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Electrochemical Studies of Reactions in Small Volumes Less Than 1 Femto Litres.

Isaac Agyekum

East Tennessee State University

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Electrochemical Studies of Reactions in Small Volumes Less Than 1 Femto Litres

A thesis presented to The faculty of the Department of Chemistry East Tennessee State University

In partial fulfillment of the requirement for the Master of Science in Chemistry by Isaac Agyekum May 2011

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Keywords: Nanometer sized Electrode, Charge Transfer (CT), Electron Transfer (ET), Ion Transfer (IT), Interface Between Two Immiscible Electrolyte Solutions (ITIES)
ABSTRACT

Electrochemical Studies of Reactions in Small Volumes Less Than 1 Femto Litres
by
Isaac Agyekum

Electrochemical methods have been used to study electron transfer reactions at the interface between an aqueous phase of less than 1 femto liters in volume and a bulk organic phase. The small aqueous phase is formed at the end of a slightly recessed platinum electrode. When a negative potential is applied between the Pt electrode and the aqueous phase, Ru(NH$_3$)$_6^{3+}$ in the aqueous phase could be reduced to Ru(NH$_3$)$_6^{2+}$. Because the volume of the aqueous phase is very small, the electrochemically formed Ru(NH$_3$)$_6^{2+}$ could instantly reach the interface between the aqueous phase and the organic phase which contains 7,7,8,8-Teteracyanoquinodimethane (TCNQ), and be oxidized to form Ru(NH$_3$)$_6^{3+}$ by giving electrons to TCNQ at the interface. Our results showed a positive shift in the $E_{1/2}$ comparing the reaction undertaken in the recessed cavity and the bulk solution.
DEDICATION

This work is dedicated to my parents and the Agyekum family for their unflinching support and encouragement, Liberty Baptist Church for their support, and all friends at Sweet Divine Manner Ministries.
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CHAPTER 1

INTRODUCTION

The study of charge transfer across the liquid/liquid interface has attracted enormous interest for the past decade. Charge transfer across the liquid/liquid interfaces are fundamental physicochemical processes that are relevant to many important chemical and biological systems including sensors, batteries, drug delivery systems, solvent extraction in hydrometallurgy, catalysis, and biomembranes [1-5].

Structure of Interface Between Two Immiscible Electrolyte Solutions

The interface between two immiscible electrolyte solutions (ITIES) is created between two electrolyte solutions, “when there is low miscibility between the two solutions” [1]; usually an aqueous/organic interface. To study charge transfer across the interface between two immiscible electrolyte solutions, one needs to understand the nature and properties of the interface. Several attempts have been made to investigate these properties, structures, and their effects on a liquid/liquid interface.

The first model for the structure of the liquid/liquid interface was proposed by Verwey and Niessen which is termed Verwey-Niessen model (MVN) shown in Figure 1. It was the first model to describe the interface between two immiscible electrolyte solutions as having two diffusion layers [3, 4]. These layers are characterized by either containing excess positive or negative charges. The Verwey-Niessen model adapts the Gouy-Chapmans model that assumes the liquid/liquid interface as a mathematical plane [4].
Figure 1: A schematic diagram of the modified Verwey-Niessen model of the interfacial structure of electrified liquid/liquid interface. $\phi^w$ and $\phi^o$ are the respective potentials in the organic and aqueous phase.

The MVN model also assumes that the dielectric permittivity of the medium at any point in the diffusion layer is constant and equivalent to the bulk phase value [4, 5]. Even though most experimental findings on the structure of liquid/liquid interface agree with the MVN model, none has been able to accurately give a detailed description of the interface. This challenge is mainly attributed to the buried nature of the interface and its size that is relatively small compared to other condensed phase media [4]. Microscopic parameters obtained from most experiments agree with the MVN model, but there are still some unresolved issues [3-6]. The existence of an ion free inner layer is one of the concerns associated with the structure of liquid/liquid interface. Electrochemical experiments involving the determination of potential of zero charge (pzc) has been carried out to prove the existence of the ion free inner layer [6]. At the liquid/liquid interface, the Galvani potential difference associated with the two phases represented by $\phi_O$ and $\phi_w$ shown in Figure 1 can be separated from each other by contributions from potential difference across the inner layer and that across the charged regions in the organic and aqueous
phase[4-6]. The inner layer potential created at the interface are as a results of the dipolar interactions arising from solvent molecular orientation [4].

Other experimental findings on the structure and dynamics on the liquid/liquid interface have been reviewed. Reymond et al. [5] in their review described the structure of the interface between two immiscible solutions as very dynamic and its properties very reproducible. Strutwolf et al. [7], using a combination of scanning electrochemical microscopy and neutron reflection measurements, were able to investigate the nature of liquid/liquid interface. From their results, the reflectivity profile of the three phase system, quartz, water, and dichloromethane (DCE) indicated that the liquid/liquid interface has a root mean square roughness less than 10 Å.

Another method that has been employed to probe the surface of liquid/liquid interface is the combination of X-ray and neutron scattering. This novel technique provides detailed information about the molecular ordering and structure of the interface between two immiscible solutions and also precisely measures the width of the water/oil interface [8]. Surface-frequency generation (SFG) technique is also one of the highly specific techniques that could be applied to probe interfaces accessible to light. This technique is actually not only applicable to studies of neat liquid/liquid interfaces but also other interfaces such as neat liquid/solid interfaces, liquid mixture/vapor interfaces, etc. [9].

