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Electrochemical Evaluation of Ionic Liquids for Biphasic Extraction of Metal Ions Common to Spent Nuclear Fuel

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Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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Electrochemical Evaluation of Ionic Liquids for Biphasic Extraction of Metal Ions Common to Spent Nuclear Fuel

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by

Thomas J. Stockmann

Graduate Program in Chemistry

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Abstract

Over the past 30 years electrochemistry at a liquid|liquid interface has been used to observe and quantify simple ion transfer (IT) as well as ligand assisted, or facilitated ion transfer (FIT) reactions. Liquid|liquid electrochemistry has developed to where valuable thermodynamic constants – for example, the metal ion to ligand stoichiometry and overall complexation constant, $\beta$, in FIT - can be evaluated using cyclic voltammetry (CV). Recently, ionic liquids (ILs) have shown greater metal ion extraction efficiencies in water-IL biphasic separations relative to conventional molecular organic solvents. In this way, they are of interest to the nuclear industry for applications in spent nuclear fuel (sometimes called nuclear waste) recycling. Herein, liquid|liquid electrochemistry has been used to investigate FIT of metal ions typically found in SNF at traditional water|organic solvent (w|o) and novel water|ionic liquid (w|IL) interfaces.

Initially, the hydrophobicity of 8 commercially available ILs were evaluated and the data obtained, combined with valuable insight from the literature, was used to select the cation and anion components of an IL that was prepared in-house; trihexyltetradecylyphosphonium tetrakis(pentafluorophenyl)borate ($P_{66614}$TB). $P_{66614}$TB possessed a suitable w|IL polarizable potential window of ~0.9 V – comparable to other ILs found in the literature, but at a cost $10\times$ cheaper than that found commercially.

The formal ion transfer potential, $\Delta^{\omega}_{w|IL} \phi^{o}_{i}$, of metal ions is a point of reference for electrochemically induced FIT and was evaluated for the first time at a w|IL interface. The alkali metals Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ where found to have $\Delta^{\omega}_{w|IL} \phi^{o}_{i}$ equal to 0.565, 0.548, 0.521, 0.531, and 0.518 V, respectively, which agrees well with the trend of increasing atomic radius and thus increasing hydrophobicity.

With a suitable IL in hand, FIT of UO$_2$$^{2+}$, Sr$^{2+}$, Rb$^+$, and Cs$^+$ were examined at w/o and w|IL micro-interfaces. Ligands for contemporary SNF recycling, such as octyl(phenyl)-N,N-diisobutylecarbamoyl-methylphosphine oxide (CMPO) were employed. The w|IL interface demonstrated overall complexation constants, $\beta$, several orders of magnitude higher than that observed at w/o interface. For example, [SrCMPO$_3$]$^+$ had $\beta$ equal to $5.5 \times 10^{25}$ and $1.3 \times 10^{34}$ for the w/o and w|IL interfaces, respectively. Indicating a higher extraction efficiency using ILs versus traditional organic solvents.
Keywords
liquid|liquid electrochemistry ● biphasic mass spectrometry ● ion transfer ● facilitated ion transfer ● equilibrium complexation stoichiometry and constants ● interface between two immiscible electrolytic solutions (ITIES) ● hydrophobicity and hydrophilicity ● ionic liquids (ILs) ● spent nuclear fuel (SNF) ● biphasic extraction of dioxouranium and strontium
Co-authorship Statement

The thesis contains the work of ten published manuscripts, found in Chapters 3, 4.1, 4.2, 6.1, 6.2, 6.3, 6.5, 7.1, 7.2, and 7.3, while Chapters 2, 6.4, and 6.5 represent manuscripts submitted and in preparation. Below is a list, by chapter, of the co-authors and their contributions.

Chapter 2: T.J. Stockmann and Z. Ding, *In-preparation* (2013). Experimental approach and design were proposed by ZD. TJS performed experiments, analyzed data, and wrote the manuscript. The manuscript was edited and finalized by ZD.

Chapter 3 appears in T.J. Stockmann, Z. Ding, *J. Electroanal. Chem.* 649 (2010) 23-31. ZD proposed experimental design and developed the computational code. TJS performed electrochemical experiments, performed computational analysis, analyzed data, and wrote the manuscript. The manuscript was edited and finalized by ZD. Reprinted with permission, copyright 2013 Elsevier.

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Chapter 6.3 appears in T.J. Stockmann, A.J. Olaya, M.A. Méndez, H.H. Girault, Z. Ding, *Electroanalysis* 23 (2011) 2677-86. Experimental design and approach developed by HHG and ZD. Electrochemical experiments performed by TJS and AJO. Data analysis was performed by TJS, AJO, and MAM. TJS and AJO wrote the manuscript, which was edited by HHG and ZD. ZD finalized the manuscript. Reprinted with permission, copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. http://dx.doi.org/10.1002/elan.201100401.

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Quotes

"I am become death, destroyer of worlds."

− Dr. Robert J. Oppenheimer, from the Bhagavad Gita,
  after the first successful Trinity Nuclear Test

"For those that fight for it, life has a flavour the sheltered will never know."

− Anonymous

"I do not fight my enemies with salt."

− Inazo Nitobe, Samurai Ethics and the Soul of Japan, 1906
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<tr>
<td>a</td>
<td>activity</td>
</tr>
<tr>
<td>A</td>
<td>ampere (unit)</td>
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<tr>
<td>ACT</td>
<td>aqueous complexation and transfer</td>
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<td>$A_e$</td>
<td>electrode area</td>
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<td>AECL</td>
<td>Atomic Energy Commission Ltd.</td>
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<td>amu</td>
<td>atomic mass units</td>
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<td>aq</td>
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<tr>
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<td>Biphasic Electrospray Ionization Mass Spectroscopy</td>
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<td>BV</td>
<td>Butler-Volmer</td>
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<tr>
<td>CANDU</td>
<td>Canadian Deutrium Uranium [Nuclear Reactor]</td>
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<td>National Ignition Facility</td>
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<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
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<td>Plutonium URanium Extraction</td>
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<td>room temperature ionic liquid</td>
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<td>solution</td>
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<td>time</td>
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<tr>
<td>x</td>
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<tr>
<td>zₑᶠ</td>
<td>effective charge of a metal ion-ligand complex</td>
</tr>
<tr>
<td>α</td>
<td>transfer coefficient</td>
</tr>
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<td>α</td>
<td>phase (subscript)</td>
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</table>
\( \beta \) overall complexation constant
\( \beta \) phase (subscript)
\( \eta \) viscosity
\( \mu \) chemical potential
\( \mu m \) micrometer
Terms

\( \phi_\alpha \) potential in phase \( \alpha \)

\( \Delta^{o}_\alpha \phi \) Galvani potential difference between phase \( w \) and \( o \)

\( \Delta^{w}_\alpha \phi^{o} \) standard ion transfer potential

\( \Delta^{w}_\alpha \phi^{o} \) formal ion transfer potential

\( \Delta^{w}_\alpha \phi_{1/2} \) half-wave potential

\( \Delta^{w}_\alpha \phi_{p} \) peak potential (cyclic voltammetry)

\( \Delta^{w}_\alpha \phi_{\text{max}} \) potential at maximum current response (differential pulse voltammetry)

\( \Delta E \) pulse amplitude

\( \Delta G \) Gibbs free energy

\( \Delta G_{w \rightarrow o}^{\alpha} \) Gibbs free energy from phase \( w \) to \( o \)

\( E_{1/2} \) half-wave potential at a metal-solution interface

\( \phi \) formal redox potential

\( c_{i,\alpha} \) concentration of species \( i \) in phase \( \alpha \)

\( c_{i,\alpha}^{*} \) initial ligand concentration in phase \( \alpha \)

\( D_{i,\alpha} \) diffusion coefficient of species \( i \) in phase \( \alpha \)

\( \xi \) \( \sqrt{D_{i,\alpha}/D_{i,\beta}} \)

\( \mu_{i,\alpha}^{o} \) formal chemical potential of species \( i \) in phase \( \alpha \)

\( r_{d} \) electrode radius

\( r_{a} \) hydrodynamic radius

\( a_{g} \) external glass radius

\( R_{g} \) ratio of \( r_{d} \) to \( a_{g} \); \( r_{d} / a_{g} \)

\( i_{p,c} \) cathodic peak current

\( i_{p,a} \) anodic peak current

\( i_{ss} \) steady state current

\( k \) Boltzmann’s constant

\( k_{f} \) rate of the forward reaction

\( k_{b} \) rate of the reverse reaction

\( k^{o} \) standard rate constant

\( z_{i} \) charge of species \( i \)
Chapter 1 – Introduction

1.0 – Energy Production for the Future

As developing nations move quickly towards industrialization and modernization, powering these emerging economies, while maintaining or improving energy production in the developed world, will be a major undertaking. Indeed, energy production will be one of the dominant global concerns facing the contemporary socio-political landscape – and scientists – moving forward into the 21st century. All of these issues need to be addressed through the lens of environmental sustainability and stewardship. The main challenge will be to remove the current dependence on fossil fuels. Fossil fuels are a finite resource that is quickly being depleted and they have also played a significant role in anthropogenic climate change. Presently, several energy harvesting technologies have emerged which meet these criteria including solar, wind, hydroelectric, and geothermal power, along with nuclear fusion and fission power [1].

Solar power is quite promising; however, it suffers from several critical drawbacks. While a great deal of progress has been made with multi-junction solar cells [2], demonstrating energy conversion efficiencies of ~40-50%, most laboratory devices elicit 10 to 20% efficiency [3-6], with commercial products falling even shorter [1]. Great strides need to be made if solar power is to become the dominant energy producer. The major hindrance to solar, wind, and hydroelectric power is intermittency; power generation is currently ‘on-demand’, that is electricity is generated as it is needed. If these energy generation technologies are to become viable options, then progress needs to be made in energy storage devices [1]. Admittedly, hydroelectric power can overcome this through the incorporation of generators into dams; however, this introduces a host of other environmental concerns like flooding of areas behind the dam.

Recently, the largest and possibly most ambitious project to date to be undertaken by the Department of Energy in the United States has just come online at Lawrence Livermore National Laboratory. Dubbed the National Ignition Facility (NIF) it is the latest attempt at Inertial Confinement Fusion [7, 8] – nuclear fusion. A massive 1.1 MJ is required in order to operate the NIF ultraviolet laser, while conditions within the reactor chamber approach or exceed 100 million Kelvin with pressures greater than 10 trillion kPa [8], essentially replicating the conditions within the interior of stars. It
should be noted that even nuclear fusion isn’t entirely sustainable [9]; it requires materials like lithium and deuterium – the former having uses as an energy storage material that will be integral to the electronics and automotive industries over the next few decades. So, while the amount of energy gained from nuclear fusion is theoretically impressive, it is still based on a finite resource. Nevertheless, despite the massive funding and tremendous amount of work already accomplished, nuclear fusion as a viable power source is still considered far off [1].

This means that the most successful approach to energy production, if nations are to abandon power created using fossil fuels, is nuclear fission. While providing only ~5% of the world’s energy [1, 9], fission is a proven technology that could supplement global power. It is based on a finite resource and best estimates – considering a once through system and known uranium reserves – place a life time of 60 years for the industry [1]. The fission process, simply put, involves the $^{235}$U isotope – the highly radioactive isotope of uranium that comprises about 0.7% of natural uranium [10]. $^{235}$U, when bombarded with neutrons, breaks down into two medium sized atoms with an average mass of 118 amu [11], while releasing energy and more neutrons.

The two atoms produced, sometimes called fission fragments, have atomic masses ranging from between zinc and erbium on the periodic table (totalling more than 40 possible elements); the distribution of atomic masses of the two atoms is actually bimodal and centered around $^{94}$Sr and $^{137}$Cs [11]. The energy released is in the form of heat and used for boiling water, which in turn spins turbines, converting the energy to electricity. The neutrons emitted sustain the fission reaction; however, the fission fragments produced often have large neutron cross-sections; that is, they absorb neutrons effectively poisoning the reaction so that fission is no longer sustainable. At this point, the fuel is removed from the reactor despite the fact it contains ~95% useable uranium [10, 12] and referred to as SNF or nuclear waste.

In the early 1900’s radioactive isotopes were first being discovered by those like Rutherford [13] in his lab at McGill, or the Curies [14] in France and this eventually lead to the discovery of fission using uranium [15-17]. Up until that point, the only radioactive isotopes on the Earth were the small amount naturally occurring (with long enough half-lives), the small number present in the upper atmosphere, and the tiny
fraction prepared in those early bench-top experiments. Presently, the mass of radioactive material produced through both military and commercial applications is significant [10, 18]. It is critical, however, to view SNF not as nuclear waste, but as a potential source.

The contemporary attitude of most governments toward SNF can be characterized in three ways [10, 12]:

1. Long term deep geological disposal
2. Surface disposal or containment with continuous monitoring
3. Recycling to isolate valuable isotopes and uranium fuel – a closed loop fuel cycle

Currently, no agency has been successful in fully developing and utilizing a deep geological repository [12], which means most SNF is kept in surface facilities. However, if the industry is to become sustainable, then the fuel needs to be recycled. Indeed, it has been proposed that if a so-called closed loop cycle was imposed, and combined with breeder reactors, then this could potentially increase the life span of the industry by hundreds of years [12]. The question then becomes: how can these fission fragments be removed and the greater than 95 % useable fuel be put back into the reactor?

This question was addressed early on and several processes – predominately solvent extraction techniques [12, 18] using various ligands, dissolved in a paraffinic organic solvent, to coordinate selectively to the uranium dissolved in an acidic aqueous phase – were developed. This process is shown, for example, using dioxouranium, \( \text{UO}_2^{2+} \), the common form of uranium in SNF [10], and a typical ligand tributylphosphate [12, 18], TBP, in equation 1.1:

\[
\text{UO}_2^{2+} + n\text{TBP}_{(\text{org})} + 2\text{NO}_3^-_{(aq)} \rightarrow \text{UO}_2(\text{NO}_3)_2\text{TBP}_{n(\text{org})}
\]  

(1.1)

During the extraction, dioxouranium coordinates to two nitrate molecules (in order to maintain electroneutrality) and complexes with \( n \) TBP compounds; with \( n \) equal to 2 [19]. Two major concerns deter most programs from the reclamation of SNF: its radiotoxicity and the threat of nuclear proliferation (the production of nuclear weapons) [10, 12, 18].

Nuclear proliferation can be mitigated through stringent security measures or through careful design of separation techniques. At present, roughly 50 % of SNF is reclaimed, mostly in France and Japan [12, 18], and if power production through nuclear
fission is to become sustainable, then recycling of SNF must become more attractive. Because of the high radiotoxicity after it leaves the reactor, SNF must be handled remotely [10] so a simplified mechanical approach with minimal maintenance required is best.

1.1 – Ionic Liquids

Over the past 30 years, air and water stable ionic liquids (ILs) [20-22] have been developed and offer possible avenues for SNF recycling. ILs are defined as salts with melting points below 100ºC where the cation is typically large and organic [22-24]. These salts present a promising way of electrochemically separating SNF while simplifying the process and thus making it more cost effective and attractive [23].

Figure 1.1 illustrates typical cation and anions that comprise ILs. Cations include quaternized ammoniums/phosphoniums to imidazoliums, etc., while anions can be inorganic, Cl\(^-\), Br\(^-\), and PF\(_6\)^- or more sophisticated such as bis(trifluoromethylsulfonyl)imide (NTf\(_2\)) or tetrakis(pentafluorophenyl)borate (TB).

![Cations](image)

![Anions](image)

**Figure 1.1:** Examples of some cation and anion components of ILs.

ILs are desirable solvents owing to their wide liquid temperature range, high thermal stability, good electrochemical stability, and negligible vapor pressure [22, 24].
ILs have been used as solution phases for organic synthesis [24], while, because of their good conductivity and stability, they have also found use in a broad range of electrochemical applications [25-38]. Critically, in 1999 Dai et al. [39] demonstrated that water-IL biphasic separations had improved extraction efficiencies versus conventional water-organic solvent systems. Since that initial discovery, there has been great interest in using ILs in biphasic, water-IL, metal extractions [23, 40-48].

1.2 – Liquid|Liquid Electrochemistry

Metal ion extraction, as exemplified in equation 1.1, is accomplished through mechanical separation [12, 18]; that is, the phases containing the metal ions and ligands are physically mixed using centrifugation, or by simple shaking, such that the neutral metal-nitroto-complex partitions. Because they are ions, instead of using physical means an external potential may be applied across the boundary between the two phases, water and oil (or IL), as they do not mix. This potential is referred to as the Galvani potential difference and this type of electrochemistry is often call liquid|liquid electrochemistry.

Most analytical electrochemical investigations, indeed electrochemical processes, are the result of a potential difference between two phases or regions, \( \Delta \phi = \phi_\beta - \phi_\alpha \); where \( \phi_\alpha \) and \( \phi_\beta \) are the inner potentials within generic phases \( \alpha \) and \( \beta \). Whether this is across a metal-solution interface, \( \phi_M - \phi_S \), or across the water-organic solvent interface, \( \phi_w - \phi_o \); conceptually these are equivalent to the point where most mathematical or theoretical treatments – with regards to current responses of cyclic voltammetry (CV) or chronoamperometry (CA) – are transferable [33, 49-51].

It is commonly understood that current \( (I) \) is related to charge \( (Q) \) through the following integral [52]:

\[
dQ = \int I dt
\]  

(1.2)

In conventional electrochemistry the electron is, in almost all cases, the charge carrier, with chemical species being oxidized or reduced as shown below using the simplest reaction for a one-electron transfer:

\[
\text{Ox} + e^- \rightleftharpoons \text{Red}
\]  

(1.3)
At liquid|liquid interfaces, the ions themselves are charge carriers and simple ion transfer (IT), for example, of species $i$ with a charge $z$ moving from water, w, to an organic solvent, o:

$$i_w^z \rightleftharpoons i_o^z \quad (1.4)$$

where species $i$ is not oxidized or reduced, but simply transfers from one phase to another through a push/pull mechanism. Figure 1.2 illustrates an energy diagram taken from the perspective of a hydrophilic cation dissolved in the aqueous phase transferring from w to o; in this case, as the Galvani potential difference becomes more positive, the cation is ‘pushed’ across the interface. If the potential was then reversed, the cation would be ‘pulled’ back across the interface. Just as for the metal-solution interface where the Gibbs free energy, $\Delta G$, can be related to the formal reduction/oxidation potential, $E^\circ$, via $\Delta G^\circ = -zFE^\circ$, the same is true at the liquid|liquid interface for the formal ion transfer potential; $\Delta G_{w}^{\circ} = zF\Delta_{o}^{\circ}E^\circ$ [33, 49].

The standard IT potential along with the Nernst equation describes the partition of ions between phases as a function of the Galvani potential difference, $\Delta_{\text{G}}$, where the activities of the ion in either phase, $a_{i,\alpha}$ or $a_{i,\beta}$, are known [33, 49]. However, the formal ion transfer potential describes the system when concentrations are used as an approximation of the activities; this is detailed in equation 1.5:

$$\Delta_{\text{G}} = \Delta_{\text{G}}^{\circ} + \frac{RT}{zF} \ln \frac{a_{i,\alpha}}{a_{i,\beta}} = \Delta_{\text{G}}^{\circ} + \frac{RT}{zF} \ln \frac{\gamma_{i,\alpha}c_{i,\alpha}}{\gamma_{i,\beta}c_{i,\beta}} \approx \Delta_{\text{G}}^{\circ} + \frac{RT}{zF} \ln \frac{c_{i,\alpha}}{c_{i,\beta}} \quad (1.5)$$

Figure 1.2 also introduces another possible reaction: if a ligand, $L$, is dissolved in the organic, or IL, phase then partitioning of the ion becomes easier and less applied potential is required. This is referred to as ligand-assisted or facilitated ion transfer (FIT):

$$i_w^z + nL_o \rightleftharpoons iL_{n,\text{p}}^z \quad (1.6)$$

Equation 1.6 is equivalent to equation 1.1 and forms the bases of electrochemical evaluations of metal ion-ligand complexation reactions in biphasic systems. Equation 1.6 shows one possible mechanism whereby the ligand is hydrophobic enough that it does not transfer to the aqueous phase; in this instance it is referred to as transfer through
interfacial complexation (TIC) and transfer through interfacial decomplexation (TID) when reversed [53-55]. The TIC/TID mechanisms are illustrated in Figure 1.3A along with two others: aqueous complexation followed by transfer (ACT, Figure 1.3B) and transfer then organic phase complexation (TOC, Figure 1.3C).

**Figure 1.2:** Thermodynamic diagram of simple and facilitated ion transfer. Here the Gibbs free energy of hydration ($\Delta G_{\text{Hydration}}$) and solvation ($\Delta G_{\text{Solvation}}$) are shown in graphical relation. Additionally, the formal Gibbs free energy of transfer ($\Delta G' \text{_{i, w to o}}$) for an ion, $i$, from aqueous to organic phases (w to o) is compared to the facilitated ion transfer (FIT) through complexation and the use of a ligand, $L$, dissolved in the organic phase; please note that $\Delta_e \phi'$ is the formal potential difference between the two phases, $z$ is the charge, $R$ is the gas constant, $T$ is temperature in Kelvin, $\beta$ is the overall complexation constant, and $\mu_{i,\alpha}'$ is the formal chemical potential of species $i$ in phase $\alpha$. Note that the Gibbs free energy diagram assumes an ion with a favourable hydration versus solvation energy; *i.e.* a hydrophilic ion.
Figure 1.3: Illustrations of three possible metal ion-ligand biphasic coordination mechanisms: A, transfer through interfacial complexation/decomplexation (TIC/TID); B, aqueous phase complexation and transfer (ACT); and C, transfer followed by organic phase complexation.

The investigation of liquid|liquid, or so-called soft interfaces between two immiscible electrolytic solutions (ITIES) has a rich history that began at the turn of the 20th century with early works by Nernst and Riesenfeld [50, 56]. These initial experiments were focused on measuring ion transport numbers in organic solvents and utilized a water|phenol|water system [50, 56] along with coloured electrolytes such as KI$_3$. By 1939 Verwey and Niessen [57] described the interface as two back-to-back double layers in analogy to the working description of the metal-solution interface with its inner and outer Helmholtz planes (IHP and OHP), or space charge regions, but with an inner, overlapping diffuse layer. Continuation in this exotic field of electrochemistry would progress through the interest of early physiologists [58, 59] who were keen to elucidate the physical and chemical nature of these interfaces as they represented simplified biomimetics for cellular membranes.

With Gavach et al.’s [60, 61] discovery that the liquid|liquid interface could be polarized and that charge transfer could be produced by externally altering the Galvani
potential difference across the ITIES, the field underwent a renaissance. During the 1970’s and 80’s, aided by modern electrochemical instrumentation and techniques [50, 62-81] the four faradaic processes at liquid|liquid interfaces began to be rigorously quantified – including electron transfer (ET) [64, 66-69], simple IT [62, 64, 65, 68, 69], FIT [70, 74, 81], as well as photoinduced electrochemical reactions. With a greater understanding a more vivid thermodynamic picture was forming. Non-faradaic processes were not ignored and studies of the adsorption of material at the interface also appeared [63, 77]. The liquid|liquid double layer structure was re-examined [63, 71, 72] often using a Gouy-Chapman approach to evaluate the potential profile. As this science developed into the 90’s and 2000’s, attention switched from conventional biphasic systems like water|1,2-dichloroethane (w|DCE) [25, 54, 82-90], w|nitrobenzene (w|NB) [62, 63, 65, 67, 71, 73, 91], and w|trifluorotoluene (w|TFT) [92] to w|IL through the work of Kakiuchi et al. [93-98], Samec et al. [31, 99, 100], and Ding et al. [25, 101-103].

With this deep history and theoretical background it is possible to evaluate different ligands and biphasic w|IL systems for their possible application in the reclamation of SNF.

The study of SNF recycling is a multidisciplinary approach involving many aspects of chemistry; however, liquid|liquid electrochemistry has a great deal to offer over other analytical techniques. Electrochemistry can provide sensitive kinetic and thermodynamic information about biphasic separations that other analytical techniques, such as Inductively Coupled Plasma Atomic Emission Spectroscopy [23], have to measure indirectly. Electrochemistry can also be reduced in scale through the use of micro-ITIES such that the total size, or volume of the experiment can be reduced. This is advantageous since ILs can be expensive; therefore, reducing the volume of material needed to perform experiments is advantageous. Additionally, electrochemical experiments at liquid|liquid interfaces are easy to perform since no electrode polishing is required, as is the case for metal-solution interfaces.

1.3 – Scope of the Thesis

A great deal of research is currently underway characterizing the reclamation of SNF using various biphasic systems incorporating ILs. This thesis begins with the characterization of several ILs both with conventional electrochemistry, using
ultramicroelectrodes (UMEs), and the search for a suitably hydrophobic, commercially available IL for liquid|liquid investigations in Chapters 2 and 3. Theses Chapters include a rigorous analysis of water and organic solvent effects on the electrochemical response of electroactive species dissolved in the IL phase. Insight is provided as to the IL molecular organization within the vicinity of the electrode through changes in the diffusion coefficient of the electroactive species, determined through CV. Water and organic solvents are often contaminants in ILs; these are present through atmospheric transfer or are remaining after IL synthesis/preparation. It is important to know to what extent water and organic solvents can influence the kinetics and thermodynamics of electrochemical processes, and the results described in Chapter 2 indicate that the hydrophobicity of the IL plays a major role. Within Chapter 2 and 3, liquid|liquid electrochemistry was used to determine the hydrophobicity of the IL cation and anion components, quantitatively and separately. Because the individual IL components hydrophobicity could be discriminated, choices could then be made as to which cations and anions would make good, hydrophobic combinations.

Additionally, in Chapter 3 the micropipette geometry is explored using finite element analysis; these data provide invaluable insight into what micropipette dimensions or geometry provide the most predictable CV responses. That is, which geometries adhere best to conventional large (cm scale) electrochemical responses and, therefore, offer the most facile data treatment options.

The purchased compounds results indicated poor to satisfactory hydrophobicity; however, particular cations were identified as possible components for future ILs. Therefore, Chapter 4 details the preparation of two ILs in-house, chosen through the data acquired in Chapter 3 and using a facile metathesis reaction; the physicochemical properties, such as viscosity and conductivity, were characterized as well as the ILs performance with both conventional metal-solution electrochemistry and w|IL micro-interfaces. The micro-ITIES utilized in these studies was a 25 μm diameter interface maintained at the tip of a pulled borosilicate glass capillary; this was made possible by a novel pipette holder designed in-house. Additionally, simple IT of several ions of intermediate hydrophobicity were evaluated, while finite element simulations were used to describe the kinetics of IT and homogeneous redox reactions. This data would then be
used to approximate certain kinetic/thermodynamic constants for the investigation of FIT at w|IL interfaces. A major contribution of this work, however, was the preparation of two inexpensive, but effective, ILs; if w|IL biphasic separation is to become useful, then the cost of these materials must be reduced.

In Chapter 5 the liquid|liquid interface was used to investigate the hydrophobicity of the cationic component of ILs used as polymer additives; several of these cations were too hydrophobic to appear within the polarizable potential window (PPW) and this chapter examines how I probed beyond it to garner an approximation of their formal IT potentials. Probing beyond the PPW represents a novel innovation that can be used to estimate a wide variety of hydrophilic and hydrophobic formal IT potentials that were once thought inaccessible.

The formal IT potentials of metals of interest, like dioxouranium and strontium, serve as a point of reference when investigating FIT. Chapter 6 concerns the evaluation of these valuable constants using micro-ITIES at both the w|DCE and w|IL interfaces. A working curve method was used to evaluate the latter through the current-potential profile at the edge of the PPW. This method can be applied to any w|IL interface and is valuable since the formal IT potential is a constant not only unique to each ion species, but also to each biphasic solvent system; therefore, a universal method, such as that described in Chapter 6.5, is invaluable. Using these constants, FIT at w|IL interfaces could then be investigated.

Chapter 7 represents the culmination of all the previous work and it is here the investigations of FIT at first w|DCE and later w|IL interfaces are detailed; using ligands widely employed in industrial SNF recycling programs at both interfaces. The data obtained in this chapter describes the w|IL system as far superior to that of conventional w|o interfaces. Herein, non-radioactive isotopes of SNF elements, such as $^{87}$Sr, were used as analogs for radioactive isotopes so that simplified, but safe laboratory procedures could be implemented. The electrochemical interfacial complexation results indicate that the w|IL interface had greater efficiency of metal ion extraction then the conventional w|o interface, and agree with published reports found in the literature [39, 41]. In this way, the metal ion extraction for Sr$^{2+}$, Rb$^+$, and Cs$^+$, using octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide (CMPO), possessed decreasing $\beta$ values
according to the trend: $\text{Sr}^{2+} > \text{Rb}^+ > \text{Cs}^+$. Therefore, CMPO was concluded to be selective for $\text{Sr}^{2+}$, at the w/IL interface employed. This comparison demonstrates the value of this facile technique for investigating the separation of the more than 40 elements found in SNF, but also shows that only a small number of ions, ILs, and ligands were analyzed – more work is needed.

1.5 – References

Chapter 2 - Electrochemical behavior of tributylmethylphosphonium methyl sulfate mixtures with water and 1,2-dichloroethane

2.1 – Introduction

Ionic liquids (ILs) have undergone extensive research over the past 20 to 30 years since Wilkes et al. [1] and Knifton [2] prepared some of the first, modern air- and water-stable versions. ILs are described as large organic salts with melting points typically below 100ºC. These unique solvents have been utilized successfully in inorganic [3] and organic [4, 5] synthesis, in solar cell applications [6], in polymer films [7], and in biphasic metal ion extraction [8, 9]. With trillions of ILs speculated to be possible [5, 10] – through variation of cation and anion structure or pairing different ion combinations together – it is not surprising ILs have permeated so many materials and chemical applications since their physicochemical properties are just as varied. One needs to simply select the IL with the desired properties; the only limitation being the amount of comprehensive, physicochemical IL data available in the literature [5, 10-12].

Several common features are pervasive in ILs, including a high thermal stability, low vapour pressure, and good electrochemical stability [3, 5, 13]. This last property translates to wide electrochemical potential windows [13], that is the potential at a working electrode can be swept in electrochemistry from ±2 V to even ±3 V; the IL must be de-aerated, or the experiment run under an inert atmosphere, as both water and oxygen typically limit the potential window [14, 15]. ILs have been shown to influence the voltammetric response of electroactive species dissolved in them [13, 16, 17] and that the diffusion coefficients of the reduced and oxidized form of a particular redox species may vary dramatically.

Schröder et al. [14] carried out a rigorous electrochemical analysis of three imidazolium ILs exposed to dry and humid atmospheres and discovered a large signal enhancement, or current response increase, between dry and water saturated samples. In their work [14], they describe the mixture as non-homogeneous and the IL as possessing a "nano-structure". Several surface studies have discussed the possibility that ILs are organized at the nano-level [18, 19]. Kakiuchi et al. [18] in their studies of the ultra-slow relaxation times with applied potential across a water-IL interface analyzed through surface tension measurements as well as via x-ray reflectivity studies at an air-IL
interface [19], suggest the IL has multilayer organization/order associated with the boundary [18, 19]. This is supported by molecular dynamic simulations, performed by other groups [20-22], whose reports predict a nano-structure at interfaces but also present evidence of organization even within the bulk phase [22].

Herein, the physicochemical properties of a phosphonium IL, tetrabutylmethylphosphonium methyl sulfate (P_{4441}CH_3SO_4), while increasing organic solvent and water content are investigated electrochemically using a chronoamperometric (CA) method developed by Aoki and Osteryoung [23, 24] and two redox probes ferrocene (Fc) and ferrocenemethanol (FcCH_2OH). The measured diffusion coefficients of the redox probes are compared to gain insight into changing IL environment with increasing molecular solvent content; these changes are contrasted against a possible nano-structure present at the w|IL interface. The hydrophobicity of P_{4441}CH_3SO_4 was quantified using liquid|liquid electrochemistry at a micro interface between two immiscible electrolytic solutions (ITIES) housed at the tip of a 25 μm diameter micropipette as was shown recently [25].

2.2 – Simulation

Numerical simulations have been used successfully to describe a myriad of unique environments including electrochemistry within supercritical CO_2 [26], in SECM corrosion modelling studies [27], at liquid|liquid interfaces [28], as well as describing the fundamental responses from microelectrode arrays [29]. Herein, they are used to garner insight into the kinetics of simple one-electron reduction reactions at a ultramicroelectrode (UME).

The UME geometry (Figure 2.1) was composed of 5 boundaries enclosing a domain within which mass transfer was described by Fick’s laws of diffusion through equation 2.1:

\[
\frac{\partial c_{i,\alpha}(r,z,t)}{\partial t} = D_{i,\alpha} \left( \frac{\partial^2 c_{i,\alpha}(r,z,t)}{\partial r^2} + \frac{1}{r} \frac{\partial c_{i,\alpha}(r,z,t)}{\partial r} + \frac{\partial^2 c_{i,\alpha}(r,z,t)}{\partial z^2} \right)
\]

\[= D_{i,\alpha} \nabla c_{i,\alpha}(r,z,t) = 0 \quad (2.1)\]
where \( c_{i,\alpha} \) and \( D_{i,\alpha} \) are the concentration and diffusion coefficient of redox species \( i \) in phase \( \alpha \); \( \nabla \), or del, is the gradient or vector operator – shown here in cylindrical coordinates.

\[ c_{i,\alpha} \text{ and } D_{i,\alpha} \]

**Figure 2.1:** Cross-section of the ultramicroelectrode simulation geometry. The red dashed box describes the simplified simulation domain with boundaries 1, 2, 3, 4, and 5 defined as axial symmetry, the electrode surface, concentration, glass insulator, and concentration respectively.

The simple one electron oxidation/reduction reaction, as defined by equation 2.2, and operated at the UME surface via boundary 2:

\[ \text{Ox} + e^- \rightarrow \text{Red} \] (2.2)

where the oxidized species, Ox, is reduced to Red through addition of one electron, \( e^- \).

The reaction kinetics is assumed to follow Butler-Volmer regime represented by equations 2.3 and 2.4 for the forward \( (k_f) \) and reverse \( (k_b) \) rates:

\[ k_f = k^0 \exp\left(-\alpha f\left(E - E^{\circ}\right)\right) \] (2.3)

\[ k_b = k^0 \exp\left((1-\alpha) f\left(E - E^{\circ}\right)\right) \] (2.4)

Here \( k^0 \) is the standard rate constant, \( \alpha \) is the transfer coefficient (this was assumed to be 0.5 unless otherwise stated), and \( f = F/(RT) \); \( F \) is Faraday’s constant, \( R \) is the universal gas constant, and \( T \) is temperature in Kelvin (assumed to be room temperature, 298.15 or
$25^\circ\text{C}$). $E$ is the applied potential and $E^{\text{red}}$ the formal redox potential. A triangular waveform described the applied potential at the electrode surface such that $E$ in equations 2.3 and 2.4 is as follows:[30]

$$E = E_{\text{initial}} + \frac{2(E_{\text{final}} - E_{\text{initial}})}{\pi} \sin^{-1}\left(\sin\left[\frac{\pi vt}{2(E_{\text{final}} - E_{\text{initial}})}\right]\right)$$

(2.5)

where $E_{\text{initial}}$ and $E_{\text{final}}$ are the initial and final potentials of the CV sweep, $t$ is time, and $v$ is the scan rate.

The other boundary conditions were set as axial symmetry, concentration, insulator, and concentration for 1, 3, 4, and 5, respectively. The initial concentration of the oxidized form, $[\text{Ox}]_{\text{initial}}$, was set to zero unless otherwise stated, while $[\text{Red}]_{\text{initial}}$ varied with changing IL/DCE and IL/water mixtures; this corresponds to the initial experimental conditions where, for example, ferrocene (Fc) is the reduced form and is oxidized to ferrocenium (Fc$^+$). A detailed COMSOL model report is provided in the Appendix B.

2.3 – Experimental

2.3.1 Chemicals

All reagents were used as purchased without additional purification. 1,2-dichloroethane (DCE), ferrocene (Fc), ferrocenemethanol (FcCH$_2$OH), tetradecylammonium tetrakis(parachlorophenyl)borate (TDATPBCl), and tributylmethylphosphonium methyl sulfate ($P_{4441}\text{CH}_3\text{SO}_4$) were ordered from Sigma-Aldrich (Sigma-Aldrich Canada, Mississauga, ON). $P_{4441}\text{CH}_3\text{SO}_4$ was stored in a vacuum oven at 90°C for 24 hours prior to use. All aqueous solutions were prepared using ultrapure water (18.2 M$\Omega$, Barnstead water filtration system).

2.3.1 - Instrumentation.

Electrochemical measurements were performed using a Modulab System (Ametek Advanced Measurement Technology, Farnborough, Hampshire, United Kingdom). The Modulab has an integrated potentiostat and Femto ammeter. All data were collected at room temperature ($\sim23^\circ\text{C}$) using a two-electrode setup: a silver wire operated as both the
counter and quasi-reference electrode whilst an ultramicroelectrode (UME) fabricated in-house as the working electrode.

2.3.2 - UME fabrication.

Platinum disk UMEs were fabricated as has been described in detail in earlier publications by our group [31-33]. Briefly, a Narishige electric puller (Model #PP-83, Japan) was used to pull a glass capillary ((1.0 mm/2.0 mm inner diameter/outer diameter, Sutter Instrument, Novato, CA ) at its center generating two tapered pipettes. The tapered end of one of the above pipettes was then flame-sealed using a Bunsen burner and a 25 μm diameter Pt wire – approximately 1.0 to 1.5 cm in length – was inserted into the open end. The wire was positioned at the tapered end by dropping the pulled capillary, with wire, down through a hollow glass tube. Ensuring that the tapered end had not been damaged, the open end of the capillary was then attached to a vacuum line and the Pt wire was annealed into the glass capillary using the heating coil of the puller. After encasing the Pt wire in roughly 0.5 cm of glass, the tapered end was cut using diamond grinding pads (grits 240 and 600, Buehler, Lake Bluff, Illinois) to expose the Pt wire cross-section and establish a good \( R_g \) or ratio of the Pt disk radius, \( r_d \), to external glass radius, \( a_g \) (\( R_g = r_d / a_g \)). Subsequently, the electrode surface was polished with increasingly fine alumina polishing pads. Then a plug of solder was inserted inside the glass capillary, behind the Pt-wire, followed by a Cu-wire. In order to anneal the solder to the Pt and Cu wires the electric puller was used with reduced heat.

2.3.3 - Micropipette Fabrication.

Micropipette fabrication has been described in detail elsewhere [8, 9, 34-38] and is similar to that of UME, except that no solder or Cu wire is used. Instead, the Pt wire is etched from the capillary using a strong acid solution consisting of 3:1 HCl to HNO\(_3\) (aqua regia) for roughly 72 hours or until the Pt wire is no longer visible under an optical microscope. The micropipette was held in a modified pipette holder (HEKA Electronics Inc., Mahone Bay, NS) and can be described using the following electrolytic cell where two silver electrodes were immersed in either phase:
The aqueous phase Ag-electrode was integrated into the pipette holder that was equipped with a syringe containing the water solution. In this way, the micro-interface was held at the tip of the capillary through the use of the syringe – its position continuously monitored using an optical microscope.

2.4 – Results and Discussion

![Cyclic voltammogram](image)

**Figure 2.2**: Cyclic voltammograms acquired at 0.020 V·s⁻¹ within a potential range from 0.200 and 0.650 V using a 25 μm diameter Pt disk ultramicroelectrode immersed in \( \text{P}_{4441} \text{CH}_3\text{SO}_4 \) with (red, solid curve) and without (black, dashed curve) 8.6 mM ferrocene added.

Water and solvent content in ILs can have substantial effects on their physicochemical properties as well as voltammetric response [13, 14]. In order to investigate these solvent effects, facile electrochemistry was employed utilizing an UME with ferrocene (Fc) or ferrocenemethanol (FcCH₂OH) redox probes dissolved in the IL phase. Two mixtures, IL/organic solvent (in this case 1,2-dichloroethane, DCE) and IL/water, were evaluated by increasing mole fractions of DCE or water were added with periodic electrochemical analysis; mole fractions were denoted relative to the water or organic solvent content such that, with no water or solvent added, the solution was zero water (\( \chi_{\text{H}_2\text{O}} \)) or solvent (\( \chi_{\text{DCE}} \)) mole fraction. \( \text{P}_{4441} \text{CH}_3\text{SO}_4 \) was the IL chosen because of...
its moderate hydrophilicity/lipophilicity [25]. Fc and FeCH₂OH were used in the IL/DCE and IL/water experiments, respectively, owing to their simple one-electron oxidation reaction at an electrode and good solubility in the IL or requisite solvent [35, 36, 39].

Figure 2.2 illustrates the cyclic voltammograms (CVs) a 25 μm diameter Pt disk ultramicroelectrode, acquired without (black, dashed curve) and with (red, solid trace) 8.6 mM of ferrocene (Fc) in the IL. An anodic peak (the oxidation of Fc to Fc⁺) can be observed with a peak potential of 0.441 V during the forward sweep of the applied potential, from 0.200 to 0.600 V. During the reverse sweep, a cathodic peak was identified at a peak potential of 0.358 V and is indicative of the re-reduction of Fc⁺ back to Fc.

The CV illustrates a typical peak-shaped trace at a millimetre size electrode for a redox reaction in a homogeneous solution instead of a steady state one at an ultramicroelectrode owing to the ILs high viscosity [13, 35, 36]. Two fundamental processes took place: consumption of the electroactive species at the electrode surface and mass transport or diffusion from the bulk. The CV response is a result from balancing these two processes. Owning to the IL’s high viscosity, Fc species diffused slowly to the electrode and were rapidly consumed. There was an initial increase in the current response for the forward scan of the CV, which was followed by an period of exponential decay as Fc, in the vicinity of the electrode, is depleted [13, 15, 17, 35, 36, 40-42]. This is sometimes called ‘linear diffusion’, or ‘consumption control’, and occurs in ILs despite the use of UMEs [15, 35, 36, 42]. In conventional molecular solvents the diffusion coefficient is in the range of 10⁻⁵ cm²·s⁻¹, that is 3 to 4 orders of magnitude greater than that found typically in ILs, and this translates to a much larger volume surrounding the UME from which species can undergo mass transport in the molecular solvent case [15, 35, 36]. This is often called ‘hemispherical diffusion’, or ‘diffusion control’, and the current-potential curve is sigmoidal or s-shaped [15, 35, 36, 42], which is the result of species close to the electrode surface being quickly consumed – an exponential increase in current – followed by a plateau, or steady state current, such that Fc continuously diffused to the UME, faster than the consumption [15, 35, 36, 42].

The peak-to-peak separation between the cathodic and anodic waves was determined to be 0.083 V. This is larger than 0.059 V, which is one criterion for an
electrochemically reversible reaction. [17, 35, 36] However, large peak-to-peak separations have been observed in several ionic liquids. [13, 14, 17, 35, 36] The second criterion for an electrochemically reversible reaction is that the ratio of a cathodic peak current \(i_{p,c}\) to anodic peak current \(i_{p,a}\) should be 1; [17, 35, 36] here the ratio was determined to be 0.9 and this is defined as quasi-reversible, indication of Fc diffusion is faster than Fc\(^+\) in the ionic liquid.

The DCE/IL mixture, in various mole fractions of DCE, was evaluated through cyclic voltammetry. Figure 2.3 illustrates the CVs obtained using a 25 μm diameter Pt disk UME immersed in 8.6 mM Fc in P\(_{4441}\)CH\(_3\)SO\(_4\) with \(\chi_{DCE}\) of (A) 0.0, (B) 0.4, and (C) 0.8. The trace in Figure 2.3B closely resembles the CV shown in Figure 2.3A with no DCE added. There is a slight increase in anodic peak current intensity from approximately 0.4 to 1.0 nA and a decrease in the cathodic peak current from roughly 0.5 to 1.4 nA (baseline corrected). This means the peak current ratio has increased to 1.4. In Figure 2.3C the mole fraction of DCE has exceeded that of P\(_{4441}\)CH\(_3\)SO\(_4\) with \(\chi_{DCE}\) of 0.8 and the CV looks very different with essentially a steady state plateau, which is diffusion controlled, as commonly seen with an UME in conventional molecular solvents. The steady-state current values in the forward and backward scans were used to calculate a peak current ratio of approximately 1; indicating good reversible redox chemistry.

The half-wave potential, \(E_{1/2}\), was determined using the peak potential, \(E_p\), and its relation \(E_{1/2} = E_p - (0.028 V)/z\) for the peak shaped waves,[43] while reading the potential at half of the steady state current for the steady state wave at \(\chi_{DCE} = 0.8\). In this way, the approximate redox potentials for the Fc/Fc\(^+\) were determined to be 0.373, 0.422, and 0.424 V at \(\chi_{DCE}\) equal to 0.0, 0.5, and 0.8, respectively. Since a Ag-wire quasi-reference electrode was used, this fluctuation of +/-0.050 V from a mean value is not surprising,[44] but might indicate a lower redox potential for the Fc\(^+\)/Fc couple in P\(_{4441}\)CH\(_3\)SO\(_4\) than in DCE.

Figure 2.3 also illustrates the simulated traces (○) obtained for each mole fraction using COMSOL finite element analysis with the geometry shown in Figure 2.1. In Figure 2.3A the simulation used an initial Fc concentration of 8.6 mmol·L\(^{-1}\), a formal redox potential of 0.340 V, a \(k_0\) of 0.1 cm\(^2\)·s\(^{-1}\), along with diffusion coefficients for the oxidized and reduced forms of 0.25 × 10\(^{-8}\) and 2.25 × 10\(^{-8}\) cm\(^2\)·s\(^{-1}\), respectively.
Figure 2.3: Cyclic voltammograms (—) acquired using a 25 μm diameter Pt disk ultramicroelectrode immersed in a P4441 CH3SO4 phase containing an initial 5 mM of ferrocene with DCE mole fractions (χDCE) of 0.0 (A), 0.4 (B), and 0.8 (C), respectively. The CVs were swept from 0.200 up to 1.800 V at a scan rate of 0.020 V∙s⁻¹. Overlaid onto the experimental curves are simulation ones (○) generated using COMSOL.

The simulated CV in Figure 2.3A overlaps very well with experimental curve. For this initial case the concentration can be calculated with reasonable accuracy and so the diffusion coefficients were the predominant parameters varied in order to achieve a good simulation-experimental overlap. The large difference (a factor of 10) between the diffusion coefficients of the oxidized and reduced forms in a homogeneous IL phase has been demonstrated previously by us [35, 36] and other groups [13, 17, 45]. Compton et al. [17] reported a diffusion coefficient ratio, $D_{Fe}/D_{Fe^+}$ of 7.8 in
trihexyltetradecylphosphonium trifluorotris(pentafluoroethyl)phosphate IL, while that estimated here is 9. It has been shown that molecules with an inaccessible or buried charges demonstrate diffusion coefficient ratios much closer to 1 [13]. Hence, the disparity in the diffusion coefficient ratio found here could be the result of an enhanced interaction between the oxidized form and IL components, especially the methyl sulfate anion whose negative charge is not sterically hindered (i.e. exposed).

The high $k^o$ indicates the excellent reversibility of the system even without organic solvent added. A range of $k^o$ values were examined from $1 \times 10^{-4}$ to 1 and even $10 \text{ cm} \cdot \text{s}^{-1}$; however, any value equal to or greater than $1 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1}$ was considered reversible as no distinguishable difference between simulated CV obtained above this limit was observed as detailed recently [36]. Therefore a $k^o$ of $1 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1}$ is considered the fastest rate constant identifiable by this method.

The simulation curves displayed in Figures 2.3B and 2.3C are highly speculative owing to the inherent difficulty in calculating the concentration of the redox species after addition of DCE. It is unclear whether the IL or DCE is the solvent as the latter increases in either case. The effective total volume was assumed to be the sum of both the IL and DCE and, in this way, an effective concentration of the redox species was estimated; for values of $\chi_{\text{DCE}}$ at 0.4 and 0.8 this was determined to be 7 and 2 mmol$\cdot$L$^{-1}$, respectively. For the $\chi_{\text{DCE}}$ value of 0.4 the diffusion coefficients were optimized to be $0.6 \times 10^{-7}$ and $1.5 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ for $D_{\text{Fc}^+}$ and $D_{\text{Fc}}$, respectively, while for $\chi_{\text{DCE}}$ of 0.8 $D_{\text{Fc}^+} = D_{\text{Fc}} = 0.59 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$. These result in ratios of 2.5 and 1 for $\chi_{\text{DCE}}$ values of 0.4 and 0.8, respectively. It seems that the diffusion coefficient ratio follows the trend of the system taking on more and more molecular solvent characteristics. In both instances the $k^o$ was set equal to $10 \text{ cm} \cdot \text{s}^{-1}$, unchanged from the case without DCE and, again, indicating excellent reversibility of the system.

It should be stressed that, while the concentration and diffusion coefficients utilized to achieve the simulated curves found in Figures 2.3B and 2.3C are serious approximations, the diffusion coefficient ratios may not be as they are effectively normalized. Likewise the standard rate constant should be independent of any volumetric assumptions and indicate the overall reversibility of the system; however, because of the
indirect nature of their determination, they should be treated as effective standard rate constants.

**Figure 2.4:** Cyclic voltammograms measured in P$_{4441}$CH$_3$SO$_4$ – with initially 3.4 mM ferrocenemethanol along with 0.0, 0.4, and 0.8 mole fractions ($\chi$) of water for curves A, B, and C respectively – using a 25 µm Pt disk ultramicroelectrode. Instrument parameters include a potential range from 0.000 to roughly 0.700 V at a scan rate of 0.020 V·s$^{-1}$. Overlaid onto the experimental curves are simulated ones (○) obtained using COMSOL.

Figure 2.4 details the CV results for increasing mole fractions of water in P$_{4441}$CH$_3$SO$_4$ from 0 to 0.4 and 0.8 (curves A, B, and C), respectively, utilizing the FcCH$_2$OH redox probe with an initial concentration of 3.4 mM. As the amount of water in the water/IL mixture increases, the $i_{p,c}/i_{p,a}$ of the FcCH$_2$OH/ FcCH$_2$OH$^+$ redox couple
changes from 1.0 to 1.1 and finally 1.0 for curves A, B, and C, respectively. The peak current ratios suggest that the FcCH$_2$OH/ FcCH$_2$OH$^+$ redox couple is highly reversible in both the homogenous P$_{4441}$CH$_3$SO$_4$ as well as the water/IL mixture.

The peak-to-peak separations were also calculated for curves A, B, and C in Figure 2.4 with changes from 0.144 to 0.099 and ultimately 0.079 V, respectively. The $\Delta E_p$ values are somewhat misleading as the potential profile shifts from a linear to hemispherical diffusion regime at the electrode surface. Trace A in Figure 2.4 has well defined peak shaped current responses during the forward and reverse scans. Meanwhile curve C still has some peak-shaped character; however, its appearance is shifting towards the steady state response typical of UMEs in molecular solvents. While the peak separations suggest irreversibility this is more likely a result of a change in the diffusion regime towards that of a molecular solvent.

The half-wave potentials for FcCH$_2$OH$^+$/FcCH$_2$OH were also calculated using the peak potentials and determined to be 0.386, 0.466, and 0.404 V for $\chi_{H2O}$ equal to 0.0, 0.4, and 0.8 or curves A, B, and C, respectively. This translates again to a shift of roughly ±0.050 V from the mean value and seems satisfactory for a Ag-wire quasi-reference electrode; developing a reference electrode for such a highly specific mixture system, however, did not seem practical.

COMSOL finite element simulations were used again to evaluate the electrochemical kinetics of the water/IL mixture through the overlap of computational CVs (○) on to actual ones, as detailed in Figure 2.4. Owning to the small change in FcCH$_2$OH concentration, a constant effective concentration of 3.4 mM was assumed and only the diffusion coefficients were varied. For the initial measurements this should be reasonably accurate as the concentration can be calculated directly, however, for curves B and C in Figure 2.4 this is a gross approximation.

Moving forward, the $k^o$ for all water/IL simulations was set equal to 0.01 cm$\cdot$s$^{-1}$; values larger than this served to generate virtually identical traces that represent good reversibility. In the case of curve A, $D_{FcCH_2OH}$ and $D_{FcCH_2OH^+}$ were optimized at 1.5 and 5.5 x $10^{-8}$ cm$^2$·s$^{-1}$, while for curve B they were 0.5 and 1.0 x $10^{-7}$ cm$^2$·s$^{-1}$, and finally 5.5 and 5.5 x $10^{-7}$ cm$^2$·s$^{-1}$ for curve C, respectively. This results in diffusion coefficient ratios of 3.6, 2, and 1, respectively, and seems to mirror the trend observed in the DCE/IL
mixture series. That is, with increasing water content the system becomes more like that of a molecular solvent, while the interactions between the electroactive species and the IL become minimized, or at least not observable.

While both DCE/IL and water/IL mixtures appeared to be homogeneous, the total volume, and hence the concentration of the redox species, could not be accurately determined. Therefore, a chronoamperometry (CA) technique, developed by Aoki and Osteryoung [23, 24], was employed to determine the diffusion coefficients of $D_{Fc}$ and $D_{Fc\text{CH}_2\text{OH}}$. This method is independent of the electroactive species concentration and has been used successfully recently [15, 35, 46]; the potentiostatic curves are interpreted through the following:

$$\frac{I}{i_{ss}} = 1 + 2r_d \pi^{\frac{3}{2}} D_{i,ss}^{\frac{1}{2}} t^{-\frac{1}{2}} \quad (2.6)$$

where $r_d$ is the radius of the Pt disk UME, $t$ is time in seconds, $I$ and $i_{ss}$ are the measured current and the diffusion-limiting (steady-state) current, respectively.

At each addition of DCE, or water, three CA curves were acquired with a 5 minutes rest period between each to allow equilibration of the system. Three typical $I$-$t$ curves are illustrated in Figure 2.5A. These were recorded by stepping from zero current potential to 0.600 V for 10 seconds in a Fc solution in P$_{4441}$CH$_3$SO$_4$. The potential step program was chosen to occur well before and after the Fc oxidation reaction as displayed in Figures 2.3 and 2.4. The CA curves record the change in current over time and are the result of the rapid Fc depletion, giving rise to an exponential decay.

The CA curves depicted in Figure 2.5 underwent two data treatment steps. First, the steady state current, $i_{ss}$, from equation 2.6 was determined by plotting $I$ versus $t^{-\frac{1}{2}}$, applying a linear curve fit to all but the first 3 data points - these correspond to the steady state portion of the CA curve, while obtaining the y-intercept which was taken to be $i_{ss}$ [23, 24, 35, 46]; as depicted in Figure 2.5B.
Figure 2.5, A: Chronoamperometric (CA) curves (3 overlaid) acquired at a Pt disk ultramicroelectrode (25 µm in diameter) immersed in a solution of 5 mM ferrocene in P_4441CH_3SO_4 with a potential step from 0 to 0.600 V. Inset illustrates the current normalized CA curves versus $t^{-1/2}$ along with the linear curve fitting applied to the all but the first 3 data points. B: $I$ versus $t^{-1/2}$ (○) that was used for the determination of $i_{ss}$ through linear curve fitting of all but the first 3 data points (steady state portion of the CA curve) and extrapolation to the y-intercept.
**Figure 2.6:** Diffusion coefficients determined with increasing mole fraction of DCE (A) and water (B) in the IL for ferrocene and ferrocenemethanol, respectively. The error bars indicate $3\sigma$ from the mean of the three chronoamperometrically obtained diffusion coefficients. Inset in (A) is a magnified portion where $\chi_{\text{DCE}}$ was equal to 0 to 0.4.

Next, as shown inset in Figure 2.5A, $i / i_{ss}$ versus $t^{1/2}$ ($\circ$) was plotted for all three potential steps with the linear curve fitting overlaid (red trace) applied again to all but the first 3 data points; the y-intercept was set equal to 1 [15, 23, 24, 35]. Using the slope of this linear fitting, according to equation 2.6, the diffusion coefficients at each mole fraction increase of DCE or water were calculated.

Figures 2.6A and 2.6B detail the trends in diffusion coefficients with increasing DCE and water content, respectively. In the case of Fc in the DCE/IL mixture, $D_{\text{Fc}}$ begins at $2 (\pm 0.2) \times 10^{-8}$ cm$^2$·s$^{-1}$ and remains at approximately this value up to $\chi_{\text{DCE}} = 0.5$. The associated error for the three runs never exceeded $\pm 0.5 \times 10^{-8}$ cm$^2$·s$^{-1}$ for the entire series of experiments, calculated using three standard deviations from the mean diffusion coefficient value. After $\chi_{\text{DCE}} = 0.5$ the diffusion coefficient of ferrocene increases up to $1.3 \times 10^{-5}$ cm$^2$·s$^{-1}$ at $\chi_{\text{DCE}} = 0.8$; the latter diffusion coefficient is in the
range expected for a molecular solvent [39]. This is in good agreement with the shapes and intensities of the CV curves illustrated in Figure 2.3, such that at the highest $\chi_{\text{DCE}}$ the IL/DCE mixture has become essentially a DCE solution with $P_{4441}$CH$_3$SO$_4$ as extra supporting electrolyte. Inset in Figure 2.6A is an enlarged graph of the $\chi_{\text{DCE}}$ equal to 0.0 to 0.4 portion of the series and illustrates the little change in $D_{\text{Fc}}$ up until the saturation point at roughly $\chi_{\text{DCE}}$ of 0.5.

The early Fc diffusion coefficients of $2 \pm 0.2 \times 10^{-8}$ cm$^2$·s$^{-1}$ are in excellent agreement with that optimized using the simulation, $2.25 \times 10^{-8}$ cm$^2$·s$^{-1}$, and illustrated in Figure 2.3A. Similarly, the diffusion coefficients determined through the simulation at $\chi_{\text{DCE}}$ values of 0.4 and 0.8 are in reasonable agreement with those evaluated using CA. $D_{\text{Fc}}$ of $1.5 \times 10^{-7}$ cm$^2$·s$^{-1}$ obtained from the simulation compared to $1.8 \times 10^{-8}$ cm$^2$·s$^{-1}$ from CA at $\chi_{\text{DCE}}$ of 0.4, while $D_{\text{Fc}}$ was found to be $0.6 \times 10^{-5}$ cm$^2$·s$^{-1}$ simulated and $1.3 \times 10^{-5}$ cm$^2$·s$^{-1}$ from CA. This difference for the later IL/DCE mixtures is likely owing to the volumetric assumptions used to perform the simulations.

A slightly different trend is seen for $D_{\text{FcCH}_{\text{OH}}}$ in the water/IL mixture as drawn in Figure 2.6B. As the added amount of water increases, the diffusion coefficient of the redox species decreases slightly up to $\chi_{\text{H}_2\text{O}}$ value of 0.3 and then begins to increase. $D_{\text{FcCH}_{\text{OH}}}$ never exceeds $1.2 \times 10^{-9}$ cm$^2$·s$^{-1}$ and remains of a magnitude commonly expected in homogeneous ILs [15-17, 35, 36, 47]. This result correlates well with CV data shown in Figure 2.4 where the current intensity of the anodic peak never exceeds 1.200 nA; since $D_{\text{FcCH}_{\text{OH}}} \propto i_p$ [13, 48, 49] through the Randles-Sevčik equation:

$$i_p = 0.4463 \left( \frac{F^3}{RT} \right)^{1/2} z^{3/2} D^{1/2} A c^* v^{1/2}$$

where $F$ is Faraday's constant, $R$ is the universal gas constant, $c^*$ is the bulk concentration of the electroactive species, $A_\varepsilon$ is the electrode area, and $v$ is the scan rate. However, it has also been understood for some time that the diffusion coefficient itself is concentration-dependent [13, 47, 50]. That is, the Randles-Sevčik equation is not strictly obeyed in IL systems and the diffusion coefficient will increase with increasing concentration causing $i_p$ to be 'supra-concentration' dependent [13, 47, 50]; this linear
increase was shown by Eisele et al. [47] and Brooks et al. [50] using imidazolium-based ILs along with Fc as the redox probe. The total amount of Fc or FeCH₂OH in the electrolytic cell was never changed; however, through subsequent DCE or water additions, its concentration should have decreased. This in turn would result in a corresponding decrease in the diffusion coefficient - if the concentration-dependence held. A slight decrease in $D_{FeCH₂OH}$ is observed and in this way agrees with these previous reports [47, 50]. However, $D_{Fc}$ shows little change during the initial additions, up to $\chi_{DCE}$ of 0.5, until the sudden increase that is believed to be the saturation point. If the diffusion coefficient was concentration-dependent in the DCE/IL mixture then a corresponding drop in $D_{Fc}$ should also be observed. The absence of this drop in $D_{Fc}$ within the IL/DCE series maybe indicative of solvent interaction enhancing the current response or the mixture assuming a molecular solvent character more rapidly. Meaning $P_{4441}CH₃SO₄$ has more hydrophobic rather than hydrophilic character. This is seemly also supported by the overall limited change in $D_{FeCH₂OH}$ throughout the water/IL experiment series; it maybe concluded that water does not disrupt the IL nano-structure as much as the organic solvent owing to the ILs hydrophobicity.

It is also recognized that the increased diffusion coefficient is also a result of the decreased viscosity as the IL/DCE mixture becomes saturated with the much less viscous organic solvent. However, it has been shown that the Stokes-Einstein equation [39] relating the diffusion coefficient to viscosity, $\eta$, as shown in equation 2.8 is not always valid for IL systems [17].

$$D = \frac{kT}{p\pi r_a \eta}$$  \hspace{1cm} (2.8)

where $k$, $T$, and $r_a$ are Boltzmanns constant, temperature in Kelvin, and the hydrodynamic radius of the electroactive species, respectively, while $p$ is a constant (either 4 or 6). The viscosity, evaluated qualitatively, decreased appreciatively in the IL/DCE mixture but not as much for the IL/water case and this is seemly in agreement with the measured diffusion coefficients.

In order to evaluate further the hydrophobicity/hydrophilicity of $P_{4441}CH₃SO₄$ its solubility was tested using an electrified interface between two electrolytic solutions
In liquid-liquid electrochemistry, ions are 'pushed' or 'pulled' across the ITIES by an applied potential across the interface, called the Galvani potential difference, biased at two electrodes immersed in either phase [25, 51]; where \( \phi_w \) and \( \phi_o \) are the potentials in the water and DCE phases, respectively, and the Galvani potential difference is then \( \Delta \phi = \phi_w - \phi_o \).

Thus, if a positive potential is applied to the aqueous phase, then cations are 'pushed', or repelled, across the interface, while if this potential were then reversed, these cations would then be 'pulled', or attracted, back across the immiscible boundary [51]. This process is called simple ion transfer (IT) is described through equation 1.4.

The potential at which IT takes place is called the formal IT potential, \( \Delta o \phi' \), and is unique for each ion and biphasic system [51]. \( \Delta o \phi' \) is related to the Gibbs free energy of transfer via \( \Delta G' = zF \Delta o \phi' \), that is analogous to relationship between the formal potential of a redox species, \( E' \), and its Gibbs free energy, \( \Delta G' = -zFE' \), found in conventional electrochemistry [51]. The formal IT potentials of the individual IL components; however, can be used to estimate the ILs \( K_{sp} \), or solubility product [52, 53], since \( \Delta G'_{r,salt} = -RT \ln K_{sp} \) and thus, \( \Delta G'_{r,cation} + \Delta G'_{r,anion} \) [51-53]. Figure 2.7 illustrates the CV obtained at a 25 \( \mu \)m diameter w|DCE interface housed at the tip of a prepared capillary using Cell 2.1 (black curve) and Cell 2.1 with 0.5 mM of \( P_{4441}CH_3SO_4 \) added to the DCE phase (red trace).

The black curve in Figure 2.7 is essentially a blank and during the forward and reverse sweeps, from \(-0.400 \) to \( 0.000 \) V at \( 0.020 \) V⋅s\(^{-1}\), the CV is featureless indicating no IT takes place. After addition \( P_{4441}CH_3SO_4 \) (red curve in Figure 2.7) a peak shaped wave with a peak potential of \(-0.177 \) V is observed during the forward scan, from \(-0.400 \) to \( 0.000 \) V, and this is indicative of a cation transferring from w to o [54]. While during the reverse scan, from \( 0.000 \) to \(-0.400 \) V, another peak shaped wave was observed at \(-0.307 \) V and is suggestive of an anion transferring from w to o [54]. The diffusion regime for IT at a prepared micropipette is divided between the interior, or microchannel, and the exterior or volume of solution surrounding the ITIES upon which the pipette is immersed [54]; it is a product of the pipette geometry. In this case, the aqueous phase is
inside the pipette and the volume of material associated with the interface is small such that ions are quickly consumed, generating a peak shaped current response [54]: a linear diffusion regime. When transferring across the ITIES from outside to inside the pipette there is a larger volume of solution – relative to the size of the interface – from which to draw from. This translates to a hemispherical diffusion regime, analogous to UME redox signal when immersed in a molecular solvent, producing an “s”-shaped or sigmoidal current response with a steady state current [54]; thus, the current-potential profile and diffusion regimes at micropipette ITIES are asymmetrical. The steady state current and sigmoidal waves are not visible in the red CV in Figure 2.7, after addition of P_{4441}CH_{3}SO_{4}, because the IT of the cation and anion overlap significantly.

\[
\Delta \phi^{w} = \frac{1}{2} \Delta \phi_{i/2} = \frac{1}{2} \left( \frac{0.028}{z} \right) P_{4441}^{+} (w) \rightarrow P_{4441}^{+} (o)
\]

\[
\Delta \phi^{o} = \frac{1}{2} \Delta \phi_{i/2} = \frac{1}{2} \left( \frac{0.028}{z} \right) CH_{3}SO_{4}^{-} (w) \rightarrow CH_{3}SO_{4}^{-} (o)
\]

**Figure 2.7:** Cyclic voltammograms acquired using Cell 2.1 at a 25 µm diameter w|DCE interface with (red curve) and without (black curve) 0.5 mM of P_{4441}CH_{3}SO_{4} added to the DCE phase. Instrument parameters include a potential range from −0.400 to 0.000 V and a scan rate of 0.020 V·s⁻¹.

By convention, cation transfer elicits a positive peak current and anions generate a negative peak current when transferring from w to o [54]. In this way, the negative and positive peaks have been identified as the IT of P_{4441}^{+} and CH_{3}SO_{4}⁻ from w to o. Using the following relationship, the half-wave potential, \( \Delta \phi^{w}_{i/2} \), has been calculated for each IT using their peak potentials, \( \Delta \phi^{w}_{p} \): \( \Delta \phi^{w}_{i/2} = \frac{1}{2} \Delta \phi_{i/2} = \frac{1}{2} \left( \frac{0.028}{z} \right) \phi_{p} + (0.028 V/z) [43] \). The half-wave potentials were then calibrated using the tetraphenylarsonium tetraphenyl-borate (TATB)
assumption [55] through addition of 1.0 mM tetramethylammonium sulfate (TMA₂SO₄) to the aqueous phase. IT of TMA⁺ was used as an internal standard, with a formal ion transfer potential of 0.160 V [56], to calibrate the potential window through the following:

\[
\Delta_n^\circ \phi_{p}^\circ - \Delta_n^\circ \phi_{p,1/2} = \Delta_n^w \phi_{p}^w - \Delta_n^w \phi_{TMA^+,1/2}
\]  

(2.9)

The potential scale in Figure 2.7 has been calibrated using the TATB assumption [55]. Through these facile calculations the formal IT potentials of P₄₄₄₁⁺ and CH₃SO₄⁻ were determined to be −0.207 and −0.279 V, respectively, as has been demonstrated recently [25]. Using these values, the \( K_{sp} \) of P₄₄₄₁CH₃SO₄ was calculated to be 0.003; comparatively, the IL trihexyltetradecylphosphonium tetrakis(pentyfluoro-phenyl)borate was recently shown to have a \( K_{sp} \) of \( 8.9 \times 10^{-7} \) and is considered highly hydrophobic with an w/IL polarizable potential window of ~0.9 V.[35] In this way, P₄₄₄₁CH₃SO₄ is indicative of a moderately hydrophobic salt and agrees well with the diffusion study data in DCE/IL and water/IL mixtures.

2.5 Conclusions

The ionic liquid P₄₄₄₁CH₃SO₄ was investigated electrochemically using two redox probe molecules, Fc and FcCH₂OH, whilst – in separate experiments – the organic solvent DCE and water were added incrementally generating DCE/IL and water/IL mixtures. The diffusion coefficients where determined using a concentration-independent CA technique and used to explore the IL structure and how it changes with increasing water or organic solvent content. For P₄₄₄₁CH₃SO₄, as the \( \chi_{DCE} \) increased the IL character was maintained up to a threshold of \( \chi_{DCE} = 0.5 \), at which point the mixture rapidly acquired the diffusion regime expected for a molecular solvent; i.e. the Fc diffusion coefficient changed from being in the range of \( 10^{-8} \) cm²·s⁻¹ to \( 10^{-5} \) cm²·s⁻¹. In the water addition case, the diffusion coefficient of FcCH₂OH did not change appreciably throughout the course of the experiment. This seems to suggest that P₄₄₄₁CH₃SO₄ has more hydrophobic character and water does not affect the FcCH₂OH mass transport to the electrode surface.
Finite element analysis was utilized to explore the kinetics of electron transfer reactions at the Pt disk UME. For the IL/DCE mixture the volume was assumed to change uniformly, or that the volume of the solution was the sum of both the IL and water. Diffusion coefficient ratios of the reduced to oxidized form indicate an interaction between the IL and electroactive species is present at low DCE or water content, but disappears at high DCE or water content. Independent of the volumetric/concentration assumption, the kinetics of the CVs was determined using the standard rate constant via Butler-Volmer formalism and suggest a high degree of reversibility in the IL/DCE and IL/water electron transfer reactions.

Liquid|liquid electrochemistry at a w/DCE micro-interface housed at the tip of a pulled pipette was used to elucidate the Gibbs free energy of ion transfer and calculate the $K_{sp}$ of $\text{P}_{4441}\text{CH}_3\text{SO}_4$. The value determined, 0.003, is indicative of a moderately hydrophobic IL and this agrees well with the IL/DCE and IL/water mixture diffusion study.

This report outlines a procedure for the assessment of solvent and water effects on moderately hydrophobic/hydrophilic ILs, while providing insight into the effect of the cation and anion component towards the diffusion characteristics of electroactive species dissolved in the IL. This procedure is similar to previous reports of water/organic solvent mixtures [39]; however, incorporates liquid|liquid electrochemistry to provide a comprehensive analysis of the mixtures.

2.6 – References


Chapter 3 - Hydrophobicity of ionic liquids assessed by the Galvani potential difference established at liquid|liquid micro-interfaces

3.1 - Introduction

The predominant method of uranium extraction from water for the last 50 years has been the Plutonium URanium EXtraction (PUREX) process [1-3]. This commonly utilizes n-dodecane, or similar paraffinic molecular solvent, as the organic phase and n-tributylphosphate (TBP) as the coordinating agent. N-dodecane is considered to have low flammability, is relatively non-toxic, and gives adequate yields, which explains the industrial longevity of this solvent. The PUREX process is a complex multistep procedure whose convolution is necessary in order to achieve a high degree of selectivity and recovery of U(VI) over Fe(III) and other actinides [1-3]. Ionic liquids (ILs) present a possible avenue towards the simplification of this methodology whilst maintaining the level of selectivity and affording a higher degree of recovery [4, 5]; they also present other cursory benefits fundamental to their nature. ILs are characterized by their desirable electrical conductivity, high hydrophobicity, large liquid temperature range, and negligible vapour pressures. These features, in conjunction with the ability to tailor their properties to meet specific chemical requirements, makes them ideal alternative solvents for use in a variety of applications especially in the PUREX process [6, 7]. However, the leaching of IL materials has been shown to complicate the aqueous-IL extraction process and poses a serious environmental hazard [1]. If the hydrophobicity of the ILs could be increased, then this would prevent or minimize this leaching effect.

Electrochemistry at interfaces between two immiscible electrolytic solutions (ITIES) can be employed to investigate the lipophilicity of the target ILs. Cyclic voltammetry (CV) utilizing a micro-ITIES hosted by the orifice of a micropipette was pioneered by the work of Girault et al. [8], who characterized the diffusion mechanism of ion transfers (ITs). Micro-ITIES have the advantage of high mass transfer rates which are necessary to obtain sensitive kinetic data, a negligible iR-drop that allows the use of a simple two electrode system and affords an attractive, facile means of data treatment. Electrochemistry at micro-ITIES and large-ITIES has been investigated surrounding both simple ITs [9-12] and facilitated ion transfers (FITs) [11, 13-17], as such, it provides a rich theoretical background that is easily mined [12, 18-26]. Recently, Kakiuchi et al.
demonstrated the use of CV as a means of establishing a relative scale of polarized potential windows (PPWs) and the point of zero charge (PZC) of their synthesized ILs. The PPW established across an aqueous-IL (w|IL) interface is directly proportional to the hydrophobicity of the constituent ionic components of the IL [28, 29]. A greater separation in formal transfer potentials ($\Delta_w^\omega \phi^\omega$) of the ions present in a IL, or a larger PPW, indicates a more hydrophobic IL, which facilitates access to more IT and FIT reactions for the ions of study at the w|IL interface. This, in turn, would have the desired effect of decreasing the leaching of materials during extraction [23].

This chapter seeks to quantify the hydrophobicity of 8 ILs by utilizing the Galvani potential difference for transfers of these IL ions, characterized through CV experiments at the micro-ITIES. In order to evaluate the optimal experimental conditions to conduct the CV at the micro-ITIES, a series of simulations were performed using Comsol 3.4 software. The overall geometry of the micropipette was investigated. This study first focuses on examining quantitatively the effect of alternating the internal diameter on the half-wave transfer potential ($\Delta_w^\omega \phi_{1/2}$). Specifically, the increasing separation of the half-wave potential that occurred as the inner diameter of the capillary decreased. The discrepancy between the $\Delta_w^\omega \phi_{1/2}$ obtained for various internal radii lead to the formulation of an etching methodology, whereby the internal diameter is formed by annealing a Pt-wire of the desired diameter inside the capillary and removing it with a strong acid solution. This technique allows for the formation of replicate capillaries of consistent dimensions. The second impact of the simulations was to fix the ratio of the internal to external radius of the capillary, the $R_g$, at a value greater than 40. It was discovered that this $R_g$ would have the smallest impact on the CV and generate current values very close to that predicted by the equation for steady state current [27]:

$$i_{ss} = 4z_i F D_{i,\alpha} c_{i,\alpha} r_d$$

(3.1)

where $z_i$ is the charge of species $i$, $F$ is Faraday’s constant, $r_d$ is the internal radius of the capillary, $D_{i,\alpha}$ and $c_{i,\alpha}$ are the diffusion coefficient and concentration of species $i$ in phase $\alpha$. That the $R_g$ value of the pipette has an impact on the diffusion regime has also been examined by previous groups [12]. Girault et al. recognized that the internal diameter
played a crucial role during their AC impedance measurements of a FIT system [12, 15, 19, 23, 30]. The simulation, in combination with the corresponding experiments, leads to the conclusion that a numerical adjustment is necessary to calculate the $\Delta_o^{\phi^o}$ from the $\Delta_o^{\phi_{1/2}}$. In solid electrode chemistry, and at liquid|liquid interfaces formed at a large interface between water and 1,2-dichloroethane (DCE), where the chemical activities and diffusion properties can be considered equivalent, it is convenient to form the assumptions $E^{\phi^o} \approx E^{1/2}$ and $\Delta_o^{\phi^o} \approx \Delta_o^{\phi_{1/2}}$, respectively. This facilitates the facile calculation of Gibb’s free energy, $\Delta G^o = -n F E^{\mu}$ and $\Delta G^o = z F \Delta_o^{\phi^o} F$. However, for electrochemical studies at micro-ITIES this is not the case and in order to maintain this assumption an adjustment must be introduced. This adjustment in calculation was further proved experimentally. Kakiuchi et al. [12] examined the asymmetric diffusion of species from cylindrical and tapered pipettes in both viscous (IL, $D_{i,IL} \neq D_{i,w}$) and conventional organic solvents (IL, $D_{i,o} \approx D_{i,w}$; w: aqueous, o: organic) and noted a similar phenomenon.

In the current study the transfer potentials of a variety of ILs (see Table 3.1) were explored at both the w|IL and w|DCE interfaces, gaining data of IL hydrophobicity. Three imidazolium-based ILs were chosen and coupled with the bis(trifluoromethylsulfonyl)imide (NTf$_2$) anion that is considered highly hydrophobic [15]. Bis(2,4,4-trimethylpentyl)phosphinic acid is a component in various industrial products [31] and has been used as a ligand for actinides including uranyl ions [32]. Thus, an IL incorporating bis(2,4,4-trimethylpentyl)phosphinate as an anion was investigated and combined with a large alkylphosphonium-based cation, trihexyltetradodecylphosphonium. In order to explore the hydrophobicity of this cation, two further ILs were chosen, one with the same NTf$_2$ anion used with the imidazolium ILs and the other with dicyanamide. These phosphonium ILs were found to have the largest PPW’s while those with imidazolium cations, whose PPW could not be directly measured, showed low hydrophobicity measured through the differences in their formal IT potentials at the w|DCE interface.
Table 3.1: Ionic Liquids

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3.2 - Theory

Mass transfer, modelled using a Nernstian reversible system, in conjunction with Fick’s laws of diffusion, through finite element analysis was utilized to study aspects of simple ion transfer across the micro-ITIES. All simulations were performed using Comsol 3.4 Multiphysics software. Simple IT is described by equation 1.4. The boundary condition at the interface in a reversible system were described by the Nernst equation, equation 3.2, where \( f = \frac{z_i F}{RT} \) (\( R \) and \( T \) maintain their conventional thermodynamic significance):
\[
\frac{c'_w}{c'_o} = e^{f(\Delta_{i,\alpha}^w - \Delta_{i,\alpha}^o)} \tag{3.2}
\]

Diffusion of the ion in the aqueous and organic phases is described for a time dependent function in cylindrical coordinate geometry as expressed in equation 2.1 [33]. Current, as a function of IT, was evaluated according to:

\[
I = 2\pi z_i F \int (-D_{i,\alpha} \nabla c_{i,\alpha}(r, z, t))rdr \tag{3.3}
\]

The sign of the current was taken to be positive when a cation was driven from the aqueous phase to the organic phase. During a CV experiment, the Galvani potential difference is swept linearly from the initial potential, \(\Delta_{i,\alpha}^w \phi_i\), to the switching or final potential, \(\Delta_{i,\alpha}^w \phi_f\), and then back using a triangular waveform, equation 2.5.

The model geometry consisted of a 2-dimensional cross-section of a cylindrical capillary, symmetrical about the z-axis (perpendicular to the liquid-liquid interface) and with an inner diameter described by the r-axis. The simulation geometry is shown in Figure 3.1 as a cross-section of the capillary and is similar to previous work on scanning electrochemical microscopy performed by Ding et al. [34]. Briefly, the z-axis constitutes the axis of symmetry and a lengthwise perspective of the capillary. The radius propagates along the r-axis perpendicular to its length. Three fields compose the simulation geometry, the internal (aqueous phase), insulator (the glass capillary), and the external (organic phase) with the periphery between the internal and external fields forming the boundary of flux normal to the z-axis.

Simulated experimental conditions were chosen to best approximate the actual conditions used in the experiments. In all simulations, the initial concentration of species \(i\) with charge \(z_i\) was zero in the aqueous phase and 10 mM in the organic phase surrounding the pipette. \(\Delta_{i,\alpha}^w \phi'\) was set at 0.250 V for an anion and −0.250 V for a cation unless otherwise stated. The common convention and experimental determination in the literature towards \(D_{i,\alpha}\), in the organic and aqueous phases, is a value of \(1 \times 10^{-9} \text{ m}^2\text{s}^{-1}\) for an ion of moderate proportions [34-36]; this convention was maintained throughout the chapter.
3.3 – Experimental

3.3.1 - Chemicals

The following chemicals were purchased from Fluka/Sigma-Aldrich Canada Ltd. (Mississauga, ON): tetrabutylammonium tetraakis(4-chlorophenyl)borate (TDATPBCl) (this constituted the organic phase supporting electrolyte), 1,2-dichloroethane (99.8 %, anhydrous), lithium sulphate monohydrate (the aqueous phase supporting electrolyte), lithium chloride, tetrabutylammonium perchlorate (TBAClO₄), tetrabutylammonium tetraphenylborate (TBATPB), and tetramethylammonium sulphate (TMASO₄) along with several ionic liquids, including trihexyl(tetradecyl)phosphonium dicyanamide (P₆₆₆₁₄DC), tributylmethylphosphonium methyl sulphate (P₁₄₄₄Ms), 1-(3-cyanopropyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (CPMINTf₂), 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (DPMINTf₂), 1,3-bis(cyanomethyl)imidazolium bis(trifluoromethylsulfonyl)imide (BCMINTf₂), and tetrabutylammonium heptadecaoctanesulfonate (TBAFOS). Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (P₆₆₆₁₄P) was purchased from Strem Chemicals Inc. (Newburyport, USA) and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide (P₆₆₆₁₄NTf₂) was generously contributed by Dr. Ragogna (the University of Western Ontario, 1151 Richmond Street, London, Ontario, Canada). All chemicals were used as received without further purification; all aqueous
solutions were prepared using deionized distilled water. Fischer brand digital micropipetters were used in the volumetric preparation of all solutions.

3.3.2 - Preparation of Micropipettes
The micropipette constitutes the basis of this report’s analytical research and hence its fabrication is of the utmost importance; a full description of their fabrication can be found in section 2.3.2.

3.3.3 - Electrochemistry
The electrochemical cells are described below for the w|DCE, w|IL, and large-ITIES w|DCE systems through cells 3.1, 3.2, and 3.3, respectively:

<table>
<thead>
<tr>
<th>Ag</th>
<th>Ag₂SO₄</th>
<th>5 mM Li₂SO₄</th>
<th>IL</th>
<th>Ag(IL-anion)</th>
<th>Ag</th>
<th>(Cell 3.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(aq)</td>
<td></td>
<td></td>
<td>(IL)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ag</th>
<th>Ag₂SO₄</th>
<th>5 mM Li₂SO₄</th>
<th>0.5 mM IL</th>
<th>AgTPBCl</th>
<th>Ag</th>
<th>(Cell 3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(aq)</td>
<td></td>
<td></td>
<td>(org)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ag</th>
<th>Ag₂SO₄</th>
<th>5 mM Li₂SO₄</th>
<th>~0.5 mM IL</th>
<th>5 mM LiCl</th>
<th>AgCl</th>
<th>Ag</th>
<th>(Cell 3.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(aq)</td>
<td></td>
<td></td>
<td>(org)</td>
<td>(aq ref)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The respective experimental set-ups for the micro and large interfaces are depicted in Figure 3.2 A and B.

3.3.4 - Micro-ITIES
During electrochemical measurements at the micro-ITIES, the glass capillary was housed in a microelectrode holder (HEKA Electronics Inc., Mahone Bay, NS, Canada) equipped with a syringe and a Ag₂SO₄/Ag electrode. The aqueous phase, consisting of 5 mM solution of the supporting electrolyte Li₂SO₄, was maintained in the capillary. A silver electrode was positioned in the organic phase which consisted of a 5 mM TDATPBCl DCE solution or a neat IL. The micropipette was immersed in the organic phase as shown in Figure 3.2 A. The w|IL or w|DCE interface (cell 3.1 or cell 3.2) was monitored
and adjusted using an optical microscope and the syringe connected to the pipette holder. Electrochemical measurements were conducted using an Electrochemical Analyzer (CHI-800b, CHI Instruments, Austin, Texas, USA), where a two-electrode system was employed.

**Figure 3.2** - Experimental Set-up for A: micro-ITIES; B: large-ITIES; the latter was constructed from borosilicate glass and fabricated in Western Universities Glassblowing Shop. WE, CE, and RE are the working, counter, and reference electrode leads of the potentiostat, respectively.

3.3.5 - Large-ITIES

The large interface consisted of a cylindrical glass vessel as shown in Figure 3.2 B, where the interface was polarised by means of the two reference electrodes (RE1 and RE2) situated in the two adjacent Luggin capillaries to minimise the ohmic resistance, and the current was measured via the two Pt counter electrodes (CE1 and CE2) fused into the wall of the glass vessel. The aqueous phase in contact with CE2 and RE2 held a 5 mM Li₂SO₄ solution whilst the DCE organic phase with 5 mM of TDATPBCl and containing RE1 was interfaced the first aqueous phase and in contact with the second aqueous phase containing 5 mM LiCl and CE1 (cell 3.3). All electrochemical measurements using the large interface were conducted using a Solartron 1480 Multistat (Ametek Advanced Measurement Technology, Farnborough, Hampshire, UK).
3.4 – Results and Discussion

3.4.1 - Simulation Results

3.4.1.1 - Ion transfers at a 25 μm diameter interface

Figure 3.3 - Simulated cyclic voltammogram of cation - anion transfers at a 25 μm diameter interface; the Galvani potential difference, $\Delta^w_o \phi$, was swept at a scan rate of 10 mV·s$^{-1}$ from 0 to +500 mV, then to −500 mV, and finally back to 0 mV. The formal transfer potentials, $\Delta^w_o \phi^w$, were set at −250 mV for the cation and 250 mV for the anion, respectively.

Figure 3.3 illustrates a typical CV obtained from the simulation where a cation and anion are present in the bulk organic phase at a concentration of 10 mM. The formal transfer potentials, $\Delta^w_o \phi^w$, were set at 0.250 V for the anion and −0.250 V for the cation, respectively. Cation transfer is depicted on the left side of the CV and the anion transfer is shown on the right. The scan in Figure 3.3 begins at 0.000 V and continues in the positive direction, where a steady-state, sigmoidal wave is observed due to the hemispherical diffusion of anions to the pipette beginning at 0.200 V and with completion at approximately 0.400 V. The scan then changes direction at 0.500 V, heading towards negative potentials. This gives rise to a peak-shaped wave indicative of linear diffusion of the anions from the aqueous phase inside the pipette back to the interface, this time from 0.400 V to 0.200 V. The cation then undergoes similar transfer processes showing a steady-state wave when transferring from oil to water and a peak-shaped wave in the reverse transfer. The depiction of ITs showing the asymmetric voltammogram in Figure
3.3 is in agreement with that established by the pioneering work of Girault et al. [13, 15, 30].

It is often convenient to generalize the relationship \( E' \approx E_{1/2} \), at a solid electrode undergoing conventional reduction-oxidation chemistry, or \( \Delta_w \phi' \approx \Delta_o \phi_{1/2} \), at a large liquid|liquid interface between water and DCE. \( \Delta_o \phi_{1/2} \) can be calculated using equation 3.4 [9, 10] and \( \Delta_w \phi_p \) or the peak potential (the potential at the current maximum):

\[
\Delta_o \phi_{1/2} = \Delta_w \phi_p + 28.5/z_1 \text{ mV} \tag{3.4}
\]

The half-wave potential of the anion transfer in Figure 3.3 was determined to be 0.300 V while the formal IT potential was set at 0.250 V. It was first noted that a discrepancy of 50 mV existed between the \( \Delta_w \phi' \) entered in the simulation parameters and \( \Delta_o \phi_{1/2} \) calculated using the CV generated by the simulation. In contrast, the \( \Delta_o \phi' \) of the cation was −0.250 V and \( \Delta_o \phi_{1/2} \) was calculated at −0.300 V. Therefore, at a micro-ITIES, the relationship of \( \Delta_o \phi_{1/2} = \Delta_w \phi' \) cannot generally be considered and an adjustment of 50 mV should subsequently be applied to the value of \( \Delta_w \phi' \) observed for all experimental results; +50 mV and −50 mV for cations and anions respectively. Kakiuchi et al. [37] investigated the half-wave potential dependence on the tapering angle of the micropipette and developed a correction factor to account for the internal angle; here the pipettes have been fabricated with an internal angle of 90 degrees so that a correction factor is not required. Wilke et al. [15] sought to quantify the linear relationship between the radius and \( \Delta_w \phi' \) in their report on the IT transfer across a microhole interface and explained that a similar effect was observed in micropipettes. This 50 mV adjustment appears relevant only to the micro-ITIES with a 25 \( \mu \text{m} \) diameter and cannot be applied to other sizes.

3.4.1.2 - Influence of internal radius of micro-ITIES interface

A simulation was then conducted to determine if changing the internal radius had ramifications on the half-wave potential; the internal radius was augmented from 2 to 5, 10, 12.5, and 25 \( \mu \text{m} \) while the external radius was maintained at 500 \( \mu \text{m} \). Figure 3.4
depicts \( \Delta_o^w \phi_{1/2, \text{anion}} - \Delta_o^w \phi_{1/2, \text{cation}} \) versus \( \ln (1/r) \) and demonstrates that altering the internal diameter can influence the half-wave potential.

\[ \Delta_o^w \phi_{1/2, \text{cation}} 1 - \Delta_o^w \phi_{1/2, \text{cation}} 2 \] ; experimental conditions are the same as those laid out in Figure 3.3.

The slope of the red (●) line is approximately 46 ± 3 mV \( (R^2 = 0.999) \) and this is proportional to the potential shift experienced between the cation and anions as the radius decreases. During an investigation conducted by Wilke et al. [14] into the Galvani potential difference established at a micro-hole ITIES, they noted that alteration of the micro-hole radius influenced \( \Delta_o^w \phi_{1/2} \). This was such that the half-wave potential of ions of opposite charge, but of equal magnitude, shifted proportionally in opposing directions along the PPW with decreasing hole radius [14]. The experimental data collected by Wilke et al. [14] indicated a shift of 43 ± 5 mV between TEA\(^+\) and ClO\(_4^-\) as the micro-hole radius was changed from 5 to 25 μm. These data are in close agreement with the potential shift shown by the simulation data concerning the micropipette of 46 mV.

The simulation was then changed to include two ions of the same charge (blue, +, trace) and the difference in the half-wave potential between them was monitored (data not shown); a slope of approximately 0 mV was achieved indicating no change in half-wave potential. Therefore, if experimental results were to remain reproducible, a capillary
fabrication method that could produce a consistent internal diameter would be necessary; as described above. Based on this trend it was also considered prudent to select internal references such that cations were calibrated using cationic standards and anions using anionic standards.

3.4.1.3 - Influence of \( R_g \) on Cyclic Voltammetry
Subsequently, the \( R_g \) was modified from 2 to 40 with the internal radius held constant at 12.5 \( \mu \)m; all other parameters were preserved from the internal radius simulations. Figure 3.5 depicts the CVs obtained for the ion transfer of a single species. The \( R_g \) with the highest peak current is 2 whilst the subsequent \( R_g \) values tested fall at the same peak current and hence their CVs overlap extensively. Table 3.2 lists the half-wave potentials determined using two methods: (i) by investigation of the steady-state wave (\( \Delta_{o,ss}^w \phi_{1/2} \)) and (ii) by the peak current calculation of the half-wave potential (\( \Delta_{o,p}^w \phi_{1/2} \)) described by Bard et al. [14] in equation 3.4. In both cases an adjustment of approximately \(-50\) mV, for the anion transfer, is required.

![Figure 3.5](image)

**Figure 3.5.** Effect of \( R_g \) on \( \Delta_o^w \phi_{1/2, anion} \); where \( R_g = 2 \) shows the highest peak current and \( R_g \) values 5, 10, and 40 have identical peak peak currents; \( \Delta_o^{w,po} = 250 \) mV, \( \Delta_o^w \phi_{initial} = 0 \) mV, \( \Delta_o^w \phi_{high} = 500 \) mV, \( \Delta_o^w \phi_{low} = 0 \) mV, and \( v = 10 \) mV·s\(^{-1}\).

The theoretical value of the steady state current was calculated as \( 4.82 \times 10^{-8} \) A according to equation 3.1 and this is in close agreement with the steady state current obtained from the simulations of \( 4.93 \times 10^{-8} \) A for high \( R_g \) capillaries. Those values observed during the simulation are included in Table 3.2 and indicate that, as the \( R_g \) is increased to more than
10, the steady state current approaches the theoretical value. Based on these data, a capillary with a high $R_g$ is desirable to better approximate the theoretical value. The micropipette in the experimental evaluation of the following ILs was of an $R_g > 40$, as measured using an optical microscope.

Table 3.2. Effect of $R_g$ on $\Delta_w^o \phi_{1/2}$ and $i_{ss}$ for IT.

<table>
<thead>
<tr>
<th>$R_g$</th>
<th>$\Delta_w^o \phi_{1/2, ss}$ (V)</th>
<th>$\Delta_w^o \phi_{1/2, p}$ (V)</th>
<th>$i_{obs, SS}$ ($A \times 10^{-8}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.296</td>
<td>0.303</td>
<td>5.25</td>
</tr>
<tr>
<td>4</td>
<td>0.293</td>
<td>0.300</td>
<td>4.93</td>
</tr>
<tr>
<td>10</td>
<td>0.293</td>
<td>0.300</td>
<td>4.93</td>
</tr>
<tr>
<td>40</td>
<td>0.293</td>
<td>0.300</td>
<td>4.93</td>
</tr>
</tbody>
</table>

3.4.2 - Hydrophobicity of ILs and the size of the w|IL PPW at the micro-ITIES

Figure 3.6. PPWs of w|IL interfaces using cell 3.2. ILs were of the $P_{66614}$ cation series with (A) NTf$_2$, (B) DC, and (C) P anions. The following instrument parameters were used for $P_{66614}$NTf$_2$: $\Delta^w_{IL} \phi_{initial} = -10$ mV, $\Delta^w_{IL} \phi_{high} = 200$ mV, $\Delta^w_{IL} \phi_{low} = -450$ mV, and $v = 20$ mV·s$^{-1}$. Similar parameters were used for $P_{66614}$DC and $P_{66614}$P: $\Delta^w_{IL} \phi_{initial} = -250$ mV and $\Delta^w_{IL} \phi_{high}$ was equal to $-95$ and $-250$ mV for the two ILs respectively.
The initial experiments focused on the direct evaluation of the PPW at a w|IL interface (cell 3.1). Figure 3.6 illustrates the CV obtained at the w|IL micro-ITIES established using P_{6614} as the common cation accompanied by NTf_{2}, DC, or P anions for curves A, B, and C, respectively. As the hydrophobicity of the anion increases, the PPW widens [37].

The PPW is limited by the transfer of the anion at positive potentials and the cation IL component at negative potentials. Thus, as the common cation, P_{6614} limits the PPW with its transfer at the ITIES at approximately −320 mV. The anions then limit the PPW towards the positive end of the potential scale at −280, −270, and +95 mV for P^−, DC^−, and NTf_{2}^−, respectively. Using this as a basis for the formation of a hydrophobicity scale, beginning with the most hydrophobic anion and following in a descending order of hydrophobicity: NTf_{2} > DC > P. The less hydrophobic anions shows a narrow PPW, approximately 100 mV wide for DC and P anions, this is most likely owing to the ability of water molecules to easily access the negative charge of the anion and participate in hydrogen bonding and dipole-dipole interactions. There might also exist a lower degree of electrostatic interaction between the cationic and anionic components of the IL. This would seem to indicate that the electrostatic interaction present between NTf_{2}^− and P_{6614}^+ is greater relative to the DC and P anions. Ultimately, however, P_{6614}NTf_{2} is a desirable IL owing to its higher degree hydrophobicity compared to P_{6614}DC and P_{6614}P. The larger PPW allows access to determine a wider range of IT and FIT of other ions.

### 3.4.3 - W|DCE micro-ITIES investigation

It was discovered that the w|IL interface could not be easily established at a micro-ITIES if the PPW is narrow. An alternative method to determine the size of the PPW is to calculate the difference in formal transfer potentials of the cation and anion components of the ILs dissolved in an organic solvent at a w|o interface [38]. In order to determine the optimal IL with a large PPW the formal IT potentials of the anionic and cationic components of the 8 ionic liquids were evaluated using the 25 μm w|DCE interface (cell 3.2). The first example uses one to the phosphonium based IL, P_{6614}NTf_{2}, that was shown to have a large PPW during the w|IL experiments and is depicted in Figure 3.7.
The blank is shown as a black dashed line in Figure 3.7, while the system with the dissolved IL is shown in red. Only one IT is visible within the w|DCE PPW: that of the anion NTf$_2^−$. The cation component is too hydrophobic to transfer within the limits of the supporting electrolytes. This is encouraging since it indicates a wide PPW and coincides with the PPW observed in the w|IL system given above. The CV of NTf$_2^−$ demonstrates a steady state wave describing a hemispherical diffusion pattern, and a peak-shaped wave denoting linear diffusion. The scan is initiated at $−450$ mV, continuing in the positive direction to a maximum of 150 mV revealing a steady state wave. 150 mV is the switching potential at which point the scan direction was changed and the potential becomes more negative; the potential was then swept from 150 mV to $−450$ mV revealing the peak-shaped wave given by linear egress at a peak potential of $−11$ mV. Like the simulation, the CV is in agreement with the theory of micro-ITIES diffusion developed by Girault et al. [38]. Asymmetric diffusion, linear within the pipette (egress) and hemispherical outside (ingress), gives rise to peak-shaped and sigmoidal steady state waves, respectively, and provides a unique method of identifying components within the system.

Figure 3.7. Cyclic voltammograms at w|DCE using cell 3.1 with blank (black dashed line) and P$_{66614}$NTf$_2$ as the IL (red curve), and the P$_{66614}$NTf$_2$ solution with TBACIO$_4$ added as an internal standard (blue curve); the radius of the interface was 25 μm, $Δ_oφ_{\text{initial}} = −450$ mV, the potential range was set from +150 to $−450$ mV, and $v = 20$ mV·s$^{-1}$.

The blue curve in Figure 3.7 shows the system after the addition of the calibrant, TBACIO$_4$. The formal transfer potential of ClO$_4^−$ was taken as $−170$ mV [9, 10]. The
formal transfer potential \( (\Delta_{\text{w|RTIL}}^{\phi_{\text{RTIL}}^{\prime}}) \) was then calculated according to the TATB assumption [39] and equation 2.9. This facile calculation is also made possible by the assumption that the diffusion coefficients of the ionic species are equivalent in the aqueous and DCE phases. Based on this assumption the average formal transfer potential of the NTf\(_2\)\(^-\) component of P\(_{66614}\)NTf\(_2\) was determined to be approximately 17 ± 3 mV. The 50 mV correction factor was cancelled since both of the reference and analyte ions are like charges.

The value found in the literature for this anion at a micro-ITIES (25 μm in diameter) was 95 mV [40, 41]. The literature reference on NTf\(_2\)\(^-\) is a similar IL [40, 41], with the imide paired with tributylmethylammonium. In comparison, it was shown that the same imide anion paired with the imidazolium cation, DPMI, had a transfer potential, 76 ± 20 mV, very similar to that found in the literature. It is proposed that this discrepancy is the result of increased electrostatic interaction between the cationic and anionic components and that each IL is subject to its own individual solvation environment. Matsumiya et al. [31] described the variation in viscosity they observed when comparing phosphonium-based ILs with their ammonium counterparts as being related to the electrostatic interaction experienced between the IL components. They observed that ammonium-based ILs were more viscose owing to higher electrostatic interaction than those composed of phosphonium [42]. It is possible that this phenomenon is responsible for influencing the ion transfer properties of these ILs.

Another example CV showing a w|DCE system with dissolved CPMINTf\(_2\) is shown in Figure 3.8; the blank CV with just the supporting electrolytes in solution is coloured black while the red curve was taken after the addition of the CPMINTf\(_2\). The potential was scanned from −250 mV up to 350 mV, giving a peak-shaped wave, at 53 mV, that is the linear diffusion of the cationic component of the IL (CPMI\(^+\)) out of the capillary. The potential is then swept back in the negative direction giving another peak-shaped wave at −10 mV; this indicates the anionic (NTf\(_2\)\(^-\)) component. The blue curve in Figure 3.8 shows the system after reference addition, in this example the salt TBAClO\(_4\) was added. The additional anionic peak observed is therefore ClO\(_4\)\(^-\). In this particular instance, no steady state wave is seen as the cation and anion peaks overlap; this indicates that the size of the PPW, at a w|IL interface, for this IL would be very narrow,
approximately 32 mV. For this reason the CPMI\(^+\) cation, along with the other imidazolium-based cations, were not considered ideal candidates.

**Figure 3.8.** Cyclic voltammograms acquired at a w/DCE micro-ITIES using cell 3.1 with no IL added or the blank (black, dashed line), CMPINTf\(_2\) as the IL (red curve), and with TBACIO\(_4\) added to the DCE phase as an internal standard. Instrument parameters were as follows: the radius of the interface was 25 μm, \(\Delta^{\nu}_o\phi_{\text{initial}} = -250\) mV, the potential range was set from +350 to −250 mV, and \(v = 20\) mV·s\(^{-1}\).

**Table 3.3:** \(\Delta^{\nu}_o\phi^{\nu'}\) and \(\Delta^{\nu}_o G_{\nu\rightarrow\nu'}^{\nu'}\) of the 8 IL components.

<table>
<thead>
<tr>
<th>Abbr.</th>
<th>(\Delta^{\nu}<em>o\phi^{\nu'}) (</em>{\text{RTIL-cation}}) (mV)</th>
<th>(\Delta^{\nu}<em>o\phi^{\nu'}) (</em>{\text{RTIL-anion}}) (mV)</th>
<th>(\Delta^{\nu}<em>o G</em>{\nu\rightarrow\nu'}^{\nu'}) (_{\text{cation}}) (kJ/mol)</th>
<th>(\Delta^{\nu}<em>o G</em>{\nu\rightarrow\nu'}^{\nu'}) (_{\text{anion}}) (kJ/mol)</th>
<th>PPW (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(_{66614})NTf(_2)</td>
<td>17 ± 3</td>
<td></td>
<td>-1.6</td>
<td></td>
<td>400(^a)</td>
</tr>
<tr>
<td>P(_{66614})P</td>
<td>-262 ± 14</td>
<td></td>
<td>25.3</td>
<td></td>
<td>100(^a)</td>
</tr>
<tr>
<td>P(_{66614})DC</td>
<td>-268 ± 16</td>
<td></td>
<td>25.9</td>
<td></td>
<td>100(^a)</td>
</tr>
<tr>
<td>BCMINTf(_2)</td>
<td>307 ± 13(^c)</td>
<td>26 ± 11</td>
<td>29.6</td>
<td>-2.5</td>
<td>141(^b)</td>
</tr>
<tr>
<td>CPMINTf(_2)</td>
<td>181 ± 7</td>
<td>18 ± 17</td>
<td>17.5</td>
<td>-1.7</td>
<td>82(^b)</td>
</tr>
<tr>
<td>DMPINTf(_2)</td>
<td>-29 ± 13</td>
<td>76 ± 20</td>
<td>-2.8</td>
<td>-7.3</td>
<td>53(^b)</td>
</tr>
<tr>
<td>TBAFOS</td>
<td>-263 ± 5</td>
<td>77 ± 8</td>
<td>-35.0</td>
<td>-7.4</td>
<td>170(^b)</td>
</tr>
<tr>
<td>P(_{1444})Ms</td>
<td>-204 ± 11</td>
<td>-410 ± 10</td>
<td>-19.7</td>
<td>39.6</td>
<td>103(^b)</td>
</tr>
</tbody>
</table>

\(^a\)PPW determined directly at a w|IL interface

\(^b\)PPW calculated based on formal transfer potentials of anion and cation at a w|DCE interface

\(^c\)includes ±1 σ
The formal transfer potentials, the values of Gibb’s free energy of transfer, and an estimate of the PPWs for the 8 ILs of study are listed in Table 3.3. These values indicate that the imidazolium-based ionic liquids would suffer from a small PPW and, hence, would be hydrophilic. Whilst the imidazolium ILs appear unsuitable, the alkyl phosphonium-based ILs afford a larger PPW that could be used to accommodate the FIT of uranyl ions or other actinides. Three ions were used as internal standards in these measurements: tetramethylammonium (TMA\(^{+}\)), perchlorate (ClO\(_{4}^{-}\)), and tetraphenylborate (TPB) with formal transfer potentials of 160 [42], −170 [39], and 342 mV [39], respectively. These three standards were chosen so as to minimize the overlap of the analyte and reference peaks, and additionally to satisfy one of the criteria born from the simulation results; because of the asymmetric diffusion regime, an anion formal IT potential should always be standardized using a known anion transfer potential and vice versa for a cation. Sometimes IT overlap prevented the determination of half-wave potential of the cell using the steady state wave, therefore the half-wave potential was calculated using the peak potential through the relationship described by Bard et al. [43] in equation 3.6 above. The peak potential, \( \Delta_{\phi} \), was determined using the potentiostat software and cross-referenced using a graphing program. The published value for methyl sulphate, −350 mV [37], was found to be close to that discovered herein, −410 mV.

The literature value for TBA\(^{+}\) is −225 mV [44] whilst the measured value at the micro-ITIES was −263 ± 5 mV which is in good agreement with the literature. This particular IL was of significant viscosity (established qualitatively) and, despite evidence that the PPW at the w||IL interface should be quite large, a micro-ITIES would not form. The type of electrostatic interaction observed by Matsumiya et al. [13] could be disrupting the establishment of a cohesive w||IL interface thus preventing us from measuring the PPW directly. As mentioned previously, the cation component of the P\(_{66614}\)NTf\(_{2}\) IL did not appear within the PPW afforded by the w||DCE interface. While this does not permit the calculation of the size of the PPW, the transfer of P\(_{1444}^{+}\) at −204 mV indicates the trend of increasing hydrophobicity and correlates well with the measured PPW at the w||IL interface of P\(_{66614}\)NTf\(_{2}\).
3.4.4 - Determination of $\Delta'_w\phi$ at a Large $w|\text{DCE}$ interface

In order to verify the formal transfer potential values obtained using the micro-ITIES, a large $w|\text{DCE}$ interface (Cell 3.3) was employed. The large interface is distinguished from the micropipette counterpart in that only linear diffusion exists; hence, ITs will exhibit peak-shaped waves in both the forward and reverse potential scans. Figure 3.9 shows the CV obtained at the large $w|\text{DCE}$ interface for a blank solution containing only the supporting electrolytes (black dashed curve) and after addition of 1 drop each of 5 mM $\text{P}_{66614}\text{NTf}_2$ and 5 mM TBAP in DCE. The initial and switching potentials were set at $-0.350 \text{ V}$ and $0.450 \text{ V}$, respectively. The transfer of two ions can be discerned and these have been identified as $\text{NTf}_2^-$ and $\text{ClO}_4^-$. Using $\text{ClO}_4^-$ as the internal standard with a formal transfer potential of $-0.170 \text{ V}$ [42] the formal transfer potential of the imide ion was calculated as 16 mV and is in excellent agreement with the value obtained at the micro-ITIES of 17 mV. The accuracy of this value constitutes the success of applying the theoretical correction factor to the experimental data. It also highlights the necessity to standardize the transfer potentials using the same sign of ions, i.e. cations should be used to standardize cations and anions used for anion calibration, in the case of micro-ITIES where, unlike the large ITIES, the asymmetric diffusion regime can influence the half-wave potential.

![Cyclic voltammetry at w|DCE large-ITIES utilizing Cell 3.3 for blank (black, dashed curve) and after addition of 1 drop each of 5 mM solutions of $\text{P}_{66614}\text{NTf}_2$ and TBAClO$_4$ (red curve) to the DCE phase; the potential range was set from $-350$ to $450 \text{ mV}$, with $\Delta'_w\phi_{\text{initial}} = -350 \text{ mV}$, and $v = 30 \text{ mV} \cdot \text{s}^{-1}$.](image_url)

**Figure 3.9:** Cyclic voltammetry at $w|\text{DCE}$ large-ITIES utilizing Cell 3.3 for blank (black, dashed curve) and after addition of 1 drop each of 5 mM solutions of $\text{P}_{66614}\text{NTf}_2$ and TBAClO$_4$ (red curve) to the DCE phase; the potential range was set from $-350$ to $450 \text{ mV}$, with $\Delta'_w\phi_{\text{initial}} = -350 \text{ mV}$, and $v = 30 \text{ mV} \cdot \text{s}^{-1}$.
3.5 - Conclusions

The finite element analysis of cyclic voltammetry at the micro-ITIES hosted by a micropipette proved invaluable in determining the optimal experimental conditions to attempt the hydrophobicity study of ILs. It was discovered that a constant inner diameter of the pipette was necessary in order to generate a consistent CV experiment which could easily be reproduced. This led to the development of the Pt-wire etching methodology. The pipette $R_g$ was maintained at a factor greater than 40 in order to obtain a steady-state current value for ion transfer predicted by theory. The simulation study provided a 50 mV correction factor for IT at a 25 μm diameter pipette. This correction factor could be cancelled mathematically by using internal references of like charges relative to the ion of interest when calculating its IT formal transfer potential and ultimately the Gibb’s free energy of IT. The experimental study of 8 ILs distinguished a possible ion-pair effect that differentiates the hydrophobicity of ammonium-based ILs from phosphonium analogues and the data was further corroborated by the use of a large-ITIES. The imidazolium ILs studied showed limited PPWs making them unsuitable for IT or FIT study and ultimately eliminates them as useful dilutants in uranium extraction in the nuclear fuel cycle; this is in agreement with current research [39]. It is hoped that this study furthers continued interest in IL characterization towards their potential use in improved metal extraction techniques, utilizing their superior distribution coefficients to achieve greater selectivity and recovery.

3.6 - References


Chapter 4.1 - Hydrophobic alkylphosphonium ionic liquid for electrochemistry at ultramicroelectrodes and micro liquid|liquid interfaces

4.1.1 – Introduction

Owing to their unique properties, room temperature ionic liquids (ILs) have been the subject of widespread research as alternatives to traditional molecular solvents in multiple chemical disciplines including organic synthesis [1, 2], electrochemistry [3-10], and inorganic chemistry [11-13]. ILs have performed well in applications such as fuel cells, electrochemical sensors, semiconductor thin film fabrications [14, 15], and solvent extractions [16-19].

Recently, ILs have been sought as replacement solvents in extraction processes after they demonstrated high metal distribution ratios [16-19]. The extraction of uranium and transuranic elements has been performed for the last 50 years using the Plutonium URanium EXtraction (PUREX) process with tributylphosphate (TBP) as a ligand and an aqueous/n-dodecane solvent system [20, 21]. This process operates at low pH where a neutral metal-nitrito complex is generated via coordination of TBP to the metal center, and can be transferred selectively to the organic phase [22, 23]. IL investigations surrounding the PUREX process have mainly utilized imidazolium-based ILs [18, 19], many of which have been shown to be hydrophilic, with the exception of those imidazoliums containing long chain alkyl substituents. Further investigation using the aqueous-imidazolium IL system showed that at moderate pH (low HNO₃ concentrations) a cation exchange process predominated [18] whereby the imidazolium component of the IL leached into the aqueous phase in exchange for a charged ligand-metal-nitrito complex (e.g. UO₂TBPNO₃⁺). At low pH this process was not observed; however, moderate pH aqueous rinses are used to retrieve the metal at the end of the reclamation process. Therefore, this leaching could become a significant problem. In order to prevent this cation loss, other hydrophobic ILs have been investigated [4, 7, 24, 25]. It is interesting to note that the above extractions are tightly related with charge transfer at the interface between two immiscible electrolytic solutions (ITIES) [26, 27]. Ding et al. therefore have tested eight ILs that were selected from commercially available resources [4], expecting a very high degree of hydrophobicity for further electrochemical study of the above metal extraction at the water|IL (w|IL) interfaces.
While most ILs do show a large potential window for conventional redox reactions in homogeneous electrolyte solutions [3], the 8 ILs investigated were not hydrophobic enough for charge transfer reactions at w|IL interfaces [4]. Some cations such as imidazolium are sometimes not lipophilic enough as represented by their ion transfer potentials. Sometimes the anions such as phosphinates, imides, and sulphates are quite hydrophilic[4]. Either one of them in combination limits the polarizable potential window (PPW) for direct w|IL biphasic electrochemistry. Kakiuchi and his co-workers[7-9, 24, 28-30] and Samec’s group[25, 31, 32] have been pioneers investigating charge transfer at w|IL interfaces, and used ammonium cations paired with fluorinated tetraphenylborate anions. These ILs are very hydrophobic but generate ILS of high to moderate viscosity [9, 25] while also being expensive. The w|IL electrochemistry has recently been the subject of a rigorous review by Samec, Kakiuchi, and their co-worker [26].

Fundamentally, it would be of great interest to explore the IL double layer structure and its influences on charge transfer (CT) reactions, applicability of existing CT theory, and dynamic responses of the water|IL interface to the applied Galvani potential difference[3, 5, 6, 8, 26, 30, 33-37].

It has been discovered that phosphoniums such as trihexyltetradecylphosphonium are very hydrophobic and their transfer at the water|1,2-dichloroethane (w|DCE) interface cannot be observed [4]. Thus, in the present chapter, a phosphonium-based IL, trihexyltetradecylphosphonium tetrakis(pentafluorophenyl)borate (P_{66614}TB), was prepared, which, while viscous (1.2 Pa·s at 60 ºC), has a moderate cost of synthesis ($10 /g at the time of submission) in comparison to many commercialized ILs. A simple and facile preparation strategy is also discussed along with a cursory examination of the ferrocene/ferrocenium (Fc/Fc⁺) redox chemistry at a solid ultramicroelectrode (UME). On the other hand, experimental methodology for testing the hydrophobicity of the prepared IL at the ITIES housed at the tip of a micropipette [4, 38, 39] has been further improved. This technique has been designed to use a modicum of IL sample and the size of the PPW formed at the ITIES has been shown to be directly proportional to the hydrophobicity of the IL [26]. The PPW was measured and calibrated investigating simple ion transfers (ITs) at the w| P_{66614}TB micro-ITIES.
Simulations based on the Butler-Volmer kinetics model and finite element analysis through Comsol 3.5a Multiphysics software are employed to describe the kinetics of CT and IT at UME/IL and w/IL interfaces, respectively.

4.1.2 - Theory

Figure 4.1.1: Simulation geometry for (A) solid Pt disc UME; (B) liquid|liquid micro-ITIES

Simulations were conducted using COMSOL 3.5a Multiphysics software with finite element analysis. The two geometries are illustrated in Figure 4.1.1A and B and mimic a vertical cross-section of the solid Pt-UME and the liquid|liquid micro-ITIES respectively. In Figure 4.1.1A, starting at the bottom left and working counter-clockwise, the boundaries consisted of the electrode surface, insulator, concentration, and an axis of
symmetry. Figure 4.1.1B includes the glass capillary with an aqueous reservoir at the top and the interfacial boundary housed at the tip of the micro-channel, with a radius of 12.5 µm. The ionic liquid phase surrounds the pipette tip with the outer surfaces designated as concentration boundaries and the pipette walls as insulator.

The ions and redox species in the simulation domains were diffusion controlled, following Fick’s second law as described in equation 2.1. The electrochemical reactions under consideration are the simplest: a one-electron, one step quasi-reversible reaction (equation 2.2), and single IT, from aqueous to ionic liquid phases (w to IL), shown respectively as:

\[ i_w \xrightleftharpoons[k_f]{k_b} i_{IL} \]  

These were simulated using the Butler-Volmer kinetic model with the rates of the forward \((k_f)\) and reverse \((k_b)\) reaction given using equations 2.3 and 2.4. In the case of liquid|liquid electrochemical simulations, these terms are identical except that, by convention, \(E\) and \(E'\) become \(\Delta w_{IL} \phi\) and \(\Delta w_{IL} \phi'\) which are the applied Galvani potential difference across the w|IL interface and the formal IT potential, respectively.

The current generated at the electrode/ITIES surface was calculated as a function of the integral of the flux of either the ions or redox species using equation 3.3. The potential of the CV was swept linearly, forward and backward, using a triangular waveform, equation 2.5 [40]. COMSOL simulation specifications and codes are available in Appendix B.

4.1.3 - Experimental

4.1.3.1 Chemicals

All chemicals were of reagent grade and used as purchased without further purification. Trihexyltetradeccylphosphonium chloride (P66614Cl) was purchased from Strem Chemicals Inc. ($1.04 /g, Newburyport, MA). 1,2-dichloroethane (DCE) (anhydrous), dichloromethane (CH2Cl2), chlorotrimethylsilane, potassium chloride, ferrocene, sodium tetraphenylborate (NaTPB), tetraphenylarsonium chloride (TPAsCl), lithium carbonate, and tetramethylammonium nitrate (TMANO3) were obtained from Fluka/Sigma-Aldrich (Mississauga, ON). Potassium tetrakis(pentafluorophenyl)borate (KTB) was purchased
from Boulder Scientific Company ($6.50 /g, Mead, Colorado). All aqueous solutions were prepared using Milli-Q water (18.2 MΩ).

4.1.3.2 Preparation of Micropipettes to house micro-ITIES

Fabrication of the micro-ITIES pipette has been described in detail in section 2.3.3.

![Figure 4.1.2: Experimental apparatus for monitoring the liquid|liquid interface. Inset is a photograph taken using the CCD camera with magnifying lens assembly of the micropipette tip.](image)

Figure 4.1.2 shows the micro-ITIES experimental setup. The micropipette fabrication and setup can be found in section 2.3.3. Careful attention was paid to maintaining the aqueous|organic interface at the orifice of the micropipette using the attached syringe and monitoring using a Moticam 2000 CCD camera (Motic, Richmond, BC) equipped with a variable 12× zoom lens assembly (Navitar, Rochester, NY). Figure 4.1.2 inset shows a digital image acquired using this setup of the micropipette submerged into the IL phase. The electrochemical cells utilized during the micro-ITIES experiments are detailed below:

\[
\text{Ag} | \text{Ag}_2\text{SO}_4 | 5 \text{ mM Li}_2\text{SO}_4(aq) | \text{P}_{6614} \text{TB} | \text{AgTB} | \text{Ag} \quad \text{(Cell 4.1.1)}
\]

\[
\text{Ag} | \text{Ag}_2\text{SO}_4 | 10.0 \text{ mM Li}_2\text{SO}_4(aq) | 1.5 \text{ mM TPAsCl} | \text{P}_{6614} \text{TB} | \text{AgTB} | \text{Ag} \quad \text{(Cell 4.1.2)}
\]
\[
\text{Ag} \mid \text{Ag}_2\text{SO}_4 \mid 10.0 \text{ mM Li}_2\text{SO}_4(aq) \parallel \text{P}
_{66614}\text{TB} \mid \text{AgTB} \mid \text{Ag} \quad (\text{Cell 4.1.3})
\]

\[
\text{Ag} \mid \text{Ag}_2\text{SO}_4 \mid 5.0 \text{ mM Li}_2\text{SO}_4(aq) \parallel \text{P}
_{66614}\text{TB} \mid \text{AgTB} \mid \text{Ag} \quad (\text{Cell 4.1.4})
\]

### 4.1.3.3 Ultramicroelectrodes

UME disk electrodes were prepared as described in section 2.3.2. All UME experiments were performed in pure IL or IL with dissolved ferrocene (Fc) (6.0 mmol·L\(^{-1}\)) using a silver counter/quasi-reference electrode and purged with argon gas for 30 minutes. The quasi-Ag-reference electrode demonstrated good reproducibility between consecutive CVs and the oxidation potential for Fc\(^+\)/Fc was measured as 0.257 ± 0.020 V in the experimental scale. Comparatively, a silver wire is a low cost alternative to commercially available reference electrodes.

#### 4.1.3.4 Preparation of P\(_{66614}\)TB IL

50 mL of CH\(_2\)Cl\(_2\) was added to a mixture of P\(_{66614}\)Cl (5.182 g, 10.0 mmol) and KTB (7.195 g, 10.2 mmol); the solution was stirred at room temperature for 48 hours as shown in Figure 4.1.3. After 48 hours, the organic phase changed colour from clear to amber and the presence of KCl was confirmed qualitatively by its distinct granular appearance relative to KTB, which appears as a fine powder.

![Reaction Equation](image)

**Figure 4.1.3**: Ionic liquid preparation in dichloromethane at room temperature with stirring for 48 hours.

The organic suspension was then vacuum-filtered, using a Büchner funnel, to remove solid KCl, and then extracted ten times with Milli-Q water. The aqueous washings were retained and analyzed using ion chromatography (IC) to test for chlorine content using the
calibration curve method \( (R^2 = 0.99) \) eliciting \( \text{Cl}^- \) concentrations of 59.52, 7.65, 1.75, 0.54, 0.16, 0.14, 0.08, 0.07, 0.06, and 0.06 ppm for extractions 1 to 10, respectively; 0.06 ppm is equivalent to 1.7 µmols/L of \( \text{Cl}^- \). The organic solvent was removed by rotary evaporation and the resultant viscous yellow liquid (11.3184 g, 9.7 mmol, 97.5 % recovery) was analyzed using NMR and ESI-TOF MS. A small amount (~ 5 mg) was dissolved in DCM and the pH of this solution was tested qualitatively using pH paper (pHydrion Paper, Micro Essential Laboratory, Brooklyn, N.Y.); the IL solution was found to be in the 1.1 – 2.1 pH range. It has been shown that ferrocene (Fc) oxidizes to ferrocenium (Fc\(^+\)) in ILs under low pH [46], therefore, the IL was dissolved in DCM and extracted with lithium carbonate saturated aqueous washings until the organic phase demonstrated a neutral pH result. The organic phase was subsequently washed with Milli-Q water with the rinses analyzed by IC; the seventh extraction contained 0.40 ppm lithium concentration. The source of this low pH was found to be the \( \text{P}_{66614}\text{Cl} \) starting material whose common contaminant is HCl [47].

**4.1.3.5. Instrumentation**

*Electro-Spray Ionization-Time of Flight Mass Spectrometry (ESI-TOF MS).* All ESI-TOF MS data was collected using a Micromass LCT Mass Spectrometer (Waters, Milford, MA) in the positive ion mode with capillary, sample cone, and extraction cone voltages of 5000, 7, and 0 V respectively. The acquisition and interscan delay time were set to 4 and 0.4 s, respectively.

*NMR.* NMR experiments were carried out using a Varian Mercury 400 MHz NMR spectrometer. NMR spectra can be found in Appendix C.

*Rheometry.* Viscosity measurements of the ionic liquid were characterized by measuring the shear stress versus shear rate using an AR1500ex Rheometer from TA Instruments (Grimsby, Ontario) with a 40 mm upper plate diameter and a plate gap of 800 µm. Temperature of the plates was controlled using a circulating water heater.

*Density.* Temperature controlled density measurements were performed using a DMA 4500 Density Meter (Anton Paar Canada, Saint Laurent, Quebec).
Ion Chromatography (IC). IC experiments were conducted using the following components: Waters 746 Data module, Varian 2510 HPLC pump, Varian CM-2 conductivity monitor, and using a Hamilton PRP-X100 IC column (250 mm in length with 10 µm particle size).

Electrochemistry. Electrochemical measurements were performed using the Modulab System from Solartron Analytical (Ametek Advanced Measurement Technology, Farnborough, Hampshire, United Kingdom) equipped with a Femto ammeter and using a feedback control loop. All electrochemical experiments were conducted using a temperature controlled water circulator (VWR, Mississauga, ON) maintained at 60 °C unless otherwise stated.

Conductivity. The complex impedance method was used to determine the conductivity of ionic liquid and organic solvent samples. This method involves the measurement of cell impedance versus AC potential frequency which was swept linearly from 10 kHz to $10^{-2}$ Hz. The cell consisted of two parallel glassy carbon-plated electrodes with a cell constant, $l/A_e = 8.5 \text{ cm}^{-1}$; where $l$ is the distance between the electrodes and $A_e$ is the electrode area. The cell constant was determined through calibration using standard solutions of KCl. Data were obtained using models 1287 potentiostat and 1252 frequency response analyzer from Solartron Analytical (Ametek Advanced Measurement Technology, Farnborough, Hampshire, United Kingdom). Temperature was controlled using a circulating water bath (VWR, Mississauga, ON).

Computations. All simulations using COMSOL 3.5a took between 3-5 minutes and were performed using an Acer Aspire laptop (Acer America Corporation (Canada), Mississauga, ON) with a 1.66 GHz Intel Core 2 Duo processor and 2 GB of DDR2 RAM. Curve fitting was performed using Igor Pro 6.12a (Wavemetrics Inc., Portland, OR) with between 10 and 200 iterations. Custom Igor procedures are available upon request.
4.1.4. Results and Discussion

4.1.4.1 $P_{66614}TB$ Structural Elucidation

The $^1$H NMR spectroscopy revealed the following chemical shifts (δ) (ppm, CDCl$_3$): 0.87 (12H, m), 1.27 (32H, m), 1.44 (16H, m), and 1.931 (8H, m) for the prepared IL. The multiplet at 0.87 ppm appears to be two overlapping triplets and, with an integration value of 12H, indicates that this can most likely be assigned to the methyl groups at the ends of the alkyl chains. The four -CH$_2$ groups adjacent to the phosphorus atom probably generate the most down shifted signal at 1.931 ppm, which integrates to 8H. The other -CH$_2$ components of the alkyl chains are difficult to assign and generate the signals that appear at 1.27 and 1.44 ppm. The total integration is in good agreement with the chemical structure and the chemical shifts are consistent with those previously reported in the literature [48] for ionic liquids with this cation. It is important to note that no further $^1$H signals were observed indicating that the fluorination of the TB anion is complete (no $^1$H signals in the aromatic region) and this is indicative of the excellent quality of the KTB salt. The IL was stored in a desiccator under vacuum; no additional $^1$H signals could be attributed to water which is indicative of its dryness. ESI-TOF MS showed a large m/z peak at 485.3 corresponding to the $P_{66614}$ cation and three peaks at 1646.6, 2810.4, and 3977.3 which correlate to $(P_{66614})_2TB^+$, $(P_{66614})_3(TB)_2^+$, and $(P_{66614})_4(TB)_3^+$ clusters with calculated values of 1646.7, 2809.6, and 3972.4 m/z respectively. It is important to note that no peak corresponding to the reactant, $P_{66614}Cl$, was observed. While it is still necessary to perform solvent extractions of the CH$_2$Cl$_2$ phase with water, using a single polar organic solvent can greatly reduce or eliminate the number of extractions required to remove KCl relative to performing this reaction in a methanol/water solvent mixture [49, 50].

4.1.4.2 Cyclic Voltammetric and Chronoamperometric investigation on Ferrocene diffusion in the IL at a Pt-UME

$P_{66614}TB$ was employed as electrolyte solution to run cyclic voltamogramms (CVs) of Fc at a Pt disc-UME. Figure 4.1.4 shows CVs taken at 60 °C with a blank IL solution (A), and with 6.0 mmol/L of Fc in the IL (B), respectively. The blank CV was initiated at 0.000 V with a potential range from 1.900 V to −1.800 V and a scan rate of
0.050 V/s. The CV in Figure 4.1.4A illustrates a wide potential window (~3.5 V), which is critical for electrochemical applications; a common trait amongst ILs [51]. Before each CV, the IL was purged with argon gas for approximately 30 minutes; however, some dissolved oxygen was still present and limited the potential window towards more negative potentials. With increased Ar purging a larger potential window can be obtained (~4.0 V) (data not shown); the use of a glovebox is currently being investigated.

**Figure 4.1.4:** CVs of a 25 µm diameter Pt disc electrode immersed in P_{66614}TB ionic liquid (A) without Fc; initial potential of 0.000 V and a potential range from -1.800 to 1.900 V at 0.050 V∙s\(^{-1}\). (B) with 6.0 mmol∙L\(^{-1}\) of Fc; initial potential of -0.250 V and a potential range from -1.500 to 1.800 V at 0.050 V∙s\(^{-1}\). Potential versus Ag (quasi-ref).

Additionally, it is interesting to note that the blank CV is clean, without anomalous peaks indicative of impurities. The absence of these peaks demonstrates that the IL preparation is facile and effective in generating quality IL for electrochemistry. After addition of Fc, the scan was initiated at -0.250 V and proceeds in the forward direction towards more positive potentials. An anodic peak with a peak current, \( i_{p,a} \), of 0.3 nA was observed at 0.257 V (\( E_{p,a} \)), indicating oxidation of Fc to Fc\(^{+}\). The limit of the potential window was reached at 1.800 V with a sharp increase in current and was
subsequently scanned in the reverse direction towards more negative potentials. A cathodic peak with a peak current, $i_{p,c}$, of −0.4 nA was observed at 0.170 V ($E_{p,c}$), indicative of the reduction of Fe$^+$ generated in the forward scan to Fc. The edge of the potential window was reached at −1.500 V and the potential was then swept in the forward direction to a final potential of −0.250 V. The Fc/ Fe$^+$ redox couple in Figure 4.1.4B shows a peak current ratio $i_{p,c} / i_{p,a} \approx 1.22$, failing one condition for a reversible electrochemical reaction. The CV also demonstrates a peak-to-peak separation of $\Delta E_p = E_{p,a} - E_{p,c} = 0.087$ V exceeding the value of 0.066 V, the other criterion for a reversible reaction.

Since the measured current is in the range of 0.3 nA and the resistance of the IL between the Pt-UME and reference electrode is 7.3 MΩ, the potential drop is expected to be less than 2.2 mV. It is therefore unlikely that the uncompensated ohmic resistance plays a role in the large peak-to-peak separation. Table 4.1.1 shows conductivity of P$_{66614}$TB IL at 25, 35, 45, 60, and 70 °C, anhydrous 1,2-dichloroethane (DCE), 5 mM DCE solutions of P$_{66614}$TB and tetradecylammonium tetrakis(parachlorophenyl)borate (TDATPBCl) at room temperature. The IL shows an increase in conductivity from 96.8 to 112.9 µS·cm$^{-1}$ in the temperature range of 25 and 70°C. These values are comparable to those of other ILs [51]. Both pure IL and 5 mM IL in DCE have similar conductivity to that of 5 mM TDATPBCl in DCE, a commonly used organic phase supporting electrolyte [4]. These conductivity measurements support the point that the IL resistance does not affect the peak separation in the cyclic voltammetry of ferrocene.

**Table 4.1.1:** Conductivity measurements obtained using the complex impedance method.

<table>
<thead>
<tr>
<th>System</th>
<th>Conductivity /µS·cm$^{-1}$</th>
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<tbody>
<tr>
<td>P$_{66614}$TB at 25°C</td>
<td>96.8</td>
</tr>
<tr>
<td>P$_{66614}$TB at 35°C</td>
<td>94.4</td>
</tr>
<tr>
<td>P$_{66614}$TB at 45°C</td>
<td>93.2</td>
</tr>
<tr>
<td>P$_{66614}$TB at 60°C</td>
<td>102.0</td>
</tr>
<tr>
<td>P$_{66614}$TB at 70°C</td>
<td>112.9</td>
</tr>
<tr>
<td>DCE</td>
<td>17.6</td>
</tr>
<tr>
<td>5 mM P$_{66614}$TB in DCE</td>
<td>124.8</td>
</tr>
<tr>
<td>5 mM TDATPBCl in DCE</td>
<td>84.9</td>
</tr>
</tbody>
</table>
Additionally, the high viscosity of the IL causes a decrease in the diffusion coefficients of ferrocene and ferrocenium. This elicits a decline in peak current intensity for redox couples in ILs relative to traditional molecular solvents of low viscosity as can be seen from equation 2.7 [52]. Since both anodic and cathodic currents show a peak shape varying with applied potential, the diffusion coefficient for Fc ($D_{Fc}$) was determined using equation 2.7 [52] through a series of CV experiments by altering the scan rate; this is termed herein as the CV method.

Double potential step chronoamperometry (CA) was also used to estimate the diffusion coefficients of the reduced and oxidized forms of Fc at the 25 μm electrode, which is similar to that at mm size electrodes [35], using two methods: the first was formulated by Aoki and Osteryoung [53, 54] (referred to as method 1) and demonstrated recently by Kosmulski et al. [55] and Quinn et al. [3]; the second technique was developed by Shoup and Szabo [56] (referred to as method 2) and has been shown to be effective in the characterization of diffusion regimes in ionic liquids by the work of Compton et al. [57].

The technique pioneered by Aoki and Osteryoung [53, 54] began with the assumption that the diffusion coefficient of the reduced and oxidized species were equal; therefore, the analysis of the second potential step is done only as an estimate of ferrocenium diffusion. Typical $I-t$ transient curves obtained during CA of Fc oxidation and generated Fc$^+$ re-reduction, for the first and second steps, respectively, are shown in Figure 4.1.5A where the potential was held at -0.250 V, stepped to 0.600 V, then stepped back to -0.250 V; each step lasted 20 seconds for each potential. Figure 4.1.5B shows a typical $I-t^{-1/2}$ plot for each step of the chronoamperogram, from which $i_{ss}$, the steady state current was determined through extrapolation from this curve to the y-intercept. Diffusion coefficient values using method 1 of 12.8 and $1.9 \times 10^{-9}$ cm$^2$/s were obtained in $P_{66614}$TB at 60°C respectively for Fc and Fc$^+$ from the slopes of the lines of best-fit to equation 2.6 [54]. These values ascertain a diffusion ratio of $D_{Fc}/D_{Fc^+}$ of 6.74 which is similar to that observed by Compton et al. [57] of 7.80 for $D_{Fc}/D_{Fc^+}$ in trihexyltetradecylphosphonium trifluorotris(pentafluoroethyl)phosphate.
Figure 4.1.5: (A) Chronoampermetry curves taken in a 6.0 mmol·L⁻¹ Fc P₆₆₆₁₄ TB solution; potential stepped to 0.600 V and held for 20 s, then stepped to -0.250 V and held for 20 s. (B) $I$ vs $t^{1/2}$ curve. (C) $I/i_{ss}$ vs $t^{1/2}$.

Method 2 employed equations 4.1.5 and 4.1.6 below, fitting the $I$-$t$ curve without modification [56].

\[
I = 4nFDr_0 f(\tau) \quad (4.1.5)
\]

\[
f(\tau) = 0.7854 + 0.8863\tau^{-1/2} + 0.2146\exp(-0.7823\tau^{-1/2})\]

where, \( \tau = \frac{4Dt}{r_d^2} \) \quad (4.1.6)
**Table 4.1.2**: Diffusion coefficients, peak-to-peak (ΔEₚ) separations, and 𝑖_{𝑝,𝑐} / 𝑖_{𝑝,𝑎} for the ferrocene/ferrocenium redox couple in (A) P₆₆₆₁₄TB and (B) P₆₆₆₁₄NTf₂ at temperatures indicated. Included are the densities and viscosities of these two ILs at temperatures.

Diffusion coefficients have been determined through three methods: CV method, method 1(Aoki and Osteryoung), and method 2 (Shoup and Szabo). ΔEₚ and 𝑖_{𝑝,𝑐} / 𝑖_{𝑝,𝑎} are listed for three scan rates: 0.025, 0.049, and 0.100 V∙s⁻¹.

<table>
<thead>
<tr>
<th>A</th>
<th>P₆₆₆₁₄TB</th>
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<tr>
<td></td>
<td>temp °C</td>
<td>CV method</td>
<td>step 1</td>
<td>step 2</td>
<td>step 3</td>
<td>0.025 V⁻¹</td>
<td>0.049 V⁻¹</td>
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The temperature of the system was varied from 25 to 35, 45, 50, 60, 70, 80, and 90°C and the diffusion coefficients determined for each temperature and analytical method have been compiled into Tables 4.1.2A and 4.1.2B for P₆₆₆₁₄TB and commercially available IL, trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)-imide (P₆₆₆₁₄NTf₂), respectively. As expected, the diffusion coefficient of Fc increased with increasing temperature, 0.3 × 10⁻⁹ cm²∙s⁻¹ at 25°C to 84.3 × 10⁻⁹ cm²∙s⁻¹ at 90°C for P₆₆₆₁₄TB using method 1, step 1 and 9.8 × 10⁻⁸ cm²∙s⁻¹ at 25°C to 115.6 × 10⁻⁸ cm²∙s⁻¹ at 90°C for P₆₆₆₁₄NTf₂ using method 1, step 1. This tendency agrees well with that of viscosity changes determined by rheometry as listed in Table 4.1.2A and 4.1.2B: the viscosity changes from 17993.8 to 245.7 mPa∙s and 332.3 to 36.3 mPa∙s with increasing temperature from 25 to 90°C for P₆₆₆₁₄TB and P₆₆₆₁₄NTf₂, respectively. Surprisingly, the diffusion coefficient determined using the CV method, method 1, and method 2 for the commercially available P₆₆₆₁₄NTf₂, at 25°C shown in Table 4.1.2B, of 20.6, 9.8, and 32.1 × 10⁻⁸ cm²∙s⁻¹, respectively, are in poor agreement with one another, while method 1
is in fair agreement with that reported in the literature at a gold nanoelectrode assembly [49] using the scan rate approach; \(2.0 \times 10^{-8}\) cm\(^2\)s\(^{-1}\). Additionally, the density measured in this report at 25°C, 1.0684 g·cm\(^{-3}\), correlates well with that described by the manufacturer, 1.07 g·cm\(^{-3}\), and the viscosity is in fair agreement with that previously reported [58]: 277 mPa·s.

Comparing the values of \(D\) obtained using the three methods, the greatest correlation in \(P_{66614}\)NTf\(_2\) occurs at low temperatures, whilst the values diverge as the temperature increases. While it is unclear as to which method is the most accurate there exists a large disparity in the values obtained. Method 1 consistently gave the lowest result, followed by the CV method, and method 2 generated the highest result.

The peak current responses observed in the CV experiments at 25 °C and 0.049 V·s\(^{-1}\) (Table 4.1.2A, \(i_{p,c}/i_{p,a}\)) demonstrate a cathodic to anodic peak current ratio of 1. Therefore, while the viscosity is known to slow down the diffusion of both ferrocene and ferrocenium, it can therefore be concluded that no homogeneous kinetic deviations are present (or at least detectable) and the system conforms to contemporary electrochemical theory. It is interesting to note that this peak current ratio varies with scan rate and temperature. In general \(i_{p,c}/i_{p,a}\) for \(P_{66614}\)TB seems to increase with increasing temperature, showing a moderate decrease with increasing scan rate. A different trend is seen in \(P_{66614}\)NTf\(_2\). Whereby the peak current ratio is 1.43 at 25°C and 0.025 V·s\(^{-1}\) and decreases to almost 1 at 90°C.

The \(\Delta E_p\) values for both ionic liquids at 0.025, 0.049, and 0.100 V·s\(^{-1}\) are also listed in Table 4.1.2A and B for the various temperature settings. \(\Delta E_p\) for \(P_{66614}\)TB shows a minor decrease with increasing temperature, whilst in \(P_{66614}\)NTf\(_2\) it increased. It was noticed that the commercial IL approaches a steady state diffusion regime and, therefore, these high peak-to-peak separations are not commensurate with any IL phenomena.

The viscosity of the prepared IL at 25°C is high compared to similar hydrophobic ILs [24, 25, 28, 30, 51]; however, the low melting point of \(P_{66614}\)TB (below room temperature) has practical benefits commensurate with a wider temperature range that is not typical of other hydrophobic ILs.

The large increase in diffusion coefficients and decrease in viscosity, shown in Table 4.1.2, are not accompanied by proportional increase in conductivity over the same
temperature range, as described in Table 4.1.1. This is rather a surprise. Conductivity measurements are usually an indication of electrochemical properties. Nevertheless, it should be reiterated for these conductivity measurements to be viewed as an approximation owing to the unexplained lack of increase in conductivity with temperature.

Ion-pair formation in IL systems has been observed elsewhere. The cationic component of an ionic liquid has been shown to stabilize the halogen leaving group in a carbon-halogen bond cleavage, which makes the reaction more favourable [36]. It has also been shown that ILs can influence not only the selectivity of an organic reaction but also its direction, as demonstrated by Earle et al. [1] who investigated the preparation of nitrobenzene and nitrotoluene in imidazolium ionic liquids. By varying the anion component of the IL they showed that not only could they alter the selectivity of nitrating the 2, 3, and 4 position of toluene but that they could also oxidize toluene to benzoic acid [1].

Therefore, it is possible that the diffusion of Fc\(^+\) may be influenced not only by the viscosity of the IL but also by anionic coordination or ion-pair-like interactions. Thus the movement (i.e. diffusion) of Fc\(^+\) away from the electrode surface is impeded and this is reflected as a decrease in \(D_{Fc^+}\), but results in an increase in \(i_{p,c}\) intensity. Any Fc\(^+\) remains closely associated with the electrode surface and thus is readily available for re-reduction resulting in an increase in the cathodic peak current; i.e. the effective concentration, \(c^*_o\) from equation 4.1.7, of Fc\(^+\) at the electrode surface generates the observed \(i_{p,c}\) increase.

Furthermore, as the temperature increases the ratio of cathodic to anodic peaks increases from a 1:1 ratio at 25 °C up to 1.4:1 at 45 °C. It is proposed that this is the result of an increase in availability of the IL anion, TB, to participate in intermolecular interactions. These interactions generate a depression in the Fc\(^+\) diffusion coefficient, which prevents electrochemically generated Fc\(^+\) from moving into the solution. At lower temperatures, the diffusion of each redox species through the IL is equally inhibited by the solutions high viscosity; i.e. that the physical parameters of the IL predominate. As the temperature of the system increases the order of the IL system will decrease allowing more coordination or pseudo-ion-pair formation of TB\(^-\) with Fc\(^+\); this increased
coordination would result in an increase in the effective Onsager radius from Fc to Fc⁺, thus resulting in a lowered diffusion coefficient.

4.1.4.3 Physical insight into ET kinetics

Figure 4.1.6: Experimental (—) and simulated (○) CVs taken using 6.0 mmol·L⁻¹ Fc P₆₆₆₁₄TB solution with a potential range from −0.250 to 0.600 V, an initial potential of −0.250 V and scan rates as indicated. Simulation parameters: \( k^0 = 5 \times 10^{-4} \text{ cm} \cdot \text{s}^{-1} \), \( D_{\text{Fc}} = 3.2 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1} \), and \( D_{\text{Fc}^+} = 5.0 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1} \). Potential versus Ag (quasi-ref).

Figure 4.1.6 illustrates the experimental (—) and overlaid simulated (○) CVs for the 60 °C P₆₆₆₁₄TB Fc/Fc⁺ system. The simulation was first optimized for the 0.025 V·s⁻¹ CV with the initial Fc concentration equal to 6.0 mmol·L⁻¹. Curve fitting was performed qualitatively through visual inspection of the two curves, and once the final parameters for \( D_{\text{Fc}} \), \( D_{\text{Fc}^+} \), and \( k^0 \) were determined, they were fixed and the scan rate was altered. The final values of \( D_{\text{Fc}} \), \( D_{\text{Fc}^+} \), and \( k^0 \) were \( 3.2 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1} \), \( 0.5 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1} \), and \( 5 \times 10^{-4} \text{ cm} \cdot \text{s}^{-1} \) with the scan rates for CVs shown in Figure 4.1.6 A, B, C, D, E, and F being 0.025, 0.036, 0.049, 0.064, 0.081, and 0.100 V·s⁻¹ respectively. The CVs in Figure 4.1.6
show good overlap at low scan rates with some minor deviation in peak current at 0.081 and 0.100 V·s⁻¹; overall this indicates the success of the simulation. The final value of $D_{Fc}$ is in excellent agreement the value obtained experimentally using the scan rate method of $3.5 \times 10^{-8}$ cm²·s⁻¹. The diffusion coefficient of Fc and the value of $k^\circ$ recently reported by Compton and co-workers [57, 59] in imidazolium and phosphonium ILs were both a factor of 10 greater and this is commensurate with the lower viscosity demonstrated by those ILs: P₆₆₆₁₄TB equal to 1206.2 mPa·s whilst Compton’s groups range between 30 and 460 mPa·s [59].

Similar disparities in the diffusion coefficients of other reduced and oxidized species have been observed [35, 60, 61], correlating well with ionic liquid viscosity. Additionally, $k^\circ$ values obtained using scanning electrochemical microscopy (SECM) [34, 35, 60] have reported results similar to those reported using CA [57, 59]. Most groups support the possibility of IL interaction with the charged component of the electroactive species, but suggest that the $k^\circ$ values obtained from such studies should be considered apparent values until the structure of the metal-IL interface can be elucidated [34, 35, 37, 57, 59, 61].

4.1.4.4 Simple Ion Transfer at Micro-ITIES

![Figure 4.1.7: CV obtained at the w/P₆₆₆₁₄TB micro-ITIES (25 µm in diameter) using Cell 4.1.1. The following potentiostat parameters were used: initial potential equal to −0.100 V; upper and lower potentials equal to 0.300 and −0.700 V, respectively; and with a scan rate of 0.020 V·s⁻¹. Potential versus Ag (quasi-ref).]
Figure 4.1.7 shows the CV obtained using Cell 4.1.1 equipped with a heating circulator controlling the temperature at 60 °C. The scan was initiated at −0.100 V at a scan rate of 0.020 V·s⁻¹ and scanned in the forward direction, with increasing potential, until the limit of the PPW was reached at approximately 0.300 V. It is assumed that the positive end of the PPW is limited by the transfer of the supporting electrolytes, Li⁺ transfer from w to IL and the IL component TB⁻ from IL to w. Owing to recently published results [62] for the standard transfer potentials of Li⁺ and TB⁻ at the w|DCE micro-hole ITIES of 0.649 and 0.710 V, respectively, it is probable that Li⁺ transfer is the major contributor. The CV was subsequently swept in the reverse direction from 0.300 to −0.700 V, where the decrease in current is owing to the transfer of the other supporting electrolyte ions, SO₄²⁻ and P₆₆₆₁₄⁺. While the use of polyfluorinated phenylborates as anionic components in ILs has been previously demonstrated to generate wide PPWs at the aqueous-ionic liquid ITIES [7, 24, 25, 30, 31], and so has the use of alkylphosphonium ionic liquids [4]. Their combination is shown here for the first time to elicit a PPW that is comparable to most ILs systems [4, 25, 30] of ~0.8 V, approaching the largest value reported in the literature, ~1.0 V, generated using tetraheptylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (THpATFPB) [24]. It should be noted, however, that the melting point range of THpATFPB is 58–59 °C. Wide PPWs are desirable electrochemical features as they allow for the investigation of a larger array of species through simple ion transfer (IT) and facