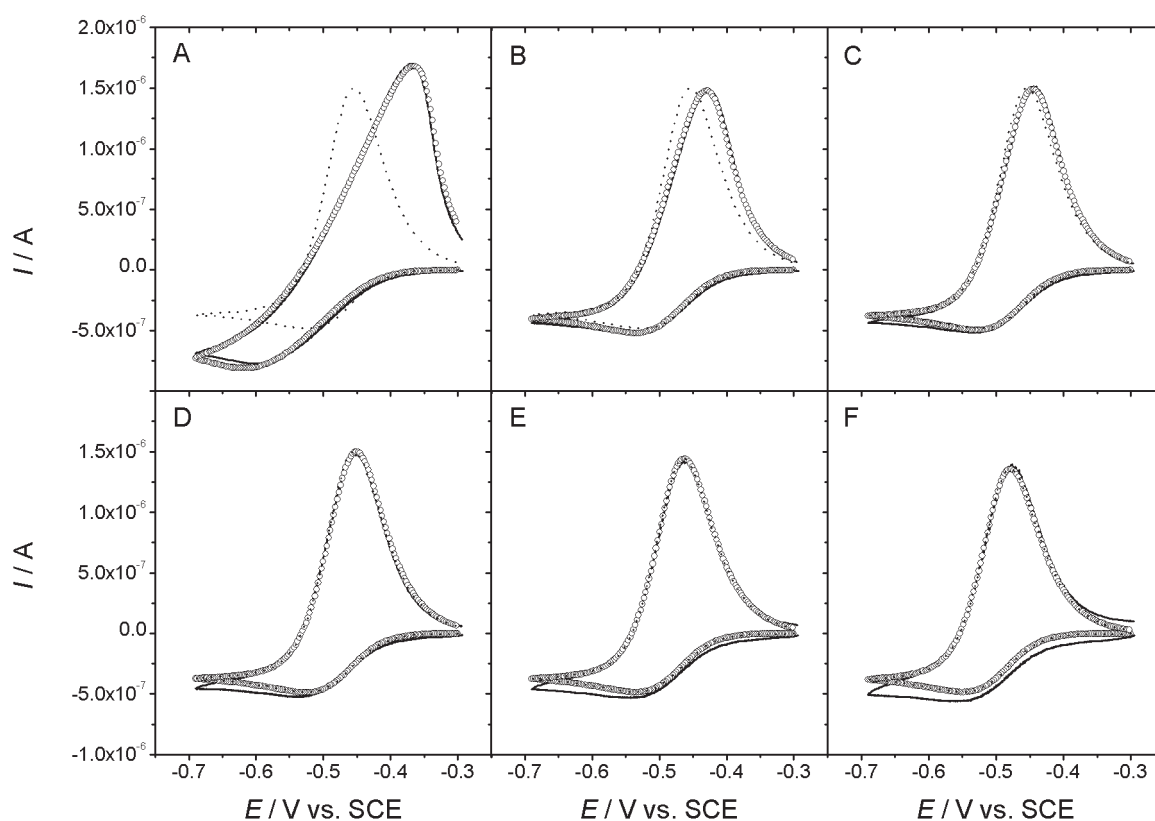


Figure 7.3: Comparison between the experimental (solid lines) and theoretical (open circles) voltammograms simulated using the model described in section 7.3.2. Voltammograms simulated under purely diffusional conditions are shown for comparison (dotted lines). The labels A-F refer to the supporting electrolyte concentrations employed in Fig. 7.2.

rate constant of the $\text{Tl}^+/\text{Tl}_{(\text{Hg})}$ couple.^{5,6,16,17} Figure 7.3 compares the experimental and simulated voltammograms, for the various supporting electrolyte concentrations employed in Fig. 7.2. The theoretical curves were calculated using the following parameters: $D_{\text{soln}} = 1.65 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$;³ $D_{\text{Hg}} = 1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$;⁴ $D_{\text{M}^+} = 1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; $D_{\text{X}^-} = 1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; $k^\circ = 1 \text{ cm s}^{-1}$;¹⁶ $r_e = 45 \text{ m}$; $\alpha = 0.5$;⁶ $E_f^0 = -0.45 \text{ V (vs SCE)}$. The value of the formal potential was calculated by employing the extended Debye-Huckel theory to estimate the activity coefficient of Tl^+ . An excellent agreement is found between the experimental and theoretical voltammograms²⁰ over the entire range of supporting electrolyte concentrations, demonstrating the validity of our theoretical approach (Section 7.1.1). Even in ‘self-supported’ conditions (Fig. 7.3A), where the Debye length κ^{-1} is the largest, our assumption of a negligibly small double layer allows us to reproduce the experimental results. Arguably, specific adsorption of thallium and nitrate on mercury^{22,23} might affect the structure of the double layer and hence the potential profile in solution, but such detailed considerations are not needed to justify our assumption. Indeed, in the present conditions, the characteristic thickness of the double-layer has a value $\kappa^{-1} = 4.3 \times 10^{-9} \text{ m}$ (for a 5 mM concentration of a 1:1 salt in water). By comparison, the range of non-zero potential created by the release of Tl^+ from the mercury electrode has an extent of $1 - 100 \times 10^{-6} \text{ m}^{11}$ which is more than 2 orders of magnitudes larger than the Debye length. In Fig. 7.3, a theoretical voltammogram simulated under purely diffusional conditions is also shown in each case. The plots displayed in Fig. 7.3 confirm that, upon decreasing the amount of supporting electrolyte, significant deviations from a purely diffusion-controlled behavior occur. These are clearly discernible on the backward sweep for electrolyte concentrations not exceeding ten times the amount of electroactive species (Fig. 7.3A, B and C), and can be detected even at higher concentrations on closer examination of the voltammograms.

7.3.3 General behavior of metal deposition and stripping

Fig. 7.3 illustrates the results for a given set of experimental conditions but, as stated earlier, the voltammetric response is very sensitive to many experimental parameters. Although a similar trend would be observed for other conditions, the actual values of the peak currents and potentials could be drastically different. On the other hand, the observed trends are not expected to be specific to the studied system but to apply more generally to the deposition and stripping of other metals, regardless of the actual solution composition or electrode size. Using our numerical simulations, we

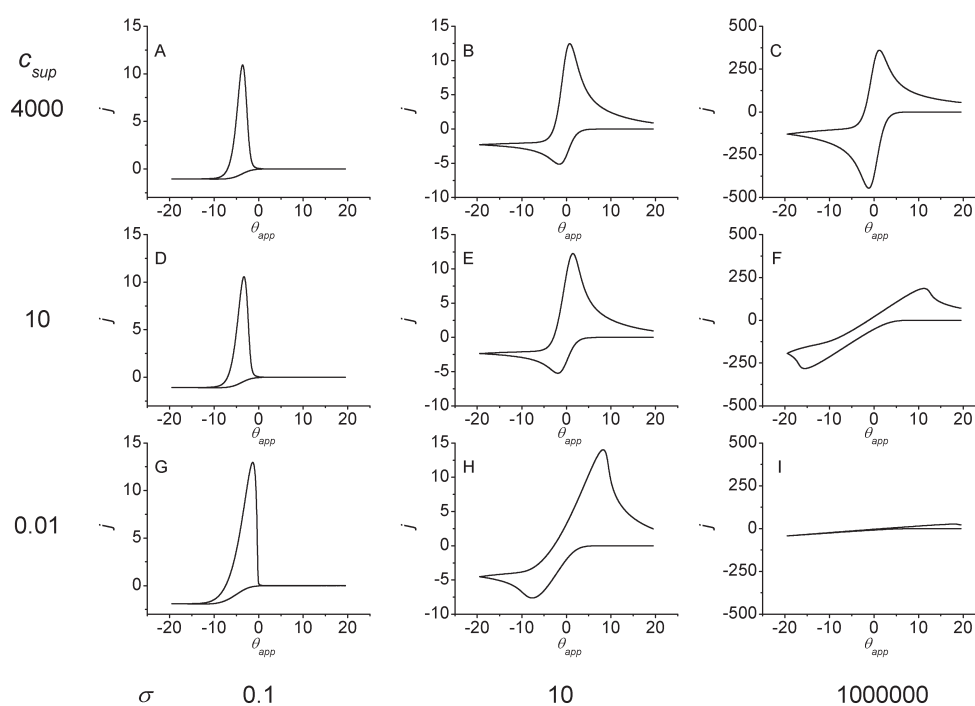


Figure 7.4: Theoretical voltammograms calculated for various values of the dimensionless parameters (columns) and c_{sup} (rows), as indicated in the graph. The diffusion coefficients of all species were assumed to be equal for the simulation.

have investigated in a systematic fashion the influence of the different parameters on the voltammetric characteristics. Numerical simulations were conducted for a set of theoretical parameters encompassing a broad range of experimentally accessible situations, in terms of scan rate, electrode radius, and electrolyte-to-analyte concentration ratio (hereafter ‘support ratio’). The metal cation was assumed to have a single positive charge, and the kinetics were taken as ‘infinitely fast’ to model a reversible system. The influence of slower kinetics can be easily included by changing the value of the heterogeneous rate constant. It is worth pointing out that if the extraction of detailed kinetic parameters is sought, the Butler-Volmer formalism might advantageously be replaced by a more refined model, but such an aim is beyond the scope of the present work. For each simulated voltammogram, the values of the peak potential and peak current were extracted, for both the deposition and subsequent stripping of the electroactive species. The data are plotted using the dimensionless quantities j , θ , σ and c_{sup} , defined in Section 7.1.1. The overall voltammetric behavior is summarized in Figure 7.4, which presents the theoretical voltammograms obtained for nine characteristic sets of parameters, the rows corresponding to different support ratios and the columns to various scan rates or electrode radii.²⁴ Under fully supported conditions (top row of Fig. 7.4) and intermediate scan rate or electrode size (Fig. 7.4 B), the voltammogram displays the ‘conventional’ shape obtained for this type of reaction and observed for instance in Fig. 7.1. Decreasing the scan rate (Fig. 7.4 A) leads to a transition from linear to hemispherical diffusion, and the current recorded during the reduction tends towards a steady-state. At very high scan rates (Fig. 7.4 C), the voltammogram has a shape reminiscent of a classical reversible process controlled by semi-infinite linear diffusion. This is because on the short time scale of the experiment, there is no significant accumulation of A^0 within the mercury hemisphere, and so the concentration gradients of A^{z+} (in the solution) and A^0 (in the amalgam) are comparable during the forward and reverse sweep, respectively. At lower support ratios (middle and bottom rows of Fig. 7.4), the transition between diffusion regime is also observed when the scan rate is changed, and the current enhancement due to migration is clearly seen for the cathodic response at the smallest scan rate and electrolyte concentration (Fig. 7.4 G). The potential drop in solution 6, 8 causes a substantial distortion of the voltammograms, which is more pronounced as the scan rate increases, in line with the shorter timescale involved, or when the support ratio decreases. An extreme situation is seen in Fig. 7.4 I, where the potential drop is so significant that the cathodic peak is moved beyond the negative limit of the voltammetric window.

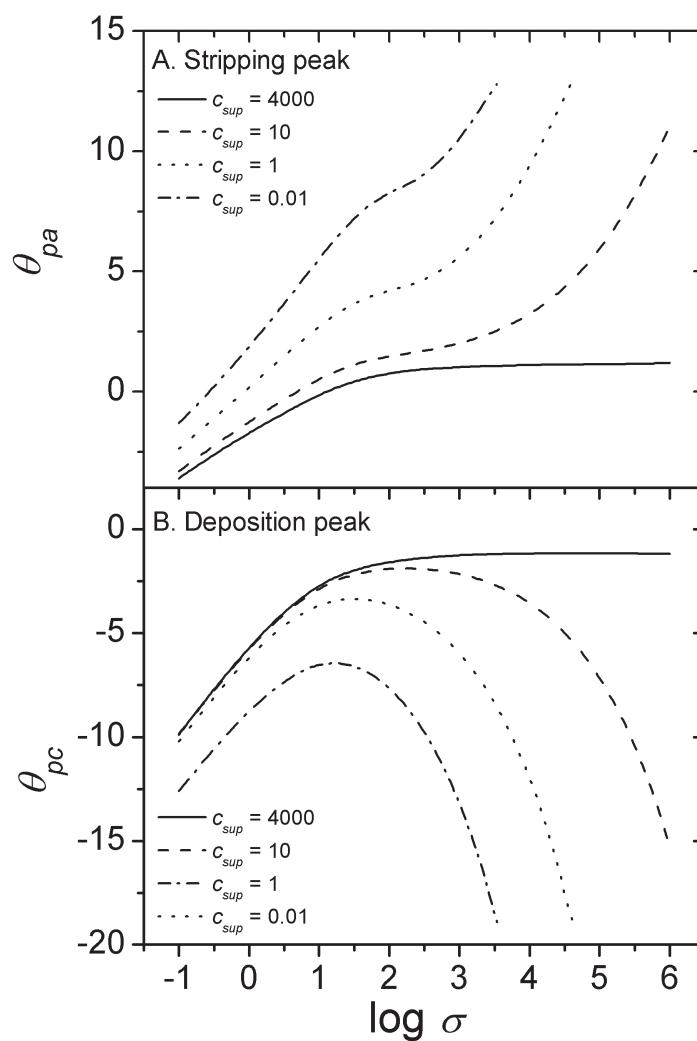


Figure 7.5: Evolution of the stripping (Panel A) and deposition (Panel B) peak potentials with the dimensionless parameter (in semi-logarithmic scales), for selected values of the support ratio c_{sup} .

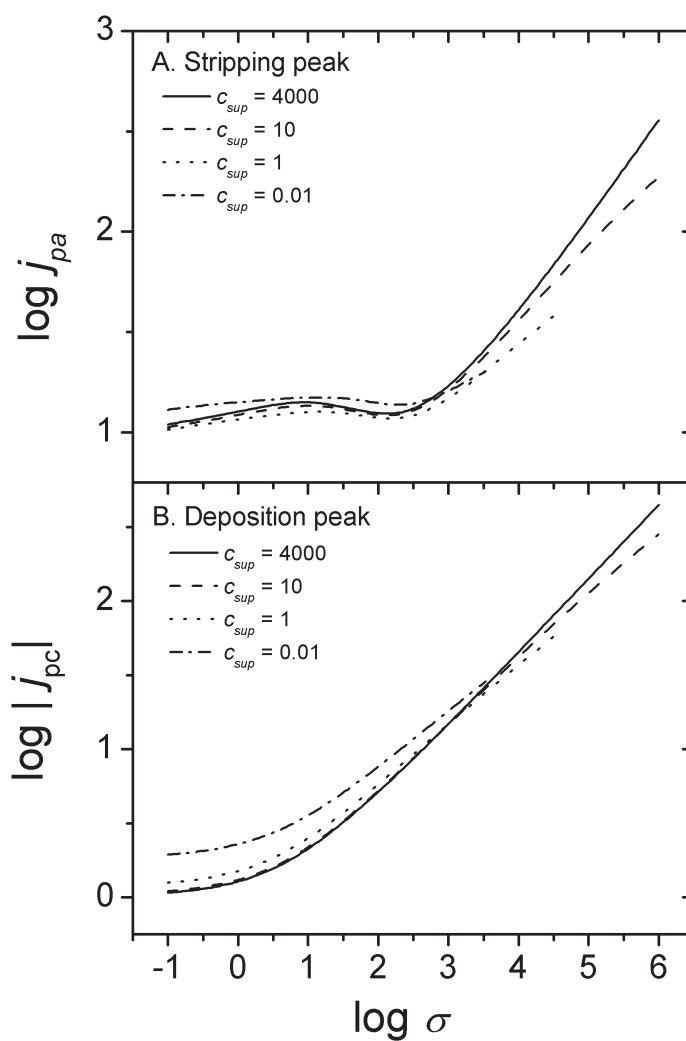


Figure 7.6: Evolution of the stripping (Panel A) and deposition (Panel B) peak intensities with the dimensionless parameter (in logarithmic scales), for selected values of the support ratio c_{sup} .

The dependences of the peak potentials (θ_{pc} , θ_{pa}) and currents (j_{pc} , j_{pa}) on the dimensionless parameters are presented in Figure 7.5 and 7.6. For the sake of clarity, only few values of c_{sup} are shown in the figures; Focusing first on well-supported conditions ($c_{sup} = 4000$), the anodic and cathodic peak potentials take at high scan rates a constant value $\theta_p = \pm 1.1$, consistent with a semi-infinite linear diffusion-controlled process. Accordingly, the peak intensities increase linearly with the square root of the scan rate, as inferred from the value 0.5 of the $\log j_p$ versus $\log \sigma$ slope in this region. At lower scan rates, the peak potentials depart from their constant value and shift towards more negative potentials, in agreement with the trend observed experimentally and in previous works on mercury thin films or microelectrodes.^{25,26} To rationalize this fact, the finite size of the mercury hemisphere has to be taken into account.²⁷⁻³¹ At high scan rates, the size of the diffusion layer, both in solution and in the amalgam, is much smaller than the hemisphere radius, and the observed behavior is equivalent to that obtained under semi-infinite diffusion conditions (see for instance Fig. 7.4 C). However, the smaller the scan rate, the thicker the diffusion layer becomes, until it greatly exceeds the radius of the mercury hemisphere. A significant concentration of metal is thus accumulated over the timescale of the experiment, even though the concentration gradients at the electrode surface, and hence the current, remain very small. This is clearly illustrated in Figure 7.7, which presents the concentration profiles of A^0 in Hg and A^{z+} in solution, calculated at the applied potential $\theta_{app} = 0$ (or $E = E^0$), during a forward sweep at various scan rates. The cathodic current tends at low scan rates towards the expected steady-state value, $j = 1$, while the interplay between the amount of accumulated metal and the scan rate causes the anodic peak intensity to exhibit two shallow extrema. Such an appearance of a maximum in the stripping current versus scan rate dependence confirms previous experimental reports on the voltammetric deposition and stripping of various metals at mercury microelectrodes.^{25,26}

At lower concentrations of supporting electrolyte, the effect of the potential drop in solution becomes significant and higher overpotentials are needed to drive the electron transfer reactions. The cathodic peak potential is shifted in the negative direction and the anodic one in the positive direction, this effect being more pronounced at higher scan rates. As a result, θ_{pc} is predicted to go through a maximum when the scan rate is varied over a few orders of magnitude. Another consequence is that at high scan rates, the slope of the $\log j_p$ - $\log \sigma$ curves deviates from the value 0.5 obtained in well-supported conditions.

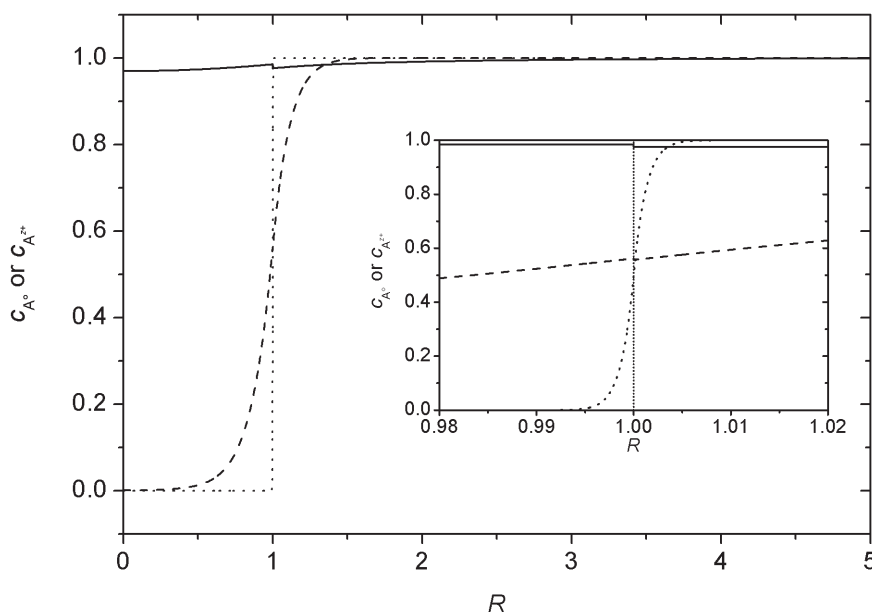


Figure 7.7: Concentration profiles of A^0 in mercury ($R < 1$) and of A^{z+} in solution ($R > 1$) calculated at $E_{app} = 0$ during a forward (deposition) potential sweep, for a support ratio $c_{sup} = 4000$ and different values of the dimensionless parameter : 0.1 (solid lines), 100 (dashed lines) and 1000000 (dotted lines). Inset: Enlarged portion of the profiles around the mercury-solution interface, symbolised by the vertical line.

7.4 Conclusions

The voltammetric features associated with the deposition of a metal in a small mercury hemisphere and its subsequent anodic stripping are very sensitive to the electrode size, scan rate and support ratio. This sensitivity arises from the subtle interplay, in potentiodynamic conditions, between diffusion (semi-infinite in solution and finite within the hemisphere), migration, and potential distribution in solution. In this study, we have proposed a model including all these effects, by implementing the Nernst-Planck-Poisson equations in conjunction with the zero-field approximation. The validity of the model was evidenced by the very good agreement found with the experimental results on the $Tl(I)/Tl(Hg)$ system. Using the model in a predictive way, we have assessed the contribution of the different factors affecting the peak potentials and intensities. Under fully-supported conditions, the voltammogram is entirely controlled by diffusion, but the size of the electrode influences the voltammogram in two ways upon varying the scan rate. First, a transition is observed between linear and spherical diffusion, causing a change in the cathodic current from a square-root dependence on the scan rate to a steady-state. Then, the finite size of the hemisphere results in the accumulation of

the metal in the mercury, leading to a significant shift of the peak potentials in the negative direction when the scan rate is decreased. These trends are further affected at lower support ratios, due to the existence of an electric field in solution, resulting at low scan rates in an enhancement of the peak intensities due to migration. The potential drop also creates an overpotential that shifts the peak potentials away from their values obtained in fully-supported conditions. This effect is more pronounced at higher scan rates, where the current increase due to migration is thus progressively counteracted.

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Chapter 8

How much supporting electrolyte is required to make a cyclic voltammetry experiment quantitatively ‘diffusional’?

Conventionally, electroanalytical experiments such as cyclic voltammetry are performed in solutions containing a large excess of inert supporting electrolyte: KCl in water and tetrabutylammonium perchlorate in acetonitrile are typical examples. The purpose of this supporting electrolyte is to ensure that the ionic strength of the solution is high, and hence that the electric field is homogeneous and near-zero, and is not perturbed by the oxidation or reduction of the analyte concerned. Under suitable experimental timescales where convection can be neglected, the theory of cyclic voltammetry is therefore reduced to a diffusion problem and the interpretation of experimental data is greatly facilitated. The use of a large amount of supporting electrolyte may introduce other problems, however: if either ion adsorbs specifically to the electrode, it will alter capacitive (non-Faradaic) currents, and the introduction of large quantities of salt is often inappropriate for analytical measurements concerning biological compounds. Further, in some otherwise appealing solvents, the dissolution of sufficient electrolyte is impossible.

Consequently it is of considerable importance to establish theoretically, and to demonstrate in practice, the minimum quantity of supporting electrolyte required for voltammetry to be indistinguishable from a diffusion-only limit. The mathematical description of migration and the role of supporting electrolyte was discussed in detail by Oldham and Zoski in the context of electrochemical mass transport,¹ although the suggested minimum support ratio of 26 derived at steady-state in their work will be shown below to be a substantial underestimate under transient conditions. Ciszowska et al. reviewed developments in weakly supported microelectrode voltammetry to 1999.² Other past theoretical work includes extensive and insightful studies by Stojek and co-workers of the effect of diffusion coefficients in such a case for reactant and product species at microelectrodes,^{3,4} and Amatore et al. recently published a theoretical discussion of microscopic ohmic drop effects.⁵

The theoretical treatment of weakly supported cyclic voltammetry at macroelectrodes has been

neglected due to the implicit practical problems of high ohmic drop associated with any experimental exploitation; the only examples are noted in the literature involve self-support for highly charged species at high concentrations, where convective effects cannot be ruled out.^{6,7} Consequently, the exact quantity of supporting electrolyte required to achieve 'diffusion-only' mass transport, to within a certain tolerance, has not yet been well established for cyclic voltammetry.

Comparison between the theory and experiment is then drawn with experimental cyclic voltammetry for the reduction of the hexaammineruthenium(III) ion, $[\text{Ru}(\text{NH}_3)_6]^{3+}$, at a Pt planar macroelectrode in aqueous solution, under varying degrees of support by KCl. The range of applicability of the model is discussed as the planar macroelectrode is compared with a hemispherical theoretical treatment.

8.1 Theoretical Introduction

8.1.1 Fully supported voltammetric analysis

The fully supported limit is defined as a situation where the electric field in solution is negligible, such that the migration term in the Nernst-Planck equation is zero everywhere and mass transport is exclusively diffusive. Under these conditions and assuming infinitely fast (Nernstian) electrode kinetics, the typical experimentally observable parameters, peak current, i_{pf} , and peak-to-peak separation, ΔE_{pp} , of a cyclic voltammogram are governed by well established expressions. In a macroelectrode limit (high σ) where diffusion is predominantly planar, i_{pf} is described by the Randles-Ševčík equation,⁸ and is proportional to $\nu^{\frac{1}{2}}$; in the same limit, ΔE_{pp} is constant with scan rate and ≈ 57 mV (at 298K). In practice, the finite potential switching window tends to fractionally increase ΔE_{pp} from this ideal limit, to ≈ 59 -62 mV. In a microelectrode limit (low σ), the waveshape is sigmoidal, so ΔE_{pp} has no real meaning, and a limiting current i_{ss} is noted, which is independent of scan rate. For a hemispherical geometry, this has the analytically determined value:⁹

$$i_{\text{ss}} = 2\pi F D_{\text{A}} C_{\text{A}}^* r_{\text{e}} \quad (8.1)$$

8.1.2 Qualitative effects of incomplete support

The electric field resulting from incomplete electrolytic support will tend to alter the observable parameters introduced above (and have been presented with great detail in previous chapters of the present work), as migration effects alter the rate of mass transport to the electrode surface, and hence the perceived current at a given potential and scan rate. In particular, i_{pf} becomes a function of c_{sup} and R_e . Further, ΔE_{pp} will be affected by the non-zero resistance of the solution. The applied (and hence recorded) potential, E , at the working electrode surface is altered from the observed potential difference between the working electrode and solution as:

$$E = E_{WE} - E_{ref} + \Delta E_{sol} \quad (8.2)$$

where E_{ref} is the constant reference electrode potential and E_{WE} is the potential difference between the working electrode and the solution at its surface. ΔE_{sol} , is the potential difference between the working electrode and the solution at its surface and is denoted as potential drop. In such a case, $\Delta E_{pp} > 60$ mV even in the limit of infinitely fast kinetics. In general, microelectrode voltammetry is expected to be substantially less sensitive to changes in c_{sup} , as the passed current is very small and so the current exchanged at the electrode is more easily dispersed. In the present Chapter we consider the necessary amount of supporting electrolyte required in order to avoid voltammetric distortions depending on the electrode radius, concentration of electroactive species and scan rate.

8.2 Experimental

All solutions were prepared with ultra pure water with resistivity $> 18.2 \text{ M}\Omega \text{ cm}^{-1}$ (at 298 K) and degassed for 30 min with N_2 (BOC, High Purity Oxygen Free) before starting each experiment. The temperature was maintained constant at 298 K using a water bath (W14, Grant). Hexaammineruthenium(III) chloride (HexRu(III), Aldrich, 98%) and potassium chloride (Aldrich $> 99\%$) were used without further purification.

A platinum disk with radius 1mm was used as a working electrode, a platinum foil was used as a counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. Diamond spray (0.3 and 0.1 μm respectively, Kemet International, UK) on soft lapping pads (Buehler, U.S.A.) was used to polish the working electrode surface.

Solutions containing 5mM of hexaammineruthenium(III) chloride with a range of concentrations of supporting electrolyte (2000, 500, 150 and 50 mM KCl) were prepared, and cyclic voltammetry was performed across a range of scan rates (50, 100, 200, 500 and 1000 mV s⁻¹) using an analog potentiostat (built in house) which was connected to an oscilloscope (TDS 3034B, Tektronix, U.S.A.) to record the data. The analog potentiostat rather than a digital equivalent was employed to prevent artefacts known to be introduced by the staircase voltage waveform, especially the broadening of peak-to-peak separation which is an essential observable for the study of migration. These effects in staircase cyclic voltammetry were first noted by Bilewicz et al.¹⁰ in purely diffusive systems, and were investigated theoretically for disk electrode systems by Barnes et al.¹¹

The capacitive current was subtracted from the cyclic voltammograms using blank voltammetry recorded in solutions without the electroactive species but containing the same degree of electrolytic support. The excess of chloride ions introduced by the hexaammineruthenium chloride into the experimental solutions was compensated for by adding 15mM of potassium chloride to the corresponding concentration of supporting electrolyte in the blank solutions.

The diffusion coefficients for the hexaammineruthenium(III) and hexaammineruthenium(II) cations in the aqueous KCl system were investigated via double potential step chronoamperometry using a 25 μ m radius platinum disk, according to the procedure established by Klymenko et al.;¹² fitted data are available in the supporting information. The values determined were $D_{\text{HexRu(III)}} = 9.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{HexRu(II)}} = 10.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. These compare well to values for HexRu(III) already in the literature ranging from $8.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ – $9.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$,^{13–15} all measured in aq. 0.1 M KCl at 298K.

8.3 Results and Discussion

Experimental voltammetry is presented at Figures 8.1-8.5 across a range of scan rates from 50 mV s⁻¹ to 1 V s⁻¹. In each case, voltammogram A is that recorded at $C_{\text{sup}} = 2\text{M}$, B at $C_{\text{sup}} = 500 \text{ mM}$, C at $C_{\text{sup}} = 150 \text{ mM}$, D at $C_{\text{sup}} = 50 \text{ mM}$. These correspond to support ratios of $c_{\text{sup}} = 400, 100, 30$ and 10 respectively. The simulated results use the same theoretical treatment as in chapter 6. Simulated theoretical fits of the voltammetry are shown by the closed circles. The following parameters were used in the simulation: $r_e = 0.71\text{mm}$ to correspond area-to-area with a disc electrode with $r_e = 1\text{mm}$; $C_A^* = 5 \text{ mM}$; $D_{\text{HexRu(III)}} = 9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ as characterised from our microelectrode double potential

step chronoamperometry as described above; $D_{\text{HexRu(II)}} = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ as also characterised from microelectrode double potential step chronoamperometry; $D_{\text{K}^+} = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{Cl}^-} = 1.95 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ which are suitable literature values in the concentration range employed.^{16,17} Parameters for electrode kinetics of $k^0 = 1 \text{ cm s}^{-1}$ and $\alpha = 0.5$ were used, which render the system effectively reversible under all pertinent conditions.¹⁸ Additionally the following parameters were used: $\epsilon_s = 78.54$ (H_2O);¹⁹ $T = 298\text{K}$.

The formal potential used, $E_f^\ominus$, was different for each support ratio; in each case reversible voltammetry was available which permitted establishment of the value. The formal potential is noted to vary consistently with ionic strength as follows: -213 mV vs. SCE for $C_{\text{sup}} = 2\text{M}$; -190 mV vs. SCE for $C_{\text{sup}} = 500 \text{ mM}$; -175 mV vs. SCE for $C_{\text{sup}} = 150 \text{ mM}$; -170 mV vs. SCE for $C_{\text{sup}} = 50 \text{ mM}$. Since the diffusion coefficients of the two species are characterised to within a close tolerance, the shift in both forward and back peaks, which is consistent in all scans, must be attributed to variation in $E_f^\ominus$. At this stage, we note this ionic strength dependence of $E_f^\ominus$ as an experimental observation, but in general we may attribute this variation to dependence of the ratio of the activity coefficients ($\gamma_{\text{HexRu(II)}}/\gamma_{\text{HexRu(III)}}$) on ionic strength, as the species have different charges: in a high ionic strength system these activity coefficients will respond differently to variations in ionic strength, as described by the Robinson-Stokes equation.

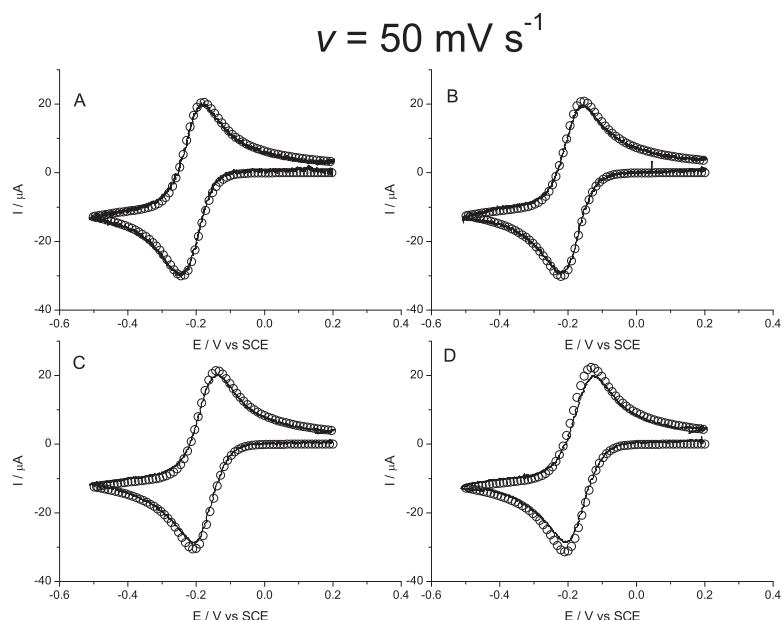


Figure 8.1: Comparison of experiment and simulation of the theoretical model for the process $[\text{Ru}(\text{NH}_3)_6]^{3+} + e^- \rightleftharpoons [\text{Ru}(\text{NH}_3)_6]^{2+}$ at a 1mm radius Pt disc, $\nu = 50 \text{ mV s}^{-1}$, $C_A^* = 5 \text{ mM}$. A: $C_{\text{sup}} = 2\text{M}$; B: $C_{\text{sup}} = 500 \text{ mM}$; C: $C_{\text{sup}} = 150 \text{ mM}$; D: $C_{\text{sup}} = 50 \text{ mM}$.

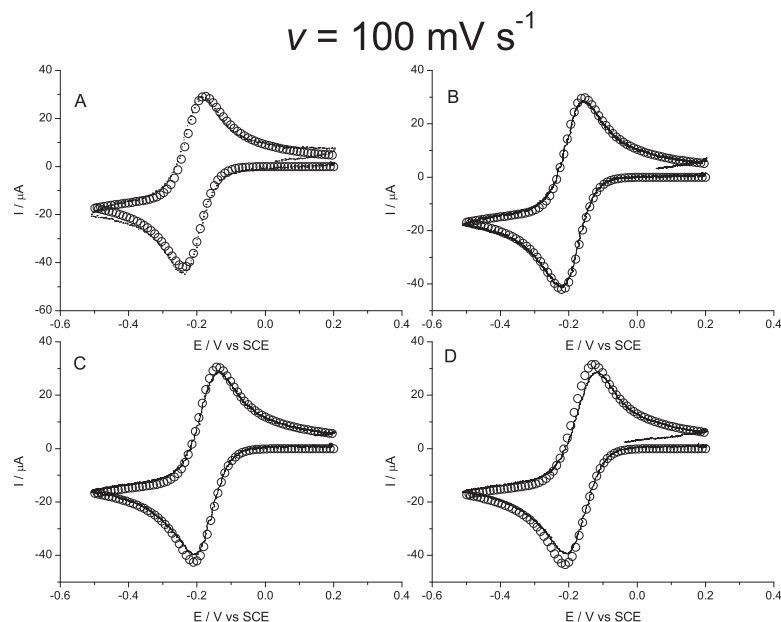


Figure 8.2: Comparison of experiment and simulation of the theoretical model for the process $[\text{Ru}(\text{NH}_3)_6]^{3+} + e^- \rightleftharpoons [\text{Ru}(\text{NH}_3)_6]^{2+}$ at a 1mm radius Pt disc, $\nu = 100 \text{ mV s}^{-1}$, $C_A^* = 5 \text{ mM}$. A: $C_{\text{sup}} = 2\text{M}$; B: $C_{\text{sup}} = 500 \text{ mM}$; C: $C_{\text{sup}} = 150 \text{ mM}$; D: $C_{\text{sup}} = 50 \text{ mM}$.

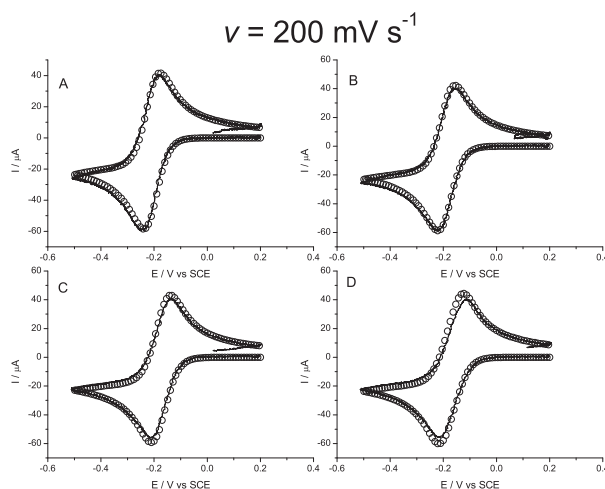


Figure 8.3: Comparison of experiment and simulation of the theoretical model for the process $[\text{Ru}(\text{NH}_3)_6]^{3+} + e^- \rightleftharpoons [\text{Ru}(\text{NH}_3)_6]^{2+}$ at a 1mm radius Pt disc, $\nu = 200 \text{ mV s}^{-1}$, $C_A^* = 5 \text{ mM}$. A: $C_{\text{sup}} = 2\text{M}$; B: $C_{\text{sup}} = 500 \text{ mM}$; C: $C_{\text{sup}} = 150 \text{ mM}$; D: $C_{\text{sup}} = 50 \text{ mM}$.

In general, we note from Figures 8.1-8.5 that the closeness of fit between the theoretical and experimental data is accurate for Cases A-C, but that peak-to-peak separation is underestimated by the theoretical model in Case D, beyond the tolerances of experimental error. In Case D, changes in the voltammetry are still predicted qualitatively, but not quantitatively; this is made clear by a plot of ΔE_{pp} against $\log \nu$ for the theoretical and experimental data, at Figure 8.6. This observable divergences are

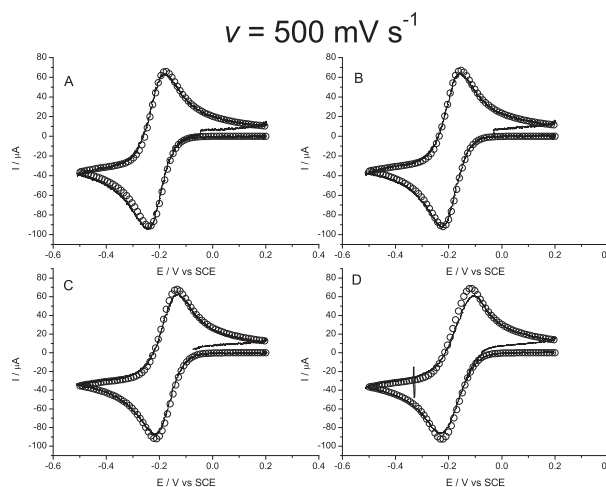


Figure 8.4: Comparison of experiment and simulation of the theoretical model for the process $[\text{Ru}(\text{NH}_3)_6]^{3+} + e^- \rightleftharpoons [\text{Ru}(\text{NH}_3)_6]^{2+}$ at a 1mm radius Pt disc, $\nu = 500 \text{ mV s}^{-1}$, $C_A^* = 5 \text{ mM}$. A: $C_{\text{sup}} = 2\text{M}$; B: $C_{\text{sup}} = 500 \text{ mM}$; C: $C_{\text{sup}} = 150 \text{ mM}$; D: $C_{\text{sup}} = 50 \text{ mM}$.

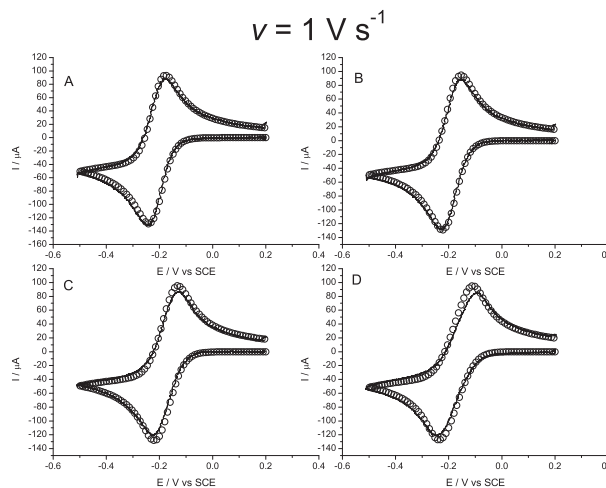


Figure 8.5: Comparison of experiment and simulation of the theoretical model for the process $[\text{Ru}(\text{NH}_3)_6]^{3+} + e^- \rightleftharpoons [\text{Ru}(\text{NH}_3)_6]^{2+}$ at a 1mm radius Pt disc, $\nu = 1 \text{ V s}^{-1}$, $C_A^* = 5 \text{ mM}$. A: $C_{\text{sup}} = 2\text{M}$; B: $C_{\text{sup}} = 500 \text{ mM}$; C: $C_{\text{sup}} = 150 \text{ mM}$; D: $C_{\text{sup}} = 50 \text{ mM}$.

due to the approximation that the theory considers a one dimensional model and the geometry used in experiment has two dimensions. Therefore in diffusion only regime, the electrode could be considered planar and with one dimension, whereas, while the concentration of supporting electrolyte drops the migration of ions along the solution goes beyond this limit, because of such, experimental divergences are observed between theory and experiment, at low concentrations of supporting electrolyte. At high supporting ratios the deviations from purely diffusional behaviour predicted by the theory are in good agreement with experimental results at different scan rates.

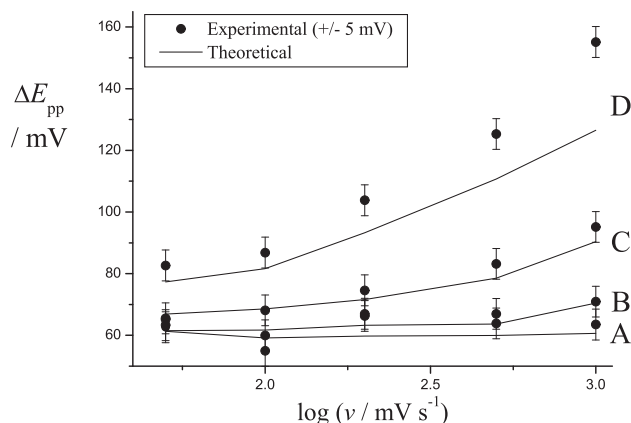


Figure 8.6: Comparison of experimental and theoretically predicted ΔE_{pp} for cyclic voltammetry of the process $[\text{Ru}(\text{NH}_3)_6]^{3+} + e^- \rightleftharpoons [\text{Ru}(\text{NH}_3)_6]^{2+}$ at a 1mm radius Pt disc, $C_A^* = 5 \text{ mM}$, support ratios A-D as above.

At this stage we are therefore able to answer the question we posted, how much supporting electrolyte is required to achieve ‘diffusional’ cyclic voltammetry? In this limit, peak current and peak-to-peak separation are as predicted by a diffusion-only model and so conclusions drawn from the observables i_{pf} or ΔE_{pp} are not prejudiced by the presence of an electric field in solution. Defining experimental distinguishability as we desire in terms of changes in i_{pf} or ΔE_{pp} , we can define, for any given combination of r_e , v , D_A , D_B , D_M and D_X , the minimum value of c_{sup} required to render the voltammetry indistinguishable from the diffusion-only case. According to our comparisons with experimental voltammetry, the theory is accurate to within an experimental error for the analog potentiostat system of $\pm 5 \text{ mV}$ for ΔE_{pp} , in the region $c_{sup} \geq 30$, and in the region where a disk-shaped macroelectrode may be approximated by a hemisphere of the same area, roughly $\sigma > 10^3$. Our conclusions will therefore be quantitatively accurate in this range.

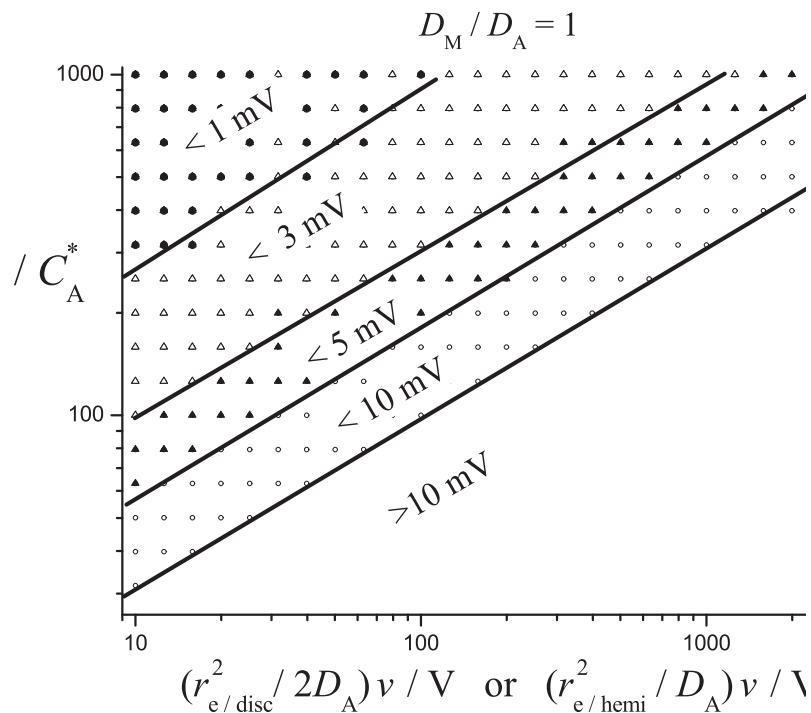


Figure 8.7: Contour plot showing the deviation $\Delta\Delta E_{\text{pp}}$ of theoretically observed ΔE_{pp} from the diffusion-only value at a hemispherical electrode for varying $c_{\text{sup}} = C_{\text{sup}}/C_A^*$ and $(r_e^2/D_A)v$, where $D_M/D_A = 1$, $A^0 \rightleftharpoons B^+ + e^-$, $K^0 = 10^5$; $R_e = 10^5$.

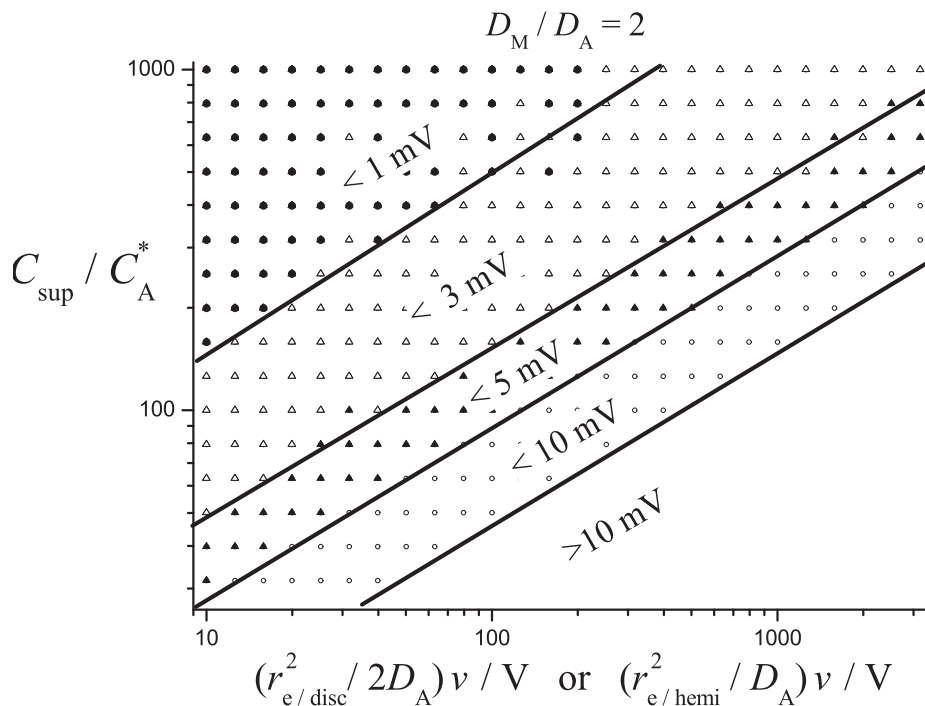


Figure 8.8: Contour plot showing the deviation $\Delta\Delta E_{pp}$ of theoretically observed ΔE_{pp} from the diffusion-only value at a hemispherical electrode for varying $c_{sup} = C_{sup}/C_A^*$ and $(r_e^2/D_A)v$, where $D_M/D_A = 2$, $A^0 \rightleftharpoons B^+ + e^-$. $K^0 = 10^5$; $R_e = 10^5$.

For three model systems, where $D_A = D_B$, $D_M = D_X$, $\epsilon_s = 78.54$ (as for water), and D_M/D_A respectively = 1, 2 and 3, voltammetry was simulated for the hemispherical electrode on a logarithmic scale varying in $(r_e^2/D_A)v$ and in c_{sup} . Each voltammogram was classified in terms of the recorded ΔE_{pp} compared to the diffusion-only case, the latter being calculated from the same program with the artificially high support ratio $c_{sup} = 10^6$. Contours are plotted (Figures 8.7-8.9) to show the regions where the deviation $(\Delta E_{pp} - \Delta E_{pp}(\text{Diffusion-Only}))$ is less than 1mV (indistinguishable), 1-3 mV (well supported, i.e. indistinguishable within typical experimental error, for a digital potentiostat), 3-5 mV (slightly distinguishable within experimental error), 5-10 mV (insufficiently supported), and greater than 10 mV (acutely unsupported).

The data are simulated here for a hemispherical electrode for which it is assumed that the voltammetry is largely indistinguishable from a disc macroelectrode under diffusion only regime, whereas as demonstrated as the concentration of supporting electrolyte decreases considerably, departure from planar behaviour is expected, it has been experimentally demonstrated that in the region of interest for the present chapter the planar electrode is in correspondence with a hemispherical of the same

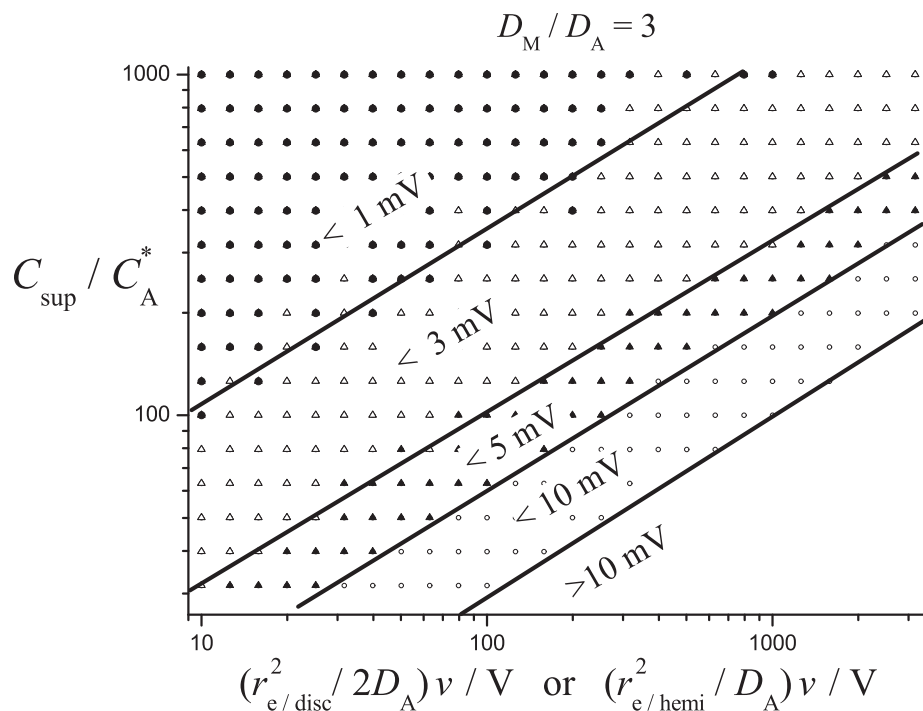


Figure 8.9: Contour plot showing the deviation $\Delta\Delta E_{pp}$ of theoretically observed ΔE_{pp} from the diffusion-only value for cyclic voltammetry at a hemispherical electrode for varying $c_{sup} = C_{sup}/C_A^*$ and $(r_e^2/D_A)v$, where $D_M/D_A = 3$, $A^0 \rightleftharpoons B^+ + e^-$, $K^0 = 10^5$; $R_e = 10^5$.

area. It is essential to note the correspondence, for equal area, that $r_{e,disc}^2 = 2r_{e,hemi}^2$, and hence the horizontal scale of the plots varies by a factor of two depending on the geometry in which r_e is taken.

The choice of switching window will affect values for ΔE_{pp} . Here, the simulation uses a $\approx 1V$ window, from $E_f^\ominus - (20RT/F)$ to $E_f^\ominus + (20RT/F)$; it is expected that in a narrower switching window the same support regions will be appropriate. Lastly, we note that the data are simulated exclusively for the one-electron oxidation of a neutral species, but at the support ratios considered (≥ 30), the contribution to electrolytic support from the counter-ion of a charged electroactive species is negligible.

8.4 Conclusion

Comparison was drawn for theory with experimental cyclic voltammetry for the aqueous $[Ru(NH_3)_6]^{3+/2+}$ system at a Pt macroelectrode; by plotting theoretical and experimental data together, the theoretical model was shown to be quantitatively accurate, within experimental error for our system, for at least the region $c_{sup} \geq 30$, across a range of typical experimental scan rates. Divergencies between theory

and experiment at low concentration of supporting electrolyte are due to the geometrical differences in both.

The contour plots presented at Figures 8.7-8.9 are intended to be instructive to the experimentalist; for any macroelectrode system, the required c_{sup} to limit deviations from the diffusion-only case to within a certain tolerance may be inferred. The experimentalist is free to choose the desired tolerance, but it would be expected that most systems to have an experimental error of approximately ± 3 mV and so real (diffusion-migration) and ideal (diffusion-only) voltammetry will be indistinguishable for tolerances of $\Delta\Delta E_{\text{pp}} \leq 3$ mV. It must be noted that the range of applicability of these plots is confined, however, to macroelectrode voltammetry and, at this stage, to electrochemically reversible systems.

These contour plots show clearly that the support ratio of 26 once proposed for the steady-state system¹ is not equally useful for transient cyclic voltammetry, but in fact is broadly inappropriate; the majority of macroelectrode systems require support ratios greater than 100 to avoid detectable peak broadening from ohmic drop. The current state and pace of development in analytical electrochemistry are such, however, that it is perhaps no longer adequate to simply apply excess electrolyte and ignore the issue of migration. To the modern electrochemist, an understanding of the microscopic and macroscopic effects associated with extended electric fields in solution is increasingly important. We consequently hope to develop the theory presented above to approach the case $c_{\text{sup}} < 30$, and indeed $c_{\text{sup}} \rightarrow 0$, by examining and revising those approximations made.

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Chapter 9

Elucidating mechanistic information by using low concentrations of supporting electrolyte

While voltammetric results obtained using diffusion-only conditions are useful, several situations exist in which kinetic and mechanistic information can be unobtainable or ambiguous. For example and in particular, stepwise two electron reactions are commonly encountered in electrochemistry and have been reviewed by Evans, himself a noted contributor to the field^{1,2}



Comproportionation between species A and C is thermodynamically favourable when the formal potential of the second step is much more negative than the first ($E_{f,A/B}^\ominus > E_{f,B/C}^\ominus$). This situation is commonly encountered because the electron added in the first step repels the electron added in the second. Insightful pioneering work by Savéant and Andrieux³ has shown that voltammetry is necessarily blind to the presence of comproportionation in situations where both electron transfers are reversible and the diffusion coefficients of species A, B and C are equal. In addition, it has been shown numerically that, when the values of the diffusion coefficients are similar, the presence or absence of comproportionation, as determined by means of voltammetric techniques, is ambiguous;⁴ the current-voltage curves are almost identical regardless of whether comproportionation takes place or not. This frequently occurs because the substrate and product in a heterogeneous reaction are often structurally very similar, leading to similar diffusion coefficients for A, B and C. It is possible to voltammetrically distinguish the presence of comproportionation in situations where the diffusion coefficients differ significantly: for example in ionic liquid solvents,⁵ where ions of higher charge interact more strongly

with the solvent, or in solvents of low polarity,⁴ where ions of different charge associate to different extents with ions of the supporting electrolyte. In each case, electroactive ions of higher charge move more slowly in solution and therefore possess smaller diffusion coefficients. In addition, Evans has demonstrated that it is possible to resolve mechanistic information when the second electron transfer is irreversible.⁶ In other situations, it is necessary to use non-voltammetric techniques to provide evidence for the comproportionation reaction. For example, Savéant and Andrieux have used electron spin resonance.³ It is useful to develop a voltammetric technique that can resolve reaction mechanisms of this type, and others, unambiguously.

One possible solution is to perform the experiments in the presence of a low concentration of supporting electrolyte. Under such conditions, as will be shown below, voltammetric equivalence is not observed, even when the diffusion coefficients of A, B and C are equal, owing to the inclusion of a migrational term in the mass transport equations.

Electrochemistry in weakly supported media is most useful when a theoretical model can be obtained, either analytically or numerically, to explain the experimental observations. In 1987, Amatore⁷ was first to construct such a model, for a simple E reaction. Several more complicated mechanisms have been studied since.^{7-9,11,12} Most publications to date have only considered systems at steady state, owing to the lack of a reliable model with which to describe transient experiments. Bond, Feldberg and Oldham were first to publish work under the latter conditions.¹³⁻¹⁵ The authors relied on simulations based on an explicit, as opposed to an implicit, system of equations. The resulting simulations could only simulate heterogeneous systems and, furthermore, all diffusion coefficients had to be similar. In addition, the authors, perhaps unknowingly, made a serious approximation by assuming the concentration and potential profiles to be linear at disc shaped electrodes over short timescales. In the experience of the present authors, while it is possible to obtain linear concentration profiles under such conditions, potential profiles are necessarily much larger and can be hemispherical. Consequently, the simulated results of Bond *et al.* compared rather poorly with experimental data.^{14,15} Recently, Streeter *et al.*¹⁶ published work on transient systems using a more robust simulation technique. The theory was based on the 'zero field' approximation which states that, when the electrode is sufficiently large ($> 1 \mu\text{m}$), it is valid to consider the electrical double layer to be infinitely thin compared to the diffusion layer. It follows, from Gauss's law, that the derivative of the potential at the outside edge of the double layer is equal to zero. The theory has been successfully applied to

experimental systems involving only heterogeneous processes as it has been studied along the present thesis.

The EE mechanism considered here has been studied numerically by Norton *et al.*,^{17,18} analytically by Amatore *et al.*¹⁹ and experimentally by Kowski *et al.*²⁰ All considered exclusively steady-state conditions and the theoretical treatments applied only to extreme cases in which comproportionation was either absent or diffusionally controlled. In the present chapter, a more general model is used to numerically simulate this process at a range of comproportionation rates, under both steady-state and transient conditions, with an arbitrary set of diffusion coefficients. In Section 9.1.4, numerical simulations, using the model of Streeter *et al.*¹⁶ described above, are used to explore the behaviour of this system as a function of several variables. The simulations are applied to the electroreduction of anthraquinone (figure 9.1) in acetonitrile, for which diffusion controlled comproportionation is shown to occur.

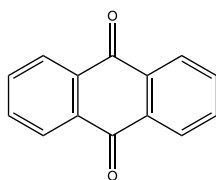


Figure 9.1: Structure of anthraquinone, AQ.

When using cyclic voltammetry to elucidate a reaction mechanism, it is good practice to compare theory and experiment over a range of scan rates. This improves the reliability of the data because the relative sensitivity of the voltammetry to each of the parameters changes with the experimental timescale. In this chapter it is shown that, in addition, the sensitivity of the voltammetry to many of the parameters varies with the concentration of supporting electrolyte. In the experimental study presented here, the validity of the data is improved considerably by comparing theory and experiment over a range of scan rates and a range of concentrations of the supporting electrolyte.

We anticipate electrochemistry in solutions of variable ionic strength is therefore likely to become widely used and is expected to greatly enhance the scope of voltammetry in detecting kinetic and thermodynamic parameters.

9.1 Theory

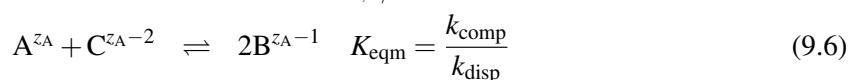
All symbols used in this chapter are defined in Tables 9.1 and 9.2.

Parameter	Definition
$\alpha_{A/B}$	Transfer coefficient of A/B redox couple / unitless
c_A	Concentration of species A / mol m ⁻³
$c_{A,0}$	Surface concentration of species A / mol m ⁻³
c_A^*	Bulk concentration of species A / mol m ⁻³
D_A	Diffusion coefficient of species A / m ² s ⁻¹
ϵ_0	Permittivity of free space ($= 8.85 \times 10^{-12}$) / Fm ⁻¹
ϵ_r	Relative permittivity / unitless
E_{app}	Applied potential / V
$E_{f,A/B}^\ominus$	Formal reduction potential of A/B redox couple / V vs. SCE
i	Current / A
j	Flux / mol m ⁻² s ⁻¹
$k_{A/B}^0$	Electrochemical rate constant of A/B redox couple / m s ⁻¹
k_{comp}	Rate constant for comproportionation / m ³ mol ⁻¹ s ⁻¹
k_{disp}	Rate constant for disproportionation / m ³ mol ⁻¹ s ⁻¹
K_{eqm}	Equilibrium constant for com/dis-proportionation / unitless
ϕ	Potential / V
ϕ_{PET}	Potential at the plane of electron transfer / V
r	Radial coordinate / m
r_e	Radius of the electrode / m
r_{max}	Maximum value of r / m
t	Time / s
ν	Scan rate ($= \left \frac{\partial E_{app}}{\partial t} \right $) / V s ⁻¹
z_A	Charge of species A / unitless

Table 9.1: List of parameters.

9.1.1 Reaction Mechanism

We consider a solution containing an electroactive species, A, which is capable of undergoing two, reversible, single electron reductions, forming species B and C respectively. These heterogeneous processes occur at a hemispherical electrode and imply an additional homogeneous comproportionation/disproportionation equilibrium



Species A is accompanied by a counterion, Y^{-z_A} , and the solution is supported by a monovalent

1:1 inert salt, M^+X^- . In this chapter, z_A is relatively small and ion pairing is assumed to be completely absent in solution. The equilibrium constant for comproportionation, K_{eqm} , varies as a function of the formal potentials for both of the heterogeneous steps, $E_{f,A/B}^\ominus$ and $E_{f,B/C}^\ominus$

$$K_{\text{eqm}} = \exp\left(\frac{F}{RT}(E_{f,A/B}^\ominus - E_{f,B/C}^\ominus)\right) \quad (9.7)$$

In this chapter, $E_{f,A/B}^\ominus \gg E_{f,B/C}^\ominus$: thermodynamically, the comproportionation reaction is favoured.

9.1.2 Mathematical Formulation

$$\begin{aligned} \frac{\partial c_A}{\partial t} &= D_A \left(\frac{\partial^2 c_A}{\partial r^2} + \frac{2}{r} \frac{\partial c_A}{\partial r} \right) + D_A z_A \left(\frac{\partial c_A}{\partial r} \frac{\partial \phi}{\partial r} + c_A \frac{\partial^2 \phi}{\partial r^2} + c_A \frac{2}{r} \frac{\partial \phi}{\partial r} \right) - k_{\text{comp}} c_A c_C + k_{\text{disp}} c_B^2 \\ \frac{\partial c_B}{\partial t} &= D_B \left(\frac{\partial^2 c_B}{\partial r^2} + \frac{2}{r} \frac{\partial c_B}{\partial r} \right) + D_B (z_A - 1) \left(\frac{\partial c_B}{\partial r} \frac{\partial \phi}{\partial r} + c_B \frac{\partial^2 \phi}{\partial r^2} + c_B \frac{2}{r} \frac{\partial \phi}{\partial r} \right) + 2k_{\text{comp}} c_A c_C - 2k_{\text{disp}} c_B^2 \\ \frac{\partial c_C}{\partial t} &= D_C \left(\frac{\partial^2 c_C}{\partial r^2} + \frac{2}{r} \frac{\partial c_C}{\partial r} \right) + D_C (z_A - 2) \left(\frac{\partial c_C}{\partial r} \frac{\partial \phi}{\partial r} + c_C \frac{\partial^2 \phi}{\partial r^2} + c_C \frac{2}{r} \frac{\partial \phi}{\partial r} \right) - k_{\text{comp}} c_A c_C + k_{\text{disp}} c_B^2 \\ \frac{\partial c_M}{\partial t} &= D_M \left(\frac{\partial^2 c_M}{\partial r^2} + \frac{2}{r} \frac{\partial c_M}{\partial r} \right) + D_M (z_M) \left(\frac{\partial c_M}{\partial r} \frac{\partial \phi}{\partial r} + c_M \frac{\partial^2 \phi}{\partial r^2} + c_M \frac{2}{r} \frac{\partial \phi}{\partial r} \right) \\ \frac{\partial c_X}{\partial t} &= D_X \left(\frac{\partial^2 c_X}{\partial r^2} + \frac{2}{r} \frac{\partial c_X}{\partial r} \right) + D_X (z_X) \left(\frac{\partial c_X}{\partial r} \frac{\partial \phi}{\partial r} + c_X \frac{\partial^2 \phi}{\partial r^2} + c_X \frac{2}{r} \frac{\partial \phi}{\partial r} \right) \\ \frac{\partial c_Y}{\partial t} &= D_Y \left(\frac{\partial^2 c_Y}{\partial r^2} + \frac{2}{r} \frac{\partial c_Y}{\partial r} \right) + D_Y (-z_A) \left(\frac{\partial c_Y}{\partial r} \frac{\partial \phi}{\partial r} + c_Y \frac{\partial^2 \phi}{\partial r^2} + c_Y \frac{2}{r} \frac{\partial \phi}{\partial r} \right) \end{aligned}$$

Each equation is composed of three terms. The first quantifies diffusion, the second migration, and the third quantifies the homogeneous chemical reaction. Since species M, X and Y are chemically inert, the latter term in the respective mass transport equations is equal to zero. This system of 6 independent equations contains 7 unknowns: the concentration for each of the 6 species and an additional term for the potential. Consequently, the description of the problem is incomplete and a further relationship must be introduced. For this purpose, we invoke the Poisson equation

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} = -\frac{F}{\epsilon_r \epsilon_0} \sum_s z_s c_s = -\frac{F}{\epsilon_r \epsilon_0} [z_A c_A + (z_A - 1) c_B + (z_A - 2) c_C + z_M c_M + z_X c_X - z_A c_Y] \quad (9.8)$$

This relationship follows from Maxwell's equations; however, many workers have attempted to

simplify the problem by invoking, instead, the electroneutrality approximation

$$0 = -\frac{F}{\epsilon_r \epsilon_0} \sum_s z_s c_s = -\frac{F}{\epsilon_r \epsilon_0} [z_A c_A + (z_A - 1) c_B + (z_A - 2) c_C + z_M c_M + z_X c_X - z_A c_Y] \quad (9.9)$$

In the experience of the present authors, this relationship, although well obeyed over the majority of simulation space, does not significantly increase simulation efficiency. It is therefore regarded in the presented work as an unnecessary, additional, approximation.

The mass transport equations and the Poisson equation can be solved in the region $r_e \leq r \leq \infty$ subject to a set of boundary conditions. However, the problem is considerably simplified, without affecting the result, by defining a finite upper limit, $r = r_{\max}$. In this chapter

$$r_{\max} = r_e + 6\sqrt{D_{\max} t} \quad (9.10)$$

where $D_{\max}$ is the diffusion coefficient of the fastest moving species in solution.²¹

Beyond the point $r = r_{\max}$, all concentrations are temporally invariant and the flux of each species at can be set equal to zero at all times. In addition, it follows, from the Poisson equation combined with electroneutrality, that at $r = r_{\max}$

$$\left. \frac{\partial^2 \phi}{\partial r^2} \right|_{r=r_{\max}} = 0 \quad (9.11)$$

Integrating this equation subject to the condition $\theta \rightarrow 0$ as $r \rightarrow \infty$ leads to a boundary condition for the potential at $r = r_{\max}$

$$\left. \frac{\partial \phi}{\partial r} \right|_{r=r_{\max}} = -\frac{\phi}{r} \quad (9.12)$$

The complete set of boundary conditions for the problem are

$t = 0, \text{ all } r$	$c_A = c_A^*$	$c_B = 0$	$c_C = 0$	$c_Y = c_A^*$
	$c_M = c_M^*$	$c_X = c_M^*$	$\phi = 0$	
$t > 0, r = r_{\max}$	$\left. \frac{\partial c_A}{\partial r} \right _{r=r_{\max}} = 0$	$\left. \frac{\partial c_B}{\partial r} \right _{r=r_{\max}} = 0$	$\left. \frac{\partial c_C}{\partial r} \right _{r=r_{\max}} = 0$	$\left. \frac{\partial c_Y}{\partial r} \right _{r=r_{\max}} = 0$
	$\left. \frac{\partial c_M}{\partial r} \right _{r=r_{\max}} = 0$	$\left. \frac{\partial c_X}{\partial r} \right _{r=r_{\max}} = 0$	$\left. \frac{\partial \phi}{\partial r} \right _{r=r_{\max}} = -\frac{\phi}{r}$	

$$\begin{aligned}
 t > 0, r = r_e \quad D_A \frac{\partial c_A}{\partial r} \Big|_{r=r_e} &= k_{A/B}^0 c_{A,0} \exp \left(-\alpha_{A/B} \frac{F(E_{app} - E_{f,A/B}^\ominus - \phi_{PET})}{RT} \right) \\
 &\quad - k_{A/B}^0 c_{B,0} \exp \left((1 - \alpha_{A/B}) \frac{F(E_{app} - E_{f,A/B}^\ominus - \phi_{PET})}{RT} \right) \\
 D_B \frac{\partial c_B}{\partial r} \Big|_{r=r_e} &= -D_A \frac{\partial c_A}{\partial r} \Big|_{r=r_e} - D_C \frac{\partial c_C}{\partial r} \Big|_{r=r_e} \\
 D_C \frac{\partial c_C}{\partial r} \Big|_{r=r_e} &= -k_{B/C}^0 c_{B,0} \exp \left(-\alpha_{B/C} \frac{F(E_{app} - E_{f,B/C}^\ominus - \phi_{PET})}{RT} \right) \\
 &\quad + k_{B/C}^0 c_{C,0} \exp \left((1 - \alpha_{B/C}) \frac{F(E_{app} - E_{f,B/C}^\ominus - \phi_{PET})}{RT} \right) \\
 D_M \frac{\partial c_M}{\partial r} \Big|_{r=r_e} &= 0 \\
 D_X \frac{\partial c_X}{\partial r} \Big|_{r=r_e} &= 0 \\
 D_Y \frac{\partial c_Y}{\partial r} \Big|_{r=r_e} &= 0
 \end{aligned}$$

The boundary condition at $r = r_e$ invokes the ‘zero field approximation’ which states that the double layer at the electrode surface is negligible in extent compared to the diffusion layer, such that the charge on the electrode is fully compensated at $r \approx r_e$. This point is called the ‘plane of electron transfer’, PET. It follows from Gauss’s law that

$$\frac{\partial \phi}{\partial r} \Big|_{r=r_e} = 0 \quad (9.13)$$

For cyclic voltammetry, the applied potential, E_{app} , varies as a function of time, t , according to

$$E_{app} = |-vt + E_{start} - E_{vertex}| + E_{vertex} \quad (9.14)$$

where E_{start} and E_{vertex} are the starting and vertex potentials respectively.

The flux at surface of the electrode, j , is calculated using

$$j = 2 \frac{\partial c_A}{\partial r} \Big|_{r=r_e} + 2 \frac{D_B}{D_A} \frac{\partial c_B}{\partial r} \Big|_{r=r_e} \quad (9.15)$$

which may be related to the current, i

$$i = 2\pi F c_A^* D_A r_e j \quad (9.16)$$

9.1.3 Numerical Methods

The problem is readily formulated in terms of a conventional set of normalised parameters, defined in Table 9.2. This procedure reduces the number of solutions by amalgamating parameters that act

Normalised Parameter	Definition
C_A	$\frac{C_A}{C_A^*}$
$C_{A,0}$	$\frac{C_{A,0}}{C_A^*}$
J	$i/(2\pi F c_A^* D_A r_e)$
K^0	$k^0 r_e / D_A$
K_{comp}	$\frac{k_{\text{comp}} c_A^* r_e^2}{D_A}$
K_{disp}	$\frac{k_{\text{disp}} c_A^* r_e^2}{D_A}$
θ_{app}	$\frac{F E_{\text{app}}}{RT}$
θ_f	$\frac{F E_f}{RT}$
θ_{PET}	$\frac{F \phi_{\text{PET}}}{RT}$
R	$\frac{r}{r_e}$
R_e	$r_e \sqrt{\frac{F^2 c_A^*}{RT \epsilon_s \epsilon_0}}$
σ	$\frac{r_e^2 F \nu}{D_A RT} = \frac{r_e^2 F}{D_A RT} \left \frac{\partial E_{\text{app}}}{\partial t} \right $
τ	$\frac{D_A t}{r_e^2}$

Table 9.2: List of normalised parameters.

as scaling factors into parameters that do not. The problem is discretised using the fully implicit finite difference method. The resulting nonlinear equations are solved using the Newton-Raphson method and the Thomas algorithm.²² It is known²³ that when K_{comp} is large, a singularity in species B exists at a time dependent point R_B . It is therefore necessary to construct a spatial mesh of high density close to the electrode surface *and* close to R_B . This can be achieved either by using a mesh that is uniformly dense²³ or, more efficiently, by using a temporally dynamic mesh that adapts to changes in the concentration profile at each timestep.^{24–26} In the latter case, the dynamically adaptive gridding techniques could handle any mechanism. In so doing, the authors sacrificed computational efficiency in favour of mechanistic generality. In this chapter a dynamically adaptive grid is used that is specifically tailored to the EE reaction, with comproportionation. The singularity in species B is only considered when $R_B > 1.1$. When $R_B < 1.1$, the mesh density close to the electrode is sufficient to resolve the singularity caused by species B. Linear interpolations are used to calculate concentration profiles at successive timesteps. The variation in grid density during the voltammogram, when K_{comp} is large, is shown in figure 9.2. The discretization quantitatively expressed as

$$R_0 = 0$$

$$R_j < \frac{R_B}{2} \quad R_j = R_{j-1} + \gamma_R (H(R_s - R_j)R_s + H(R_j - R_s)R_{j-1} - 1)$$

$$\frac{R_B}{2} < R_j < R_B \quad R_j = R_B - (R_B - R_{j-1}) + \gamma_R (H(R_s - R_j + R_B)R_s + H(R_j + R_B - R_s)(R_B - R_{j-1}) - 1)$$

$$R_j > R_B \quad R_j = R_B + (R_{j-1} - R_B) + \gamma_R (H(R_s - R_j - R_B)R_s + H(R_j - R_B - R_s)(R_{j-1} - R_B) - 1)$$

where H is the Heaviside step function. The parameters are converged to yield $< 1\%$ error ($\gamma_R = 1 \times 10^{-2}$ and $R_s = 2 \times 10^{-3}$). The mesh density is considerably higher than that used in simple ‘diffusion only’ studies^{27–29} owing to the extremely tight coupling between the migration electrical fields and concentration profiles of ionic species.^{9,30} All simulations were programmed in C++ and run on a desktop computer (Intel Core2 Quad 2.4 GHz, 2 GB RAM), with running times of 30-60 minutes per voltammogram being typical.

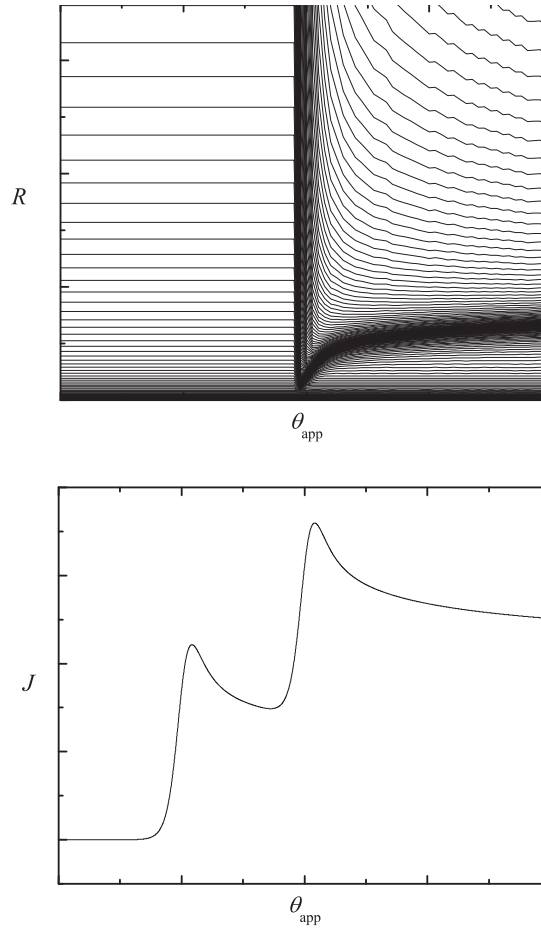


Figure 9.2: Schematic representation of the spatial grid as a function of θ_{app} . The corresponding voltammogram is shown for comparison.

9.1.4 Theoretical Results and Discussion

Preliminaries

The mechanism considered varies as a function of several parameters. Discussions in this section are based on a system in which $\frac{D_B}{D_A} = \frac{D_C}{D_A} = 1$, $z_A = 0$, $z_B = -1$, $z_C = -2$, $R_e = 2660$ and the electrode kinetics are reversible. The value of R_e is derived from $c_A = 1$ mM, $r_e = 25$ μ m and $\epsilon_r = 37.5$, which correspond to the experiments in acetonitrile considered in the experimental section.³¹

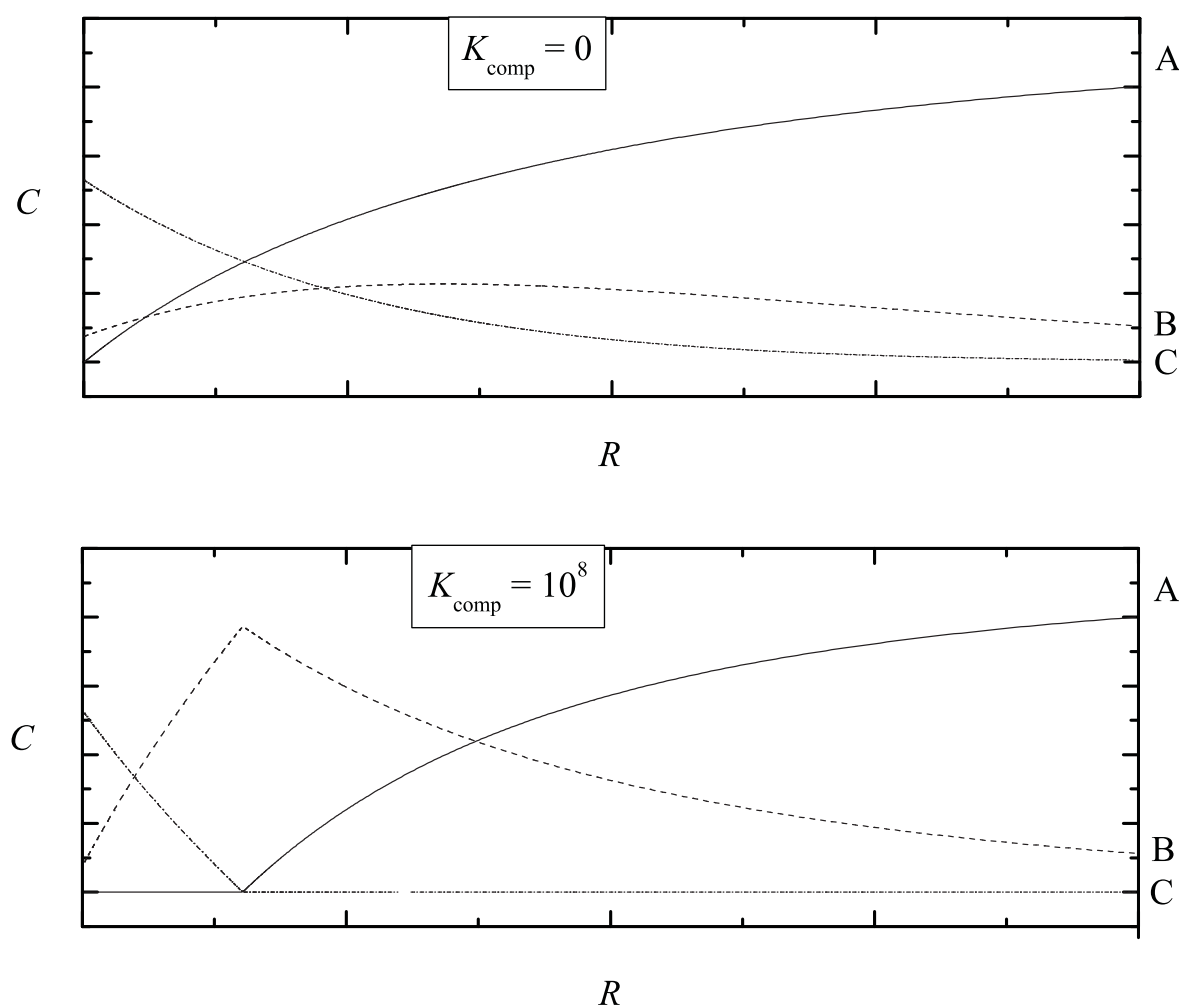


Figure 9.3: Schematic concentration profiles for $K_{\text{comp}} = 10^{-8}$ and 10^8 . The general shape of each profile is invariant to the kinetic and thermodynamic parameters simulated.

Figure 9.3 shows schematic concentration profiles for which $K_{\text{comp}} = 0$ and $K_{\text{comp}} = 10^8$ at the second peak. Trivially, when $K_{\text{comp}} = 0$, species A travels towards the electrode from bulk solution while species C travels away. Species B, formed in the first wave, has remained very close to the electrode and, consequently, is almost depleted at the second peak. The concentration profile when

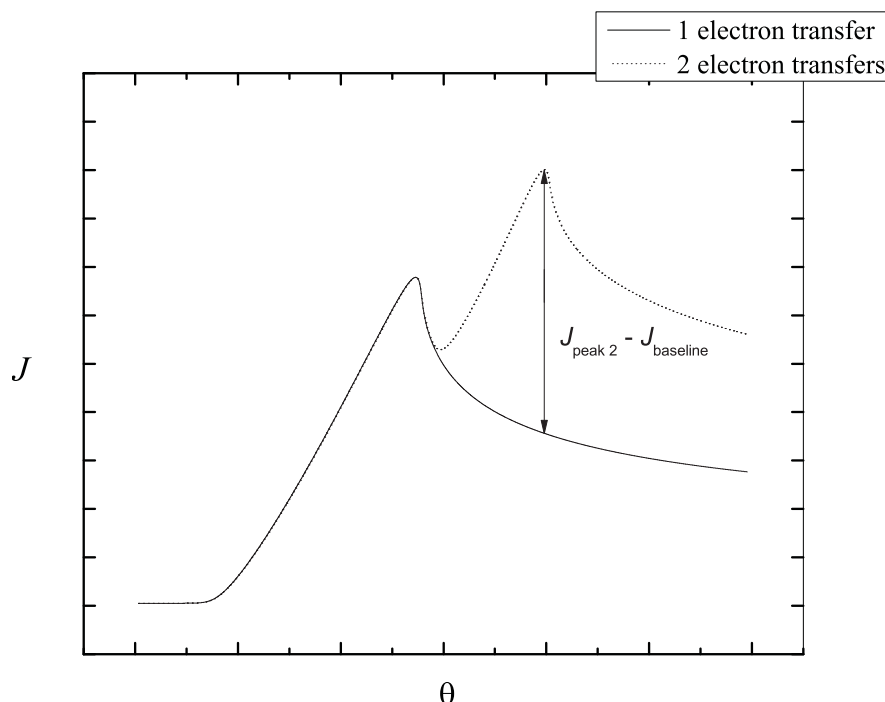


Figure 9.4: Schematic voltammograms for 1 electron, $A + e^- \rightleftharpoons B$, and two electron, $A + 2e^- \rightleftharpoons B + e^- \rightleftharpoons C$, processes. The procedure for calculating baseline corrected currents for the second peak, $J_{\text{peak 2}} - J_{\text{baseline}}$, is shown.

$K_{\text{comp}} = 10^8$ is more complicated. As before, during the second wave, all 3 electroactive species are present in solution. Species A travels towards the electrode from bulk solution while species C travels away. At an intermediate point in solution, a homogeneous comproportionation reaction occurs between species A and C leading to a maximum in the concentration of species B.

The comproportionation can be studied using cyclic voltammetry. During the second wave of the forward sweep, all three electroactive species (A, B and C) are present in appreciable quantities close to the electrode surface. It follows that the peak current for this wave (J_{peak2}) is the most sensitive measure of the rate constant, K_{comp} . As is conventional,¹⁰ this current is quoted relative to a baseline derived from the forward wave of the corresponding one electron process. This procedure is illustrated schematically in figure 9.4.

Effect of C_{supp}

Figure 9.5 shows $J_{\text{peak2}} - J_{\text{baseline}}$ as a function of C_{supp} and K_{comp} . When C_{supp} is high, the ionic strength is sufficiently high at every point in solution to suppress potential gradients. In this region, migration does not occur and the voltammetry is purely diffusional. As explained in the introduction,

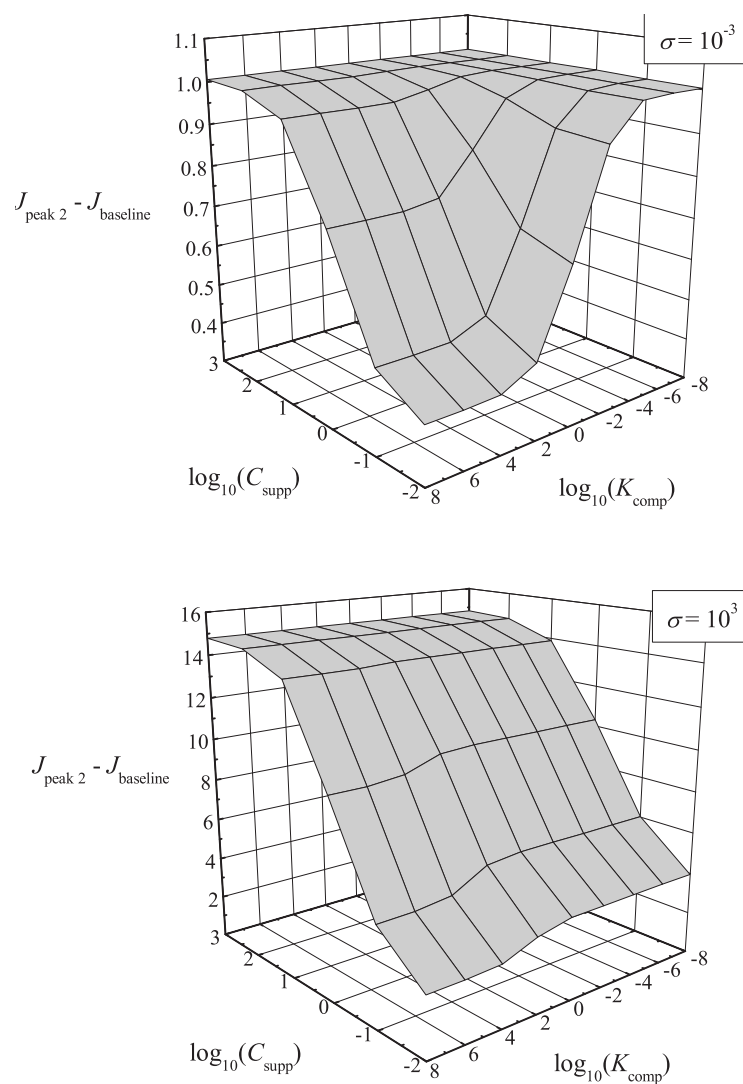


Figure 9.5: $J_{\text{peak 2}} - J_{\text{baseline}}$ as a function of C_{supp} and K_{comp} for $\sigma = 10^{-3}$ and 10^3 .

the effects of K_{comp} are not voltammetrically distinguishable under diffusion only conditions. This manifests figure 9.5, as $J_{\text{peak2}} - J_{\text{baseline}}$ is invariant with K_{comp} when C_{supp} is high. Additionally, it is known that when $\frac{D_B}{D_A}$ and $\frac{D_C}{D_A}$ both close to unity, the value of K_{comp} , though experimentally obtainable using voltammetry, is not unambiguous.⁴ As C_{supp} decreases, the ionic strength in solution decreases and the potential gradient close to the electrode increases. Migration makes a progressively more significant contribution to mass transport. In every case, the current is given by:

$$J = \frac{D_B}{D_A} \left(\frac{\partial C_B}{\partial R} \right)_0 + 2 \left(\frac{\partial C_A}{\partial R} \right)_0 \quad (9.17)$$

When $\sigma = 1000$, the timescale of the experiment is short and, during the second wave, B is present in appreciable quantities close to the surface of the electrode when K_{comp} large *and* when K_{comp} is small. Therefore, in both situations, as the value of C_{supp} decreases the current decreases. When C_{supp} is small, the current increases with decreasing K_{comp} . This occurs because the term in species B is more important for the current when K_{comp} is large, due to the higher concentration of species B close to the electrode. Lower values of C_{supp} are required to reach the self support limit as the scan rate increases. The ions of the supporting electrolyte move to nullify to effect of the potential gradient close to the electrode. As the scan rate decreases, the time over which the ions can adapt to a given potential at the electrode increases and the extent of this shielding effect becomes more significant.

When $\sigma = 0.001$, species B is almost completely depleted and this contribution to the flux is negligible. The flux is given solely in terms of the uncharged species, A. Since A is uncharged, its mass transport is independent of potential gradients in solution. As C_{supp} decreases, $J_{\text{peak2}} - J_{\text{baseline}}$ is constant. In contrast, when K_{comp} is large species A is almost completely depleted close to the electrode and this contribution to the flux is negligible. The flux is given solely in terms of the charged species, B. Since B is negatively charged, it is repelled by the negative charge at the surface of the electrode. As C_{supp} decreases, the flux of species B at the electrode surface, and $J_{\text{peak2}} - J_{\text{baseline}}$, decreases. At very low values of C_{supp} , the system begins to tend towards a limit in which the ionic strength of the solution varies as a function of only the electroactive species present in solution and its counter ion and products, and hence is independent of C_{supp} . This is called the limit of ‘self support’ as presented in the previous chapter. The comproportionation reaction is most effectively studied at, or near, steady state because the charge on the ions close to the electrode changes with K_{comp} and

leads to significant changes in the voltammetry at low support when migration is a significant form of mass transport.

Effect of D_{supp}

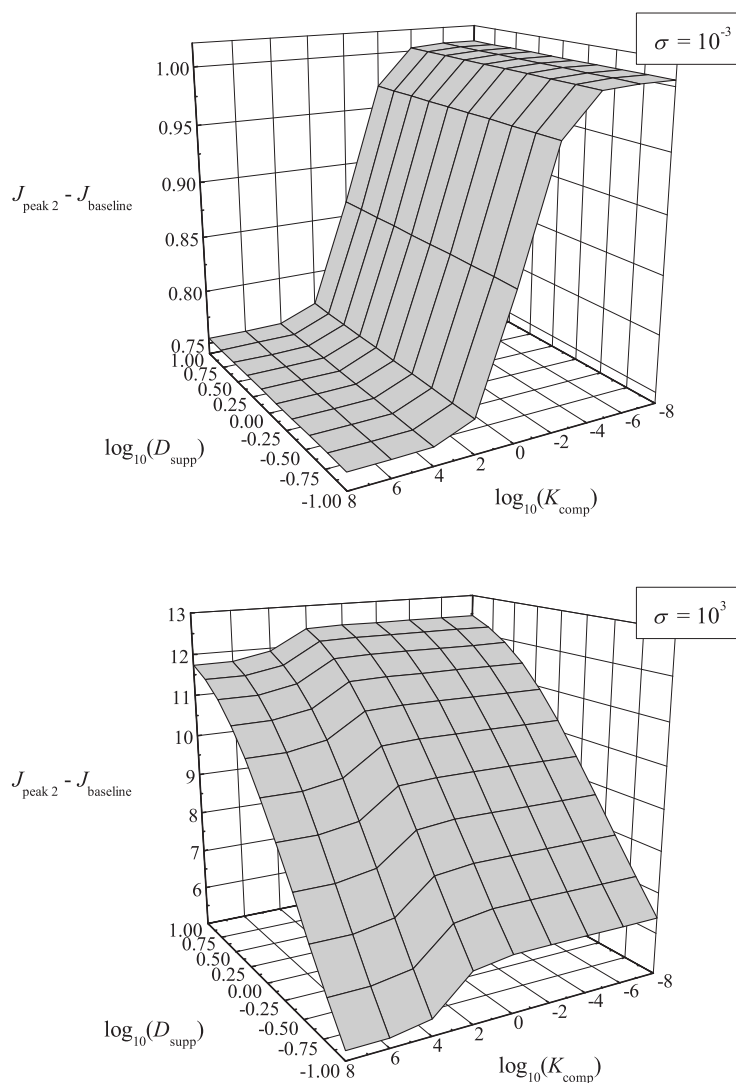


Figure 9.6: $J_{\text{peak2}} - J_{\text{baseline}}$ as a function of $D_{\text{supp}} = D_{\text{M}} = D_{\text{X}}$ and K_{comp} for $\sigma = 10^{-3}$ and 10^3 .

Figure 9.6 shows $J_{\text{peak2}} - J_{\text{baseline}}$ as a function of D_{supp} ($= D_{\text{M}} = D_{\text{X}}$) and K_{comp} . The surface is drawn for a situation in which $C_{\text{supp}} = 1$. This value represents a compromise between a support ratio low enough to allow comproportionation to be observed while allowing the effect of changing D_{supp} to be probed. As explained above, $J_{\text{peak2}} - J_{\text{baseline}}$ decreases as K_{comp} increases. As D_{supp} increases, the ions of the supporting electrolyte can move more quickly and so are more effective at maintaining the electroneutrality in the solution: the proportion of migration that must occur from the electroactive

species is smaller. As the scan rate increases, the time over which the ions can adapt increases and the rate at which the ions move becomes less significant. Therefore, when $\sigma = 0.001$, the voltammetry is insensitive to D_{supp} ; in contrast, when $\sigma = 1000$ the value of the value of $J_{\text{peak2}} - J_{\text{baseline}}$ tends towards the limit of full support as D_{supp} increases.

Effect of D_B/D_A and D_C/D_A

It was concluded in section 9.1.4 that the effect of comproportionation is most pronounced at steady state. In this section, the value of the steady-state current is studied as a function of D_B/D_A and D_C/D_A at various values of C_{supp} . When $K_{\text{comp}} = 0$, the flux is given solely in terms of species A and the voltammetry is independent of D_B/D_A and D_C/D_A . In addition, since A possesses no charge, the steady state value is independent of C_{supp} . In contrast, when $K_{\text{comp}} = 10^8$, the flux depends on upon all three electroactive species. It is therefore anticipated that the value of the steady-state current will depend upon D_B/D_A , D_C/D_A and C_{supp} .

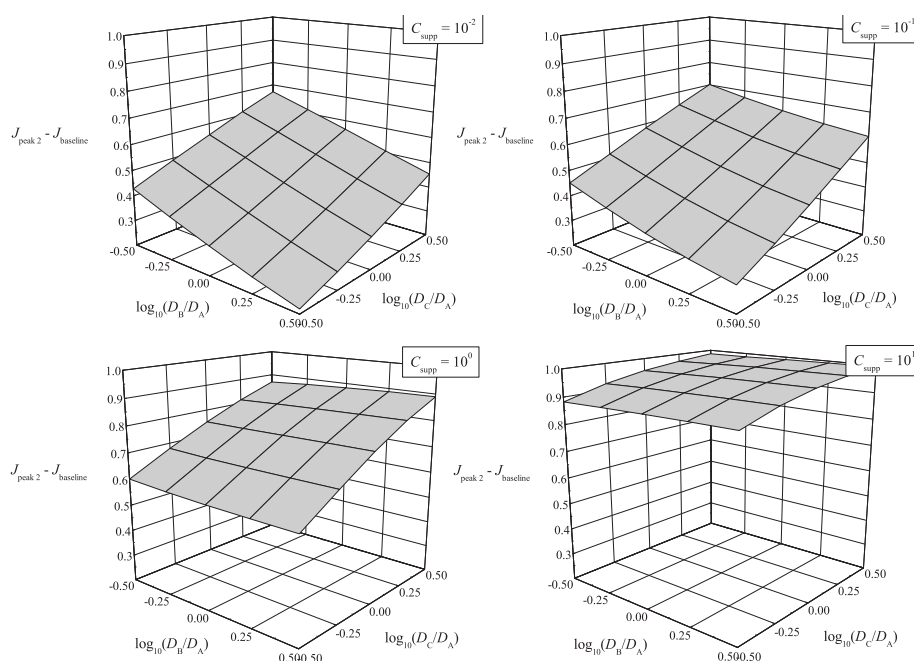


Figure 9.7: $J_{\text{peak2}} - J_{\text{baseline}}$ as a function of D_B/D_A and D_C/D_A for $\sigma = 10^{-3}$.

Figure 9.7 shows $J_{\text{peak2}} - J_{\text{baseline}}$ as a function of D_B/D_A and D_C/D_A for $\sigma = 10^{-3}$. Surfaces are drawn for several values of C_{supp} . As noted in Section 9.7, the value of $J_{\text{peak2}} - J_{\text{baseline}}$ increases with C_{supp} ; however, the rate at which this occurs changes with D_B/D_A and D_C/D_A . It has been observed experimentally,⁶ that at full support, the value of $J_{\text{peak2}} - J_{\text{baseline}}$ at steady-state when $K_{\text{comp}} = 0$ is

equal to that when $K_{\text{comp}} = 10^8$, regardless of the values of D_B/D_A and D_C/D_A . Given that most mechanisms of this type have either no comproportionation or diffusion controlled comproportionation, the presence or absence of the homogeneous step can easily be verified experimentally by comparing the value of the steady-state current under weakly supported conditions with one at full support: comproportionation is absent if the two are concordant.

At each support ratio, $J_{\text{peak2}} - J_{\text{baseline}}$ increases with D_C/D_A . Species C travels away from the electrode and make no contribution to the current; however, there is a large concentration of C close to the surface of the electrode. Species C can therefore exert strong ionic strength effects. As D_C/D_A increases, the C ions can respond more rapidly to changes in potential at the electrode surface. This leads to a decrease in ohmic drop and in the size of the potential at the plane of electron transfer, ϕ_{PET} . Unpublished numerical studies by the authors have confirmed this. It is reasonable to assume that

$$\frac{d\phi}{dr} \propto -\phi_{\text{PET}} \quad (9.18)$$

Therefore, as D_C/D_A increases, the potential gradient at the electrode surface becomes smaller. Under these conditions, negative migration of the flux determining species, species B, is less significant and the current increases.

At each support ratio, $J_{\text{peak2}} - J_{\text{baseline}}$ decreases with D_B/D_A . It follows that, from the concentration profiles shown in figure 9.3, the size of maximum in concentration of species B increases as D_B/D_A becomes smaller. The concentration gradient between this maximum and the electrode surface increases and the diffusion term becomes more significant. This leads to an increase in the current.

Effect of z_A

As explained in section 9.1.4, when $z_A = 0$, the presence of comproportionation is most easily measured at low scan rates and low support ratios. This conclusion is expected to hold in other situations when $z_A \neq 0$. Figure 9.8 shows $J_{\text{peak2}} - J_{\text{baseline}}$ as a function of C_{supp} and K_{comp} . The surface is redrawn for different values of z_A ; the case for which $z_A = 0$ has already been considered in section 9.1.4. Since both heterogeneous processes are one electron transfers, the charges of the other species follow directly from z_A . In each case, the charge on species A is balanced by a counterion of equal but opposite charge. The ionic strength of the solution, for a given C_{supp} , changes between the surfaces

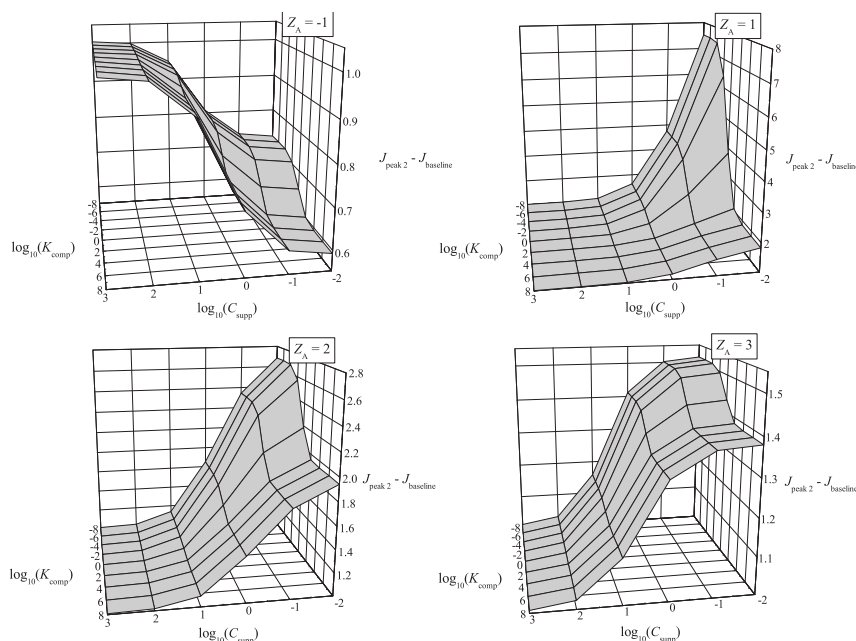


Figure 9.8: $J_{\text{peak2}} - J_{\text{baseline}}$ as a function of C_{supp} and K_{comp} for $z_A = -1, 1, 2$ and 3 .

for z_A ; however, it is still possible to identify meaningful trends in the z_A values.

In each case, when K_{comp} is close to zero, the value of $J_{\text{peak2}} - J_{\text{baseline}}$ is determined solely by the flux of species A, from eqn 9.17. As C_{supp} decreases, the mass transport of species A becomes increasingly dictated by the potential gradient at the electrode surface. The reaction considered is a reduction and the electrode is negatively charged. Therefore, when $z_A < 0$, negative migration occurs and the value of $J_{\text{peak2}} - J_{\text{baseline}}$ decreases with C_{supp} ; in contrast, when $z_A > 0$, positive migration occurs and the value of $J_{\text{peak2}} - J_{\text{baseline}}$ increases with C_{supp} . As pointed out in section 9.1.4, when $z_A = 0$, migration does not occur and the value of $J_{\text{peak2}} - J_{\text{baseline}}$ does not vary with C_{supp} .

When $z_A = -1$ and K_{comp} is very large, both species B is negatively charged and undergo negative migration close to the surface of the electrode. The difference between $K_{\text{comp}} = 0$ and $K_{\text{comp}} = 10^8$ is relatively small because each case, the flux determining species is negatively charged and mass transport is affected by negative migration.

When $z_A = 1$ and K_{comp} is very large, species B is neutral and is not affected by migration close the electrode surface. The difference between $K_{\text{comp}} = 0$ and $K_{\text{comp}} = 10^8$ is very large because in the former case, mass transport is affected by positive migration while, in the latter, mass transport is affected by positive migration. In this situation, it is even possible to voltammetrically distinguish a wide range of intermediate values of K_{comp} , between $K_{\text{comp}} = 0$ and $K_{\text{comp}} = 10^8$. The range lies

approximately between $K_{\text{comp}} = 10^{-4}$ and $K_{\text{comp}} = 10^4$.

When $z_A = 2$ or 3, and K_{comp} is very large, species B is positively charged and is affected by positive migration towards the electrode surface. The difference between $K_{\text{comp}} = 0$ and $K_{\text{comp}} = 10^8$ is small because, in both cases, mass transport is affected by positive migration. The difference is less when $z_A = 3$ because the relative difference in charge between species A and B is lower.

9.1.5 Chemicals and Equipment

All solutions were made with acetonitrile solvent (MeCN, HPLC grade, Fisher Scientific). Anthraquinone (>97%, Strem Chemicals) was used as the electroactive species, with tetra-*n*-butylammonium perchlorate (TBAP, $\geq 99\%$, Fluka) as supporting electrolyte. A three electrode cell was used: a 25 micron radius platinum disk or a 25 micron radius mercury hemispherical electrode was used as a working electrode. The latter was prepared by electrodepositing mercury on a platinum disk, and the size was controlled by passing the necessary amount of current to form a hemisphere, using the procedure stated in Bard *et al.*³² and Limon-Petersen *et al.*³³ The size of the electrode minimised the effect of ohmic drop in the solution. The geometry of the electrode ensured that the potential and concentration profiles were of the same geometry at all times. A silver wire was used as a reference electrode to avoid leaking of ionic impurities in the solution.

Note that voltammograms were recorded using a PG-STAT12 potentiostat (Autolab, Netherlands) without the ‘ohmic drop correction’ used or theorised in some early studies of weak support,^{13,15} so as to permit a clear comparison of theory and experiment.

All solutions were thoroughly degassed with N_2 before each experiment, and an inert atmosphere was maintained during the experiments.

9.1.6 Experimental Results and Discussion

The experimental data this summarised in Table 9.3. It is reasonable to expect the diffusion coefficients to be close to those used in the weakly supported media. This occurs because the charges of the ions considered in this reaction are small and ion pairing ion pairing, which increases at low support, is unlikely to occur. This was found experimentally.

The formal potentials are not given because they vary as a function of support ratio. Changing the concentration of supporting electrolyte leads to a large change in the ionic strength of the solution.

Parameter	Experimental Value	Reference
$\alpha_{\text{AQ}/\text{AQ}^-}$	0.5	
$\alpha_{\text{AQ}^-/\text{AQ}^{2-}}$	0.5	
D_{AQ}	$2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	
D_{AQ^-}	$1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	
$D_{\text{AQ}^{2-}}$	$1.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	
D_{TBA^+}	$0.68 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	Szymanska <i>et al.</i> ⁴²
D_{Cl^-}	$2.35 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	Szymanska <i>et al.</i> ⁴²
$\epsilon_{\text{r,AN}}$	37.5	Ritzoulis <i>et al.</i> ³¹
$k_{\text{AQ}/\text{AQ}^-}^0$	$\geq 0.001 \text{ m s}^{-1}$	
$k_{\text{AQ}^-/\text{AQ}^{2-}}^0$	$\geq 0.001 \text{ m s}^{-1}$	
k_{comp}	$1 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	

Table 9.3: Experimental data for anthraquinone, AQ, with tetra-*n*-butylammonium perchlorate, TBAP, in acetonitrile, AN.

This, in turn, affects the potential of any redox couple by ionic strength effects:

$$\Delta E_{\text{f}}^{\ominus} = \frac{RT}{F} \ln \frac{\gamma_{\text{red}}}{\gamma_{\text{ox}}} \quad (9.19)$$

The values of γ_{red} and γ_{ox} can be obtained analytically using the Robinson Stokes equation.^{34,35} However, the requisite parameters required for these calculations are not available in the literature. The ionic strength effects change peak position and, to a lesser extent, peak to peak separation; peak height, which is used as the main probe for comproportionation, is unaffected. It is therefore possible to obtain concordance between experimental and simulated data by treating $E_{\text{F}}^{\ominus}$ as a variable ‘fitting parameter’. The reduced species in each heterogeneous process possesses a higher charge, $\gamma_{\text{red}} > \gamma_{\text{ox}}$. The ionic strength effects change peak position and, to a lesser extent, peak to peak separation; peak height, which is used as the main probe for comproportionation, is unaffected. Given that activity coefficients increase with ionic strength, $E_{\text{F}}^{\ominus}$ values are expected to become more negative. This was observed experimentally.

Fully supported conditions

When dissolved in acetonitrile, anthraquinone is known to present two, reversible, single electron reduction peaks;³⁶ in contrast, when dissolved in water, anthraquinone presents a complex mechanism that is pH dependent.³⁷

Chronoamperograms were recorded in a solution containing 1.25 mM anthraquinone and 62.5 mM

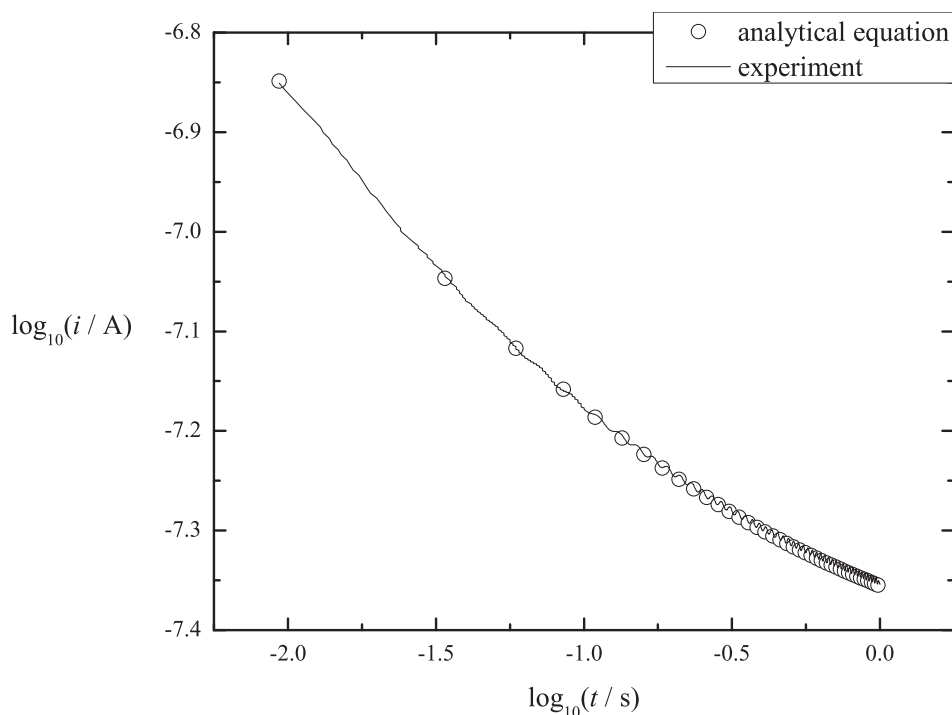


Figure 9.9: Experimental chronoamperometry compared with the analytical equation ($D_{AQ} = 2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$).

of TBAP, $C_{\text{supp}} = 50$. Under these conditions, mass transport can be considered ‘diffusion-only’. The single step chronoamperogram shown in figure 9.9 was obtained by applying a potential of -1 V vs. Ag_{wire} for two seconds. This potential lies in between the two reduction waves and therefore corresponds to rate limiting diffusion of AQ only. The value of D_{AQ} was determined by fitting the experimental transient to the analytical equation¹⁰

$$i = nF\pi r_e^2 D_A c_A^* \left(\frac{1}{\sqrt{D_A \pi t}} + \frac{1}{r_e} \right) \quad (9.20)$$

The analytical transient shown in figure 9.9 was obtained using $D_{AQ} = 1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The double potential step chronoamperogram shown in figure 9.10 as obtained by applying a potential of -1 V vs. Ag_{wire} for two seconds subsequently applying -0.3 V vs. Ag_{wire} for two seconds. The first potential lies in between the two reduction waves and therefore corresponds to rate limiting diffusion of AQ only. The second potential is more positive than either voltammetric wave and corresponds to rate limiting diffusion of AQ^- only. These experimental results were compared with numerical results obtained using a program described by Klymenko *et al.*³⁸ Concordance between the experimental and simulated data occurred when $D_{AQ} = 2.1 \pm 0.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and

$D_{AQ^-} = 1.7 \pm 0.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. These values are consistent with the literature data.³⁹

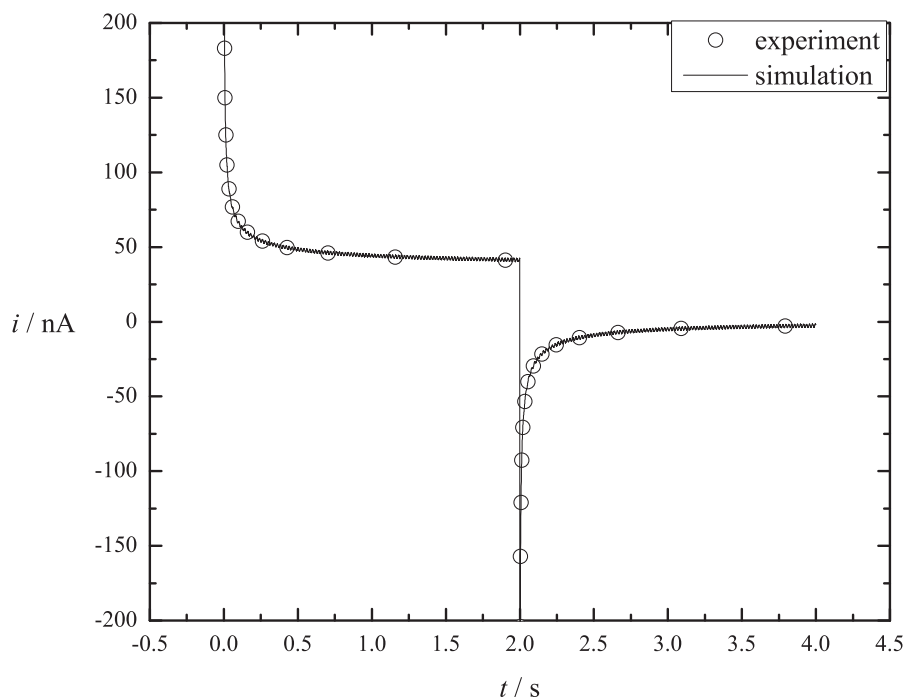


Figure 9.10: Experimental double potential step chronoamperometry compared with the simulated result ($D_{AQ} = 2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{AQ^-} = 1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$).

The quadruple potential step chronoamperogram shown in figure 9.11 as obtained by applying a potential of -1 V *vs.* Ag_{wire} for two seconds, -1.6 V *vs.* Ag_{wire} for two seconds, -1 V *vs.* Ag_{wire} for two seconds, -0.3 V *vs.* Ag_{wire} for two seconds. These potentials correspond to from open circuit step to a potential between the first and second wave, then stepping to a potential after the second wave, after coming back to a potential between both waves and finally stepping before the first wave. These potentials correspond to rate limiting diffusion of species A, B, C and B respectively. These experimental results were compared with numerical results obtained using a program described by Wang *et al.*⁴⁰ Concordance between the experimental and simulated data occurred when $D_{AQ} = 2.1 \pm 0.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_{AQ^-} = 1.7 \pm 0.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{AQ^-} = 1.6 \pm 0.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

Cyclic voltammograms were recorded at different scan rates (50, 100, 200, 500 and 1000 mV s^{-1}). The results for the highest and lowest scan rates studied are shown in figure 9.12. The voltammetry was simulated as described in section 9.1. The parameters that yielded the greatest concordance between theory and experiment are given in table 9.3. Simulated voltammograms are shown in figure 9.12 for both $k_{\text{comp}} = 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{\text{comp}} = 10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The former corresponds

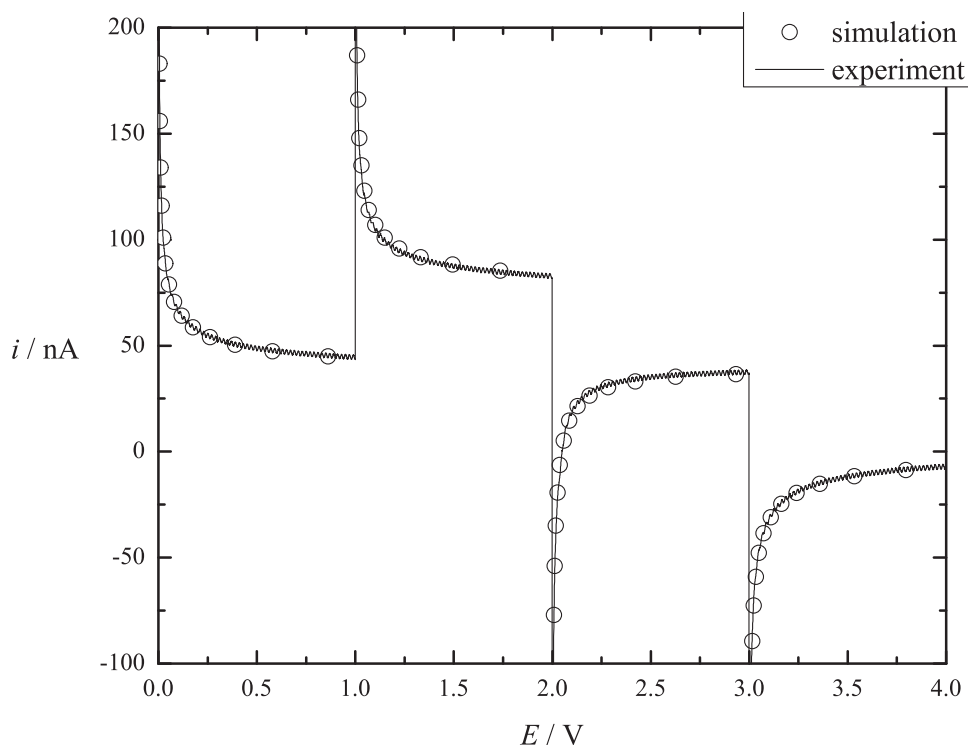


Figure 9.11: Experimental quadruple potential step chronoamperometry compared with the simulated result ($D_{AQ} = 2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $D_{AQ^-} = 1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{AQ^{2-}} = 1.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$).

to the limit of diffusion control. Both simulated voltammograms are in good agreement with the experimental results over the range of scan rates studied. This is expected because the diffusion coefficients of AQ, AQ^- and AQ^{2-} are similar.⁴ Cyclic voltammetry is unable to resolve the presence of comproportionation under conditions of full support. Graph

Weakly supported conditions

Cyclic voltammograms were recorded at low concentration of supporting electrolyte in a solution containing 1.25 mM of TBAP and 0.7mM of TBAP at various scan rates. The results are shown in figure 9.13. The peak current of the second wave decreases with support ratio due to negative migration, as explained in section 9.1. As before, cyclic voltammograms for $k_{\text{comp}} = 0 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{\text{comp}} = 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Unlike the case of full support, these simulated voltammograms are distinctly different. From this data it is possible to conclude, unambiguously, that comproportionation occurs at diffusion control. This conclusion is in accordance with Marcus theory which predicts that molecule, such as anthraquinone, that are rigid with respect to gain or loss of electrons, lead to rapid

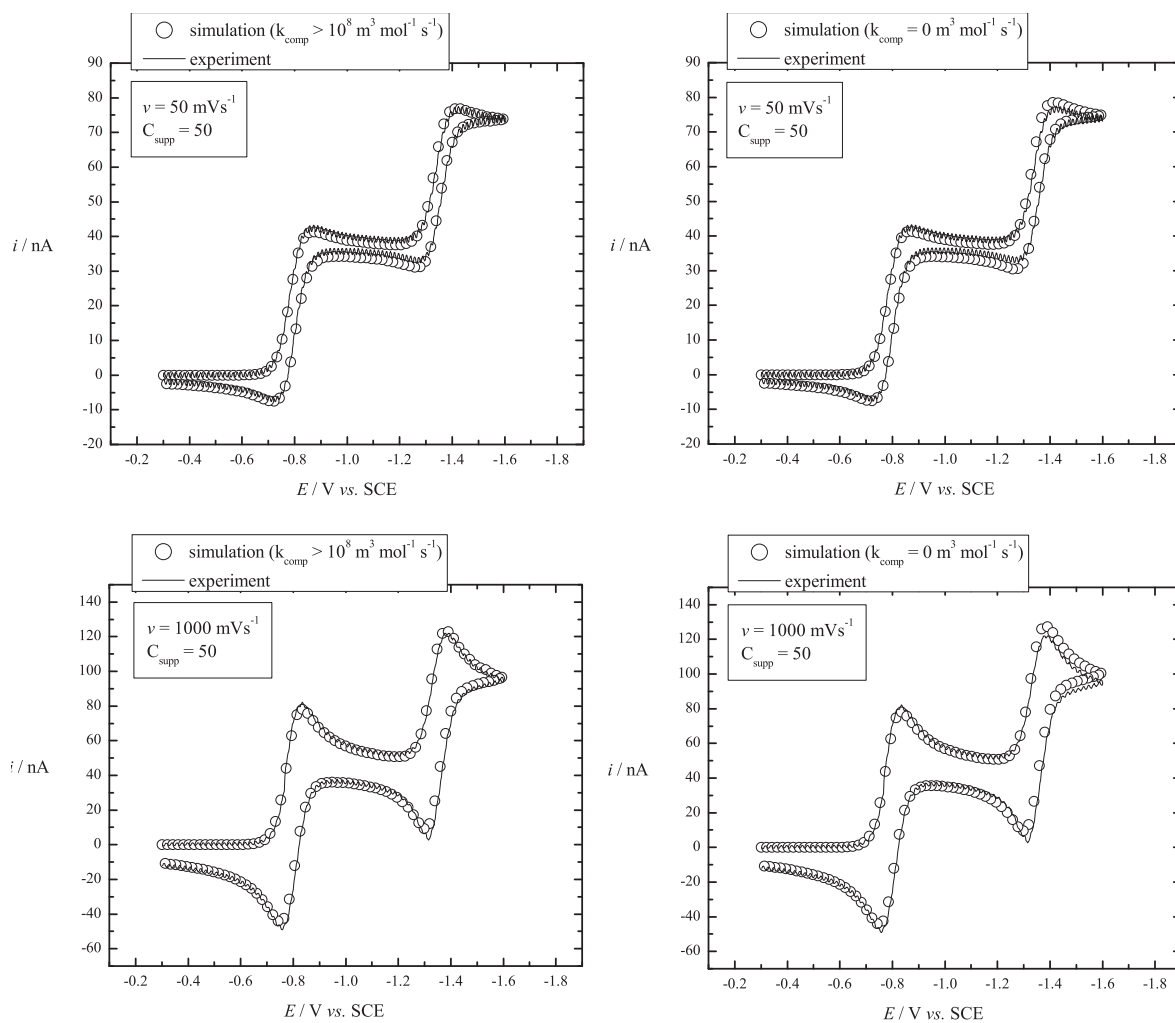


Figure 9.12: Experimental cyclic voltammetry compared with simulated results when $C_{\text{supp}} = 50$.

rate constants for reactions, such as comproportionation, involving electron transfer.⁴¹

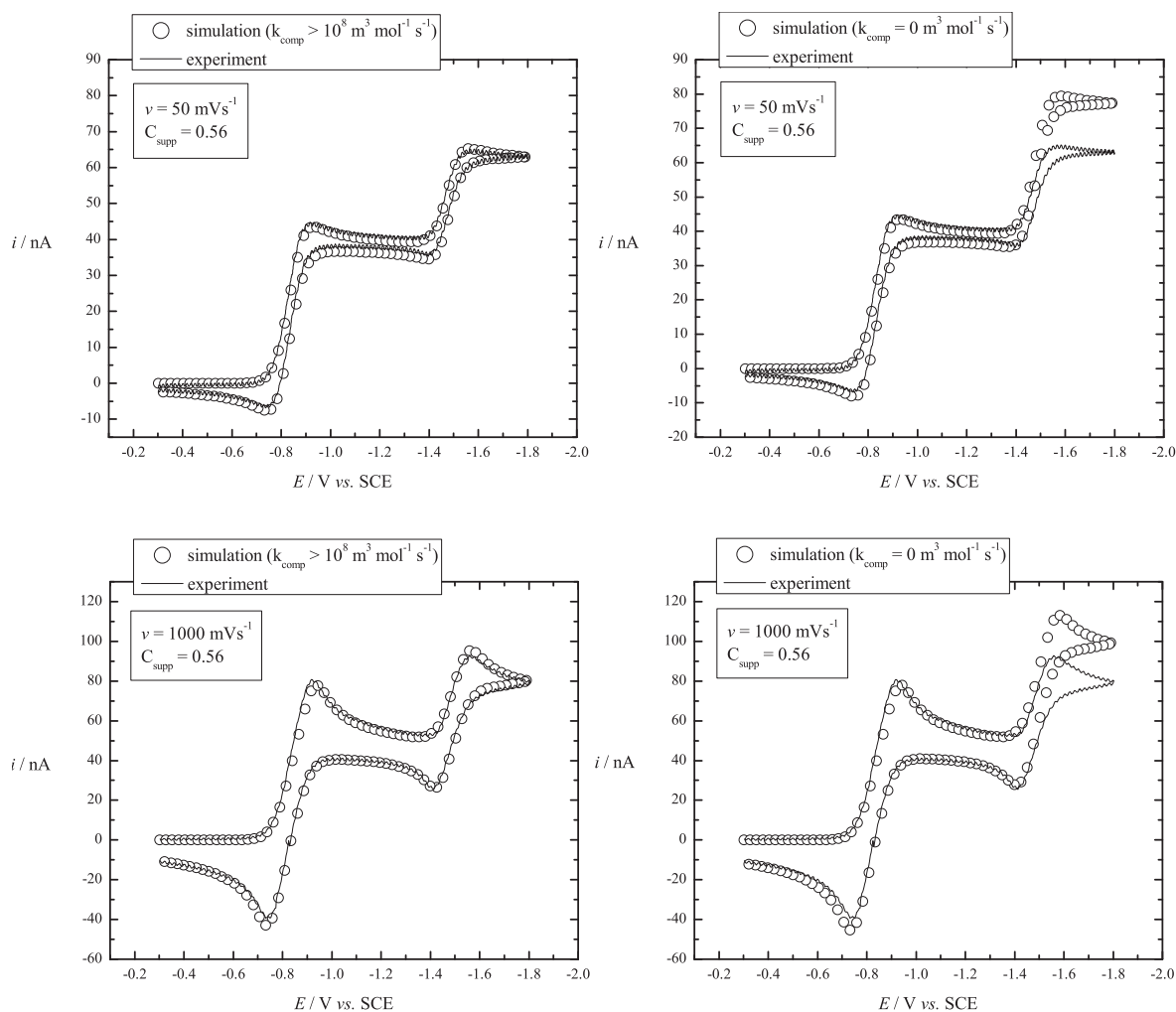


Figure 9.13: Experimental cyclic voltammetry compared with simulated results when $C_{\text{supp}} = 0.56$.

9.2 Conclusion

Cyclic voltammetry, with homogeneous kinetics, can be simulated for conditions of low support. In many cases, cyclic voltammetry is unable to determine the presence or absence of diffusion-controlled comproportionation under conventional, fully supported, conditions; in contrast, under weakly supporting conditions the distinction can be unequivocal. It has been shown experimentally that, in the case of anthraquinone in acetonitrile, comproportionation is diffusionally controlled.

In the experimental study presented here, the validity of the data is improved considerably by comparing theory and experiment over a range of scan rates and a range of concentrations of the

supporting electrolyte. We anticipate electrochemistry in solutions of variable ionic strength is therefore likely to become widely used and is expected to greatly enhance the scope of voltammetry for detecting kinetic and thermodynamic parameters.

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