Polarization of ITIES

The interface between two immiscible electrolytes solutions is categorized as either polarized or nonpolarized. This characterization is actually based on whether there exists a relationship between potential difference and the concentration of charged species present [1].
Ideal nonpolarized interface is one in which the potential difference does not change upon passing electric current through it, while for ideally polarized interface charged species there is no faradic current even though a potential difference between the interface has been applied [1, 3]. To polarize the ITIES, four electrode potentiostat systems are employed: two reference electrodes in combination with two counter electrodes. The potentiostatic polarization of ITIES is required for the study of charge transfer across liquid/liquid interfaces at a particular Galvani potential difference. There are two methods that could be employed to produce a potential drop at a liquid/liquid interface. One approach is by using a non polarized interface which has a single ion found in both phases [3]. A schematic representation of a polarized interface is shown in Figure 2 where $M^+$ is a common ion in both phases while $N^-$ and $P^-$ are ions that are either hydrophilic or hydrophobic enough to remain in their respective phases.

![Figure 2: A schematic representation of a polarized liquid/liquid interface.](image)

The Galvani potential difference could be expressed as

$$
\Delta_0^w = \Delta_0^w \phi_M^0 + \frac{RT}{F} \ln \left( \frac{a_M^O}{a_M^W} \right)
$$

Equation 1

Where $a_m$, $R$, $T$, and $\phi$ are the activity of the ion $M^+$, the molar gas constant, temperature and the Galvani potential.

The second method is simply achieved by applying an external voltage source from a reference electrode to a polarized liquid/liquid interface [3].
CHAPTER 2

CHARGE TRANSFER ACROSS ITIES

Charge Transfer across liquid/liquid interface is classified into two main types: ion transfer (IT) and electron transfer (ET).

**Ion Transfer Across ITIES**

The chemistry of ion transfer across the ITIES has been well documented. Ion transfer across ITIES usually involves the movement of an ion from the aqueous phase (w) to an organic phase (o) and vice versa. This process is achieved by giving the ion the required Gibbs free energy to move from one phase to the other. Ion transfer across ITIES is actually based on the Gibbs free energies of the ion that is confined by the potential window available for a given pair of immiscible electrolytes [1, 5]. Ion transfer across ITIES is categorized into two main types: simple ion transfer and assisted ion transfer.

**Simple Ion Transfer**

Simple ion transfer across liquid/liquid interfaces occurs when an ion is transferred directly from one phase to another.

\[ A^{n+} (w) \leftrightarrow A^{n+} (o) \]  

Equation 2

Research carried out by Laforge et al. [10] showed that this one-step mechanism for ion transfer cannot be generalized for a wide variety of ions. The mechanism for a simple ion transfer reaction at the interface between two immiscible electrolyte solutions is outlined below and a schematic representation of a simple transfer across ITIES is shown in Figure 3.
Figure 3: A schematic diagram of ion transfer across ITIES

Where $A^Z$ is the charge transferred across the Organic phase to the aqueous phase.

For a simple ion transfer

$$A^Z(w) \rightleftharpoons A^Z(o) \quad \text{Equation 3}$$

And at equilibrium the charge transfer across the interface is given as

$$\mu_i^w = \mu_i^o \quad \text{Equation 4}$$

Therefore, the Galvani Potential at the interface is expressed as

$$\Delta_{aq}^0 \phi = \phi^w - \phi^o \quad \text{Equation 5}$$

and

$$\phi_{aq} - \phi^0 = \frac{\mu_i^w - \mu_i^o}{Z_i F} + \frac{RT}{Z_i F} \ln \frac{a_i^w}{a_i^o} \quad \text{Equation 6}$$

Where $\mu_i^w - \mu_i^o = \Delta G^0_{tri \rightarrow w}$ is the standard Gibbs free energy difference across the interface.

$$\Delta G_{tri \rightarrow w} = \Delta G_{solv,d}^{0,o} - \Delta G_{solv,d}^{0,w} = \mu_i^w - \mu_i^o \quad \text{Equation 7}$$
The Standard Ion transfer potential is given by

$$\Delta^o_w \phi_i = \frac{\Delta G^o_{wi}}{Z_i F}$$

Equation 8

Therefore Equation 4 can be expressed as

$$\Delta^o_w \phi = \Delta^o_w \phi_i + \frac{RT}{Z_i F} \ln \frac{a^w_i}{a^o_i}$$

Equation 9

The ionic distribution at equilibrium between ITIES is governed by the Nernst Equation (10).

For a polarized interface, the electrochemical potential is given as

$$\mu(\alpha) = \mu^0_i + RT \ln a_i(\alpha) + Z_i f \phi(\alpha)$$

Equation 10

Where $\mu^0_i, R, T, f, \phi$ and $a_i$ are the standard chemical potential, molar gas constant, temperature, inner (Galvani potential) of the phase $\phi$, faradays constant and, the activity of the ion respectively.

At equilibrium and the Nernst equation for (11) is expressed as

$$\Delta^o_w \phi = \phi(aq) - \phi(o) = \Delta^o_w \phi_i + \frac{RT}{Z_i F} \ln \frac{a^w_i}{a^o_i}$$

Equation 11

The equilibrium concentrations of redox species involved in interfacial ion transfer reactions at the liquid/liquid interface is governed by Equation 11.

**Assisted Ion Transfer**

Assisted ion transfer across ITIES occurs when the transfer of the ion across the interface is facilitated by the addition of a compound that lowers the energy required by the ion to bring it within the potential window [5, 11]. The electrochemical reaction for an assisted ion transfer reaction is given below.
\[ A^{n+}(w) + L^{m-}(o) \rightleftharpoons AL^{n-m}(o) \]

Equation 12

Where A is the ion transferred across the interface and L is a ligand, and n, m their respective charges. This type of ion transfer has been extensively discussed by Reymond et al. [5]. Schmickler [12] stated that ion transfer across liquid/liquid interface could be significantly enhanced by complexing with a suitable ionophore. A very important consideration in most complexation reactions for facilitated ion transfer across liquid/liquid interface is the nature of the ligand ion interaction at the interface. Ligands having low distribution coefficients have been found to undergo protonation or partitioning at the interface [13].

There have been several reports on the mechanism associated with ion transfer reactions [1, 5, 14]. Marcus [14] outlined the mechanism for ion transfer reactions as initiated by desolvation of the ion from liquid and concerted solvation by another liquid. Another mechanism that involves the transient interfacial ion pairing and the transfer of hydrophilic ion across the interface of mixed solvents has been reported [10]. Studies have shown that it is possible to probe the transfer of highly hydrophilic ions at the liquid/liquid interface by limiting the mass transfer reaction of a particular ion [15].

Considering the reversibility nature of both ion and assisted ion transfer reactions, they can be used in the designing of amperometric ion sensors even though their applicability is hindered by the large ohmic drop in the organic phase and the mechanical instability nature of the interface [5]. With regards to obtaining detailed information about the transfer mechanism of assisted ion transfer, electrochemical studies involving ion transfer across the liquid/liquid interface of molecules having acid base properties can help in elucidating this mechanism [5].
Electron Transfer at ITIES

Electron transfer (ET) reactions at ITIES involves the transfer of electrons between a redox couple $O_1/R_1$ in the aqueous phase (w) and $O_2/R_2$ in the organic phase (o), where O and R are the oxidized and reduced species. The mechanism for ET reaction at liquid/liquid interface is outlined as follows:

$$
\begin{align*}
O_1^w + e^- & \rightarrow R_1^w \\
O_2^w + e^- & \rightarrow R_2^w
\end{align*}
$$

Equation 13

$$
O_1^w + R_2^O \rightleftharpoons O_2^w + R_1^O
$$

Equation 14

When equilibrium is achieved across the interface

$$
\mu_1^w + \mu_2^O = \mu_{R1}^w + \mu_{O2}^O
$$

Equation 15

and the equilibrium potential at the interface is written as

$$
\Delta_0^w \phi = \Delta_0^w \phi_{el}^o + \frac{RT}{F} \ln \frac{aO_2(o)aR_1(w)}{aR_2(o)aO_1(w)}
$$

Equation 16

Where $\Delta_0^w \phi_{el}^o$ is the standard Galvani potential difference that is expressed as

$$
\Delta_0^w \phi_{el}^o = \frac{\Delta_0^w G_{el}^o}{F} = \frac{\mu_{R1}^o(w) - \mu_{O1}^o(w) + \mu_{O2}^o(w) - \mu_{R2}^o}{F}
$$

Equation 17

The interfacial electron transfer is governed by the Nernst equation in (17).

There have been several novel techniques that have been employed to study electron transfer reactions. The most popular among the methods is scanning electrochemical microscopy (SECM).
Scanning Electrochemical Microscopy (SECM)

Scanning electrochemical microscopy (SECM) is one of the very important analytical chemistry techniques used to investigate structures and processes of micro-meter and even sub-micrometer dimensions. SECM is highly sensitivity and known for its accuracy in probing electron transfer reactions across the interface of two immiscible electrolyte solutions [16]. The versatility of this technique has seen application on other types of interfaces apart from liquid/liquid interface [17].

SECM is made up of four main parts, the micro-positioning system that is responsible for the movement of the ultramicro electrode tip in 3D, an electrochemical cell that is a combination of the ultra-micro electrode tip, reference, and counter electrode and the substrate that acts as a second working electrode, a computer for data collection, and a bipotentiostat [16-18]. A scheme of the main component of SECM is shown in Figure 3.

Control/Record: Current, potential

![Figure 4: A schematic diagram of the scanning electrochemical microscopy instrument](image-url)
Functional Principles of SECM

When the ultramicroelectrode (UME) tip is brought near the surface of a substrate, the electrochemical response at the tip of the UME is interfered by the substrate; this interference then provides information about the structure and properties of the substrate [18]. One of the modes of operation that has been used extensively for various research works is the feedback mode of the SECM.

Feedback Mode Operation of SECM

In the feedback mode of operation, the ultramicroelectrode (UME) tip is the working electrode, and the substrate is used as another electrode. In the typical SECM experiment, four or three electrode systems could be applied depending on the experimental requirement. When a positive potential is applied to the UME tip, specie O is generated from the redox mediator R initially contained in the electrochemical cell and then moves to the substrate [19].

\[ O + ne \rightleftharpoons R \text{ (at tip)} \]  
Equation 18

The faradic current generated at the UME tip by the reaction (18) above is constant when it is positioned further from the substrate. This current is given by the equation

\[ i_{T\infty} = 4nFDCa \]  
Equation 19

Where \( i_T \) is the limiting current, \( F \) is faradays constant, \( D \) is the Diffusion Coefficient of \( R \), \( C \) is the concentration of the electroactive reactant and \( a \) is the radius tip UME tip. When the tip is brought closer to the substrate, the specie \( O \) formed can be reduced to form \( R \) at the substrate and the \( R \) produced can diffuse back to the substrate. This process increases the flux of \( R \) to the tip hence termed a positive feedback mode [19]. However, on an insulator substrate where specie \( O \)
cannot react, there is the reduction of current at the UME tip, hence the term negative feedback. Other operational modes of SECM employed by electrochemists are generation/collection mode [18, 19].

Scanning Electrochemical Microscopy and Its Application at The ITIES

Other electrochemical processes such as coupling of charge transfer across liquid/liquid interfaces using SECM have also been reported by Selzer et al. [20]. A research conducted using SECM to probe charge transfer reactions at the liquid/liquid interface has being reported by Barker et al. [21]. In their report, a new method for investigating the dynamics of partitioning of electroactive solutes between two immiscible phases has been discussed. Among the numerous applications of scanning electrochemical microscopy is the probing of cellular based reactions.

Application of SECM at Cellular Interfaces

Electrochemical studies involving charge transfer across liquid/liquid interface provide a basic model that can help elucidate the complex mechanism involving charge transfer across biological membranes. Research carried out by Sun et al. [22] has shown that redox activity involving transmembrane charge transfer can be probed without destroying the cell using the feedback operation mode of SECM. Applying nanometer- size amperometric probes and SECM, they were able to carry out electrochemical experiments in cultured human breast cells. Using hydrophilic redox mediators that are unable to penetrate cell membranes, Liu et al. [23] investigated redox and acid/base activities in mammalian cell using SECM. Applying a similar technique, Cai et al. [24] reported the redox activity of Rb. Sphaeroides. Using two groups of
redox mediators to transport electrons between the SECM tip and the redox centers within the cell, they were able to probe the pathway transmembrane charge transfer in the substrate, combining nanometer size amperometric probes with scanning electrochemical microscopy. Zhan et al. [25] have also reported the detection and investigated the toxicity of Ag⁺ using a micropipette ITIES as a scanning electrochemical microscopy tip (SECM). Electron transfer reaction at SECM tip and the substrate are illustrated in Figure 5 below.

Figure 5: Schematic diagram of a feedback mode experiment using a scanning electrochemical microscopy with the UME tip positioned near a substrate.

The mediated electron transfer mechanism across the immobilized cell and the SECM tip shown in Figure 5, is outlined below.

**Reaction at the electrode tip**  \[ O + ne \rightarrow R \]  \[ \text{Equation 20} \]

**Reaction within the cell**  \[ R + O_{cell} \rightarrow O + R_{cell} \]  \[ \text{Equation 21} \]

Where R and O are the oxidized and reduced specie in the solution forming a redox mediator in the solution and \( O_{cell} \) and \( R_{cell} \) are also the redox mediators in the cell.
Other Methods Used to Investigate Charge Transfers Across ITIES

Among several other techniques used in the study of the nature and charge transfer process across liquid/liquid interfaces is Raman spectroscopy [26]. Applying Raman microscopic techniques, Edwards et al. [27] identified particulate matter at the interface between an organic and aqueous solvent. Their study also reports the mass transfer of metal ions across the interface between the two immiscible solvents, and the processes involved in the transfers are also discussed. Cheng et al. [28], using Polarization-modulation Fourier transform infrared reflection and absorption spectroscopy (PM-FTIRRA) at ITIES, established the transfer of 95% conversion of ferrocyanide ions. One of the novel techniques that has successfully been applied for studies involving liquid/liquid interface is Spatially Resolved Nuclear magnetic resonance (NMR) spectroscopy. Lambert et al. [29], using this technique created a flat cuboid as their detection volume element, discovered the diffusion coefficient at the interface was five times faster than in the bulk. Studies involving electrochemical ion transfer across micro liquid/liquid interfaces within solid state micro arrays have also been reported by Strutwolf et al. [30]. The use of “Electron paramagnetic resonance” (EPR) spectroscopy technique to probe charge transfer across liquid/liquid interfaces has been reported by Webster et al. [31]. They carried out EPR spectroscopic experiments involving the reduction of TCNQ to TCNQ\(^-\) and the oxidation of TTF to TTF\(^+\) across the interface of water/1,2-dicloromethane. A similar work carried out by the same group stated the possibility of modeling the EPR signals obtained from potential step experiments in terms of diffusional transport. EPR data and voltammetric results obtained from their experiment also showed the stability of the two semiquinones couples that is 2,3,5,6-tetrachloro-p-benzoquinone (TCBQ/TCBQ\(^-\)) and 2,3,5,6-tetrafluoro-benzoquinone (TFBQ/TFBQ\(^-\)) at the DCE/water interface [32].
CHAPTER 3

CHARGE TRANSFER REACTIONS IN VERY SMALL VOLUMES

Electrochemical studies of chemical reactions in very small volumes have come of age. Studies done with very small volumes have been motivated by the fact that very important life processes occur at liquid/liquid interface [3] and these reactions occurring in these volumes can serve as a model for cellular based reactions. Also, the introduction of samples in very small volumes and its application to current instrumentation design is of great concern to researchers. Applying various techniques, researchers have reported interesting phenomena involving charge transfer across the interface of two immiscible electrolyte solutions in very small volumes.

Microelectrochemical measurements at expanding droplets (MEMED) is one of the new techniques that has been used to investigate the kinetics of reactions occurring at Interface between two immiscible liquids involving small volumes [33]. Banks [34] in his review reiterated the usefulness of microdroplet modified electrodes. His observation was that when redox compounds are confined to an electrode surface using DME (droplets modified electrodes), one is able to determine the Gibbs free energy transfers from an aqueous phase to a non aqueous phase. Scholz et al. [35] reported the transfer of Gibbs free energy involving ion transfer across the liquid/liquid interface applying DME techniques. Gulaboski et al. [36] in their report compared the solvation properties of 2-nitrophenyl Ether, Nitrobenzene, and n-Octanol. Applying a potential to start a reaction at the three phase junction line, they were able to introduce a small amount of salt into the edge of the droplet from the aqueous phase, thereby
decreasing ohmic resistance. Electrochemical studies involving neutral and ionic redox species using a thin film and droplets deposits have also been reported by Schroder et al. [37]. In their results, they concluded that neutral and ionic redox liquids go through redox conversions, but both differed due to lack of ion conductivity in the neutral liquid.

There are several other novel techniques that have been employed to carry out charge transfer studies across the interface between a small volume aqueous phase and a bulk organic phase. Using capillary and microinjection methods, Nakatani et al. [38], reported the study of electron transfer reaction across a single micro-water-droplet/oil interface. In their report, they observed the suppression of mass transfer of the redox species due to the extremely small volume of the micro-water droplet. Using kinetic data obtained from their work, Zhang et al. [39] were able to explain the simple energy barrier model in which the Gibbs free energy is related to surface pressure of the absorbed monolayer. This experiment was carried out by investigating the kinetics of IrCl₆²⁻ ion across the water/1, 2-dicloroethane interface using microelectrode measurements at expanding droplets and scanning electrochemical microscopy.

Other novel techniques employed by research scientists to study charge transfer reactions across liquid/liquid interface have also been well documented. The inception of micro and nano pipettes and its application to the study of charge transfers across the interface between two immiscible electrolyte solutions have been very useful, especially providing an alternative means of creating micro-to nano scale ITIES [40]. Cai et al. [41] reported the study of ion transfer reaction involving tetraalkylammonium ions across the interface between dichloromethane and water. From their results, they reinforced the importance of working with nano scale ITIES, with
respect to mass transfer.

\[ M_f = \frac{i_d}{2\pi r^2 c} \quad \text{Equation 22} \]

Where \( M_f \) is the mass transfer coefficient, \( i_d \) is the limiting current, \( r \) is the radius of the electrode and \( c \) is the concentration of the redox specie. From equation 22, mass transfer rate is enhanced at nano ITIES, hence its applicability for studying faster kinetics at liquid/liquid interface.

One major concern of modern analytical instrumentation is small volume sampling. Another is the injection of small volumes of solutions during studies at the cellular level. Modern analytical techniques such as microfluidic systems and very small volume fluid injection systems would find this technique very useful. Laforge et al. [42] have reported the use of attosyringe to disperse atto-picoliter of solutions and were able to control the fluid motion using electroanalytical techniques allowing sampling of attoliter-to-picoliter (\( 10^{18} \) to \( 10^{12} \) liter) volumes of these solutions. This was achieved by changing the voltage across the liquid/liquid interface at the tip of a nanopipette. A schematic diagram of an electrochemical attosyringe is shown in Figure 6.

Figure 6: A Schematic diagram of an electrochemical attosyringe.
Because most of the reports on electron transfer reactions across very small volume interfaces were carried out in volumes within microliter range, we wanted to investigate electron transfer reaction across the interface between a very small aqueous phase whose volume is less than 1 femto liter and a bulk organic phase using a recessed platinum electrode. The use of the recessed electrode was to enable us create a cavity whose volume was less than 1 femto liter.
CHAPTER 4
EXPERIMENTAL SECTION

Chemicals Used

KNO₃ (99+%, Fisher Chemical) was used as supporting electrolytes. Ru(NH₃)₆Cl₃ was purchased from Strem Chemicals (Newburyport, MA). 1, 2-diclochloroethane (DCE) and octadecyltrimethoxysilane (90%, Aldrich) TCNQ, were purchased from Aldrich. All aqueous solutions were prepared with deionized water (Milli-Q, Millipore Co.)

Fabrication of Recessed Electrode

Two main methods were employed in the fabrication of the nanometer sized recessed electrode, the Puller made method and the Electrochemical etching method.

Puller Made Method

Nanometer sized electrodes were fabricated using P-2000 laser puller instrument (Sutter Instrument Co). These electrodes were observed under an optical microscope and found to be slightly recessed as shown in Figure 7. The observed cavity created met our experimental requirements of obtaining a very small volume at the tip of the nanometer sized electrode. After some few experiments, we were not able to obtained very good cyclic voltammograms for these electrodes and the cavity created was so small, hence the difficulty in measuring accurately the depth of the cavity.
Electrochemical Etching Method

A puller-made nanometer size recessed Pt electrode was polished such that the angle between the electrode and the rotating disk of a micropipette beveller (Sutter instrument Co, Novato, CA) is 3°. The electrode shown in Figure 8 was dried and hanged in a 50 mL vial, in which 0.5 mL of octadecyltrimethoxysilane (90%, Aldrich) was present at the bottom. The covered vial was then put into an oven at 90 °C overnight to silanize the glass wall of the electrode.

After silanization, the electrode was rinsed several times with acetone and dried at 80 °C for about 2-3 h. It was then etched with an alternating current of about 5V using a transformer. The side and top view of an electrochemically etched electrode is shown in Figures 8 and 9.
Figure 8: Optical microscopy image of an unpolished puller made nanometer size platinum electrode. Scale bar 7 \( \mu \text{m} \).

Figure 9: Scanning electrode microscopic image of the surface of a nanometer size recessed electrode.
Experiment 1

Both Working and Reference Electrodes in The Bulk Aqueous Phase

To carry out this experiment, a simple electrochemical cell was designed using a glass vial containing the test solution with our working electrode and Ag/AgCl reference electrode placed vertically in it. Cyclic voltammograms were obtained on a nanometer sized recessed electrode placed in aqueous solution of 0.1 M KNO₃ which was our blank solution. This experiment was repeated for various scan rates for over 20 scan segments until a stable cyclic voltammogram was obtained. This was done to ensure the recessed cavity at the tip of the electrode was filled with the solvent of interest. The experiment was then repeated using an aqueous solution of 1 mM Ru(NH₃)₆Cl₃ containing 0.1 M KNO₃ as the supporting electrolyte. A schematic diagram for the experimental setup using a Ag/AgCl reference electrode and the nanometer sized recessed electrode is shown in Figure 10.

(A) Aqueous phase made up 0.1 M KNO₃ and (B) aqueous phase made up of 1 mM Ru(NH₃)₆Cl₃ with 0.1M KNO₃.

Fig 10: Experimental set up for bulk aqueous phase experiment. (A) Aqueous phase made up 0.1 M KNO₃ and (B) aqueous phase made up of 1 mM Ru(NH₃)₆Cl₃ with 0.1M KNO₃.
Experiment 2

Working Electrode in Aqueous Phase and Reference Electrode in The Organic Phase

A second bulk aqueous phase experiment was carried out with aid of simply designed electrochemical setup using a glass vial and a capillary tube through which Ag wire was inserted. With the aid of a Torr seal, our capillary tube was sealed at both ends such that only 2 cm of the Ag wire was exposed to the organic solvent. The vial was 2/3 filled with 1, 2-dichloroethane (DCE) containing 2 mM TCNQ and aqueous solution of 0.1 M KNO₃ was then added. With the recessed electrode in the aqueous phase comprising 0.1 M KNO₃ which was the blank solution and the reference electrode in the Organic phase, cyclic voltammograms for this experiment were obtained at various scan rates for about 20 segments. This was then repeated with aqueous solution of 1 mM Ru(NH₃)₆Cl₃ with 0.1 M KNO₃ as the supporting electrolyte. And the corresponding voltammograms were also obtained. The schematic representation for experiment 2 is shown in Figure 11.

Figure 11: Experimental Set up for bulk phase experiment with working electrode in aqueous phase; (C) Aqueous phase made up 0.1 M KNO₃ and (D) aqueous phase made up of
1 mM Ru(NH$_3$)$_6$Cl$_3$ and 0.1 M KNO$_3$, with Ag/AgCl reference electrode in the organic phase (DCE solution containing 2 mM TCNQ solution)

**Experiment 3**

**Working Electrode in Aqueous Phase and Reference Electrode in The Organic Phase**

After several scans for experiment two, the Working electrode was now pushed into the organic phase such that the about 1/3 of its length was in the organic phase. With both electrodes in the organic phase, and having trapped enough aqueous solvent in the cavity of the recessed electrode, cyclic voltammograms for the blank solution of 0.1 M KNO$_3$ were obtained. This experiment was repeated for aqueous solutions of 1 mM Ru(NH$_3$)$_6$Cl$_3$ containing 0.1 M KNO$_3$ as the supporting electrolyte. The schematic diagram showing the magnification of the interface across a small aqueous volume and a bulk organic phase is shown in Figure 12.

![Figure 12: Schematic diagram of a recessed electrode with aqueous solution trapped between the electrode surface and the organic phase.](image-url)

Figure 12: Schematic diagram of a recessed electrode with aqueous solution trapped between the electrode surface and the organic phase.
The schematic diagram of the set up for experiment 3 is shown in Figure 13 below.

Figure 13: Schematic diagram of the experimental setup for ET reaction at the aqueous /organic interface with both W.E electrodes and reference electrode in the organic phase (1, 2-dicloroethane containing 2 mM TCNQ; (E) Aqueous solution of 0.1 M KNO₃ trapped in the cavity (F) aqueous solution of 1 mM Ru(NH₃)₆Cl₃ containing 0.1 M KNO₃ as the supporting electrolyte trapped in recessed cavity.

**Inlaid Platinum Electrode In 1,2-Dichloroethane**

To verify the electron transfer reaction occurring across the interface of the aqueous solution trapped in the recessed cavity and the bulk organic phase, an experiment was carried out on an inlaid platinum electrode using a simple electrochemical cell. This electrode was placed in a bulk solution of DCE containing 2 mM TCNQ, and the corresponding cyclic voltammograms for this experiment was obtained for various scan rates.
The schematic representation for the inlaid platinum electrode experiment in bulk 1, 2-dichloroethane is shown in Figure 14.

Figure 14: A schematic diagram for an inlaid platinum electrode in a bulk solution of DCE containing 2 mM TCNQ, with Ag/AgCl reference electrode at scan rate 50 mV/s.
CHAPTER 5

RESULTS, DISCUSSION, AND CONCLUSION

The results for various electrochemical reactions in bulk aqueous phase experiments and electron transfer reactions across the interface of an aqueous phase whose volume is less than 1 femto liters and bulk organic phase is presented in this chapter. The results obtained were verified by carrying out control experiments with a blank solution of 0.1 M KNO$_3$. Also, this chapter discusses the shift in the $E_{1/2}$ as illustrated in Table 1.

Table 1: List of $E_{1/2}$ obtained for various electrochemical experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Exp. 1</th>
<th>Exp.2</th>
<th>Exp.3</th>
<th>Inlaid Pt Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{1/2}$ mV</td>
<td>-300</td>
<td>-350</td>
<td>-100</td>
<td>-220</td>
</tr>
</tbody>
</table>

Experiment in Bulk Aqueous Phase

Applying a negative potential to a nanometer sized recessed electrode in an aqueous solution of 1 mM Ru(NH$_3)_6$Cl$_3$, electrons are given to the electrode that facilitates the reduction of Ru(NH$_3)_6^{3+}$ to Ru(NH$_3)_6^{2+}$.

The $E_{1/2}$ obtained with respect to the Ag/AgCl reference electrode for Experiment 1 was
-300 mV. The electrochemical reaction for the reduction of Ru(NH$_3$)$_6^{3+}$ is illustrated by Equation 23.

\[ \text{Ru(NH}_3\text{)}_6^{3+} + e^- \rightleftharpoons \text{Ru(NH}_3\text{)}_6^{2+} \]  
Equation 23

The cyclic voltammogram for this experiment is shown in Figure 15.

Figure 15: Cyclic voltammogram obtained on a nanometer sized recessed electrode in bulk aqueous phase containing 1 mM (Ru(NH$_3$)$_6$Cl$_3$) with 0.1 M KNO$_3$ as the supporting electrolyte, using Ag/AgCl reference electrode at a scan rate of 150 mV/s.

The electrochemical reaction occurring in the second experiment was still the reduction of Ru(NH$_3$)$_6^{3+}$ to Ru(NH$_3$)$_6^{2+}$; however, an increase in $E_{1/2}$ was observed. The increase in the $E_{1/2}$ was as a result of the interfacial barrier created between the organic phase and aqueous phase. The Gibbs free energy required to reduce Ru(NH$_3$)$_6^{3+}$ to Ru(NH$_3$)$_6^{2+}$ at the interface was greater compared to that of experiment 1. Therefore, the $E_{1/2}$ observed for this experiment,
which was -350 mV, indicated more energy was required for the reduction of Ru(NH$_3$)$_6^{3+}$ to Ru(NH$_3$)$_6^{2+}$. The cyclic voltammogram obtained for this experiment is shown in Figure 16.

![Cyclic voltammogram](image)

Figure 16: Cyclic voltammogram obtained on a nanometer sized recessed electrode in bulk aqueous phase containing 1 mM (Ru(NH$_3$)$_6$Cl$_3$) with 0.1 M KNO$_3$ as the supporting electrolyte, using Ag/AgCl reference electrode in the organic phase at a scan rate of 150 mV/s.

After running the reactions in the bulk aqueous phase for several segments and at various scan rates to facilitate the trapping of enough solvent in the cavity, the cyclic voltammogram shown in Figure 17 for the electron transfer reaction across the interface of an aqueous phase whose volume is less 1 femto liters and a bulk organic phase was obtained. This was carried out with both the nanometer sized recessed electrode and Ag/AgCl reference electrode in the organic phase.
Figure 17: Cyclic voltammogram obtained for ET reaction across the interface of aqueous solution containing 1 mM (Ru(NH$_3)_6$Cl$_3$) and 0.1 M KNO$_3$ as supporting electrolyte trapped in the recessed cavity of a nanometer-sized recessed electrode and a bulk organic phase at a scan rate of 150 mV/s.

The mechanism for electron transfer reaction occurring across the interface of the aqueous solution trapped in the recessed cavity and the bulk organic phase is outlined as follows. The negative potential given to the working electrode donates electrons to the electrode surface that facilitates the reduction of Ru(NH$_3)_6^{3+}$ to Ru(NH$_3)_6^{2+}$. The Ru(NH$_3)_6^{2+}$ produced diffuses to the interface where it donates an electron to TCNQ thereby regenerating Ru(NH$_3)_6^{3+}$. The electron gain by TCNQ reduces it to TCNQ$^-$ as shown in Equation 24.

\[
\text{Ru(NH}_3)_6^{2+} + \text{TCNQ} \leftrightarrow \text{Ru(NH}_3)_6^{3+} + \text{TCNQ}^- \quad \text{Equation 24}
\]

\[
\left[ E^{1/2}_{1/2} \text{Ru(NH}_3)_6^{2+/3+} / \text{TCNQ}^-/\text{TCNQ}^- \right]_{\text{Ag}/\text{AgCl}} = -100 \text{ mV} \quad \text{Equation 25}
\]

The regenerated Ru(NH$_3)_6^{3+}$ can be reduced by the electron at the electrode surface hence a loop is formed as shown in Figure 18.
Figure 18: Schematic diagram for the electron transfer mechanism at the interface between the aqueous phase whose volume is less than 1 femto liters and the bulk organic phase.

This experiment was repeated for different electrode sizes and the same E$_{1/2}$ was obtained as shown in Figure 19.

Figure 19: Cyclic voltammogram obtained on nanometer sized recessed electrode for electron transfer reaction at a small aqueous phase and a bulk organic phase for three electrodes of different sizes, at a scan rate of 150 mV/s using Ag/AgCl reference electrode.
Because the product Ru(NH$_3$)$_6^{2+}$ does not diffuse into the bulk organic solution, it is possible to carry out quantitative experiments in the recessed cavity of the nanometer sized electrode.

To further ascertain the ET reaction at the interface of the small aqueous phase and bulk organic phase, the experimental results were compared to the blank that showed no peaks within the range of the applied potential as shown in Figures 20 and 22. However, the blank experiment 2 for the reduction of Ru(NH$_3$)$_6^{3+}$ to Ru(NH$_3$)$_6^{2+}$ shown in Figure 21 produced some peaks. The peaks observed were as a result of redox species trapped from the previous experiment that were difficult to remove because of the very small volume (less than 1 femto liters) they occupied.

Figure 20: Cyclic Voltammogram obtained for nanometer-sized recessed electrode placed in the aqueous phase (0.1 M KNO$_3$), using Ag/AgCl reference electrode at a Scan rate of 150 mV/s.
Figure 21: Cyclic Voltammogram obtained for a nanometer sized recessed electrode in the aqueous phase (0.1 M KNO₃) using Ag/AgCl reference electrode placed in the organic phase (DCE containing 2mM TCNQ). Scan rate is 150mV/s.

Figure 22: Cyclic voltammogram obtained when the cavity of a nanometer-size electrode is filled with 0.1 M KNO₃ solution and placed in the organic phase together with the reference electrode. Scan rate is 150 mV/s.
The final experiment which was undertaken to verify the proposed reaction was carried out by placing an inlaid platinum electrode (working electrode) in DCE solution containing 2 mM TCNQ coupled with a Ag/AgCl reference electrode. The $E_{1/2}$ obtained for the reduction of TCNQ to TCNQ$^-$ was -220 mV.

$$\text{TCNQ} + e^- \rightarrow \text{TCNQ}^- \quad \text{Equation 26}$$

$$[E_{1/2} \text{TCNQ}/\text{TCNQ}^- (w)]_{\text{Ag/AgCl}} = -220 \text{ mV} \quad \text{Equation 27}$$

From the $E_{1/2}$ obtained for the inlaid platinum electrode placed in 1, 2-dichloroethane containing 2 mM TCNQ, we were certain the reaction taking place across the liquid/liquid interface was not the reduction of TCNQ to TCNQ$^-$. The $E_{1/2}$ for both the reduction of TCNQ to TCNQ$^-$ and the electron transfer reaction occurring at the interface were compared using their cyclic voltammograms shown in Figure 23.

Figure 23: Cyclic voltammograms obtained for a nanometer size inlaid platinum electrode in DCE containing 2 mM using Ag/AgCl reference electrode at a scan rate of 50 mV/s and ET reaction across the liquid/liquid interface at scan rate 150 mV/s.
The main challenge encountered during this experiment was ensuring that all the solutions containing redox active specie were removed from the recessed cavity. To solve this problem, several scans are carried out to ensure the diffusion of the redox species into the bulk solution (blank) before carrying out the proceeding experiments.

Conclusion

Electron transfer reactions at the interface between an aqueous phase of less than 1 Femto liters in volume and a bulk organic phase have been reported. This research showed a positive shift in the $E_{1/2}$ value comparing the ET reaction done across the interface of a small aqueous volume / bulk organic phase and the reduction of Ru(NH$_3$)$_6^{3+}$ in the bulk aqueous phase experiments. The $E_{1/2}$ obtained for the electron transfer reaction between the redox couple Ru(NH$_3$)$_6^{2+}$/Ru(NH$_3$)$_6^{3+}$ and TCNQ/TCNQ$^-$ across the aqueous phase whose volume is less than 1 femto liters and the bulk organic phase was -100mV which indicated less energy was required for the transfer of electrons from the redox couple in the aqueous phase to those in the organic phase. Which then implied that ET reaction between Ru(NH$_3$)$_6^{2+}$/Ru(NH$_3$)$_6^{3+}$ and TCNQ/TCNQ$^-$ required less Gibbs free energy compared to the reactions involving the reduction of Ru(NH$_3$)$_3^{3+}$ in the bulk aqueous phase experiments whose $E_{1/2}$ where -350 and 300 mV.

Because there was the possibility of trapping TCNQ in the recessed cavity that may have led to its reduction to TCNQ$^-$, the $E_{1/2}$ of -200 mV obtained for the reduction of TCNQ indicated the solution trapped in the cavity was actually aqueous solution of Ru(NH$_3$)$_6$Cl$_3$. 
The loop formed as a result of the electron transfer reactions involving the redox couple Ru(NH$_3$)$_6^{2+}$/Ru(NH$_3$)$_6^{3+}$ and TCNQ/TCNQ in both phases further goes to enhance the applicability of this study for quantitative experiments because Ru(NH$_3$)$_2^{2+}$ does not diffuse away into the bulk solution.

Having achieved our goal of studying electron transfer reactions across the interface of an aqueous phase whose volume is less than 1 femto liter and a bulk organic phase, our future studies will focus on characterizing these electrodes to carry out quantitative experiments.
REFERENCES


34. Banks, C.E.; Davies, T.J.; Evans, R.G.; Hignett, G.; Wain, A.J.; Lawrence, N.S.;


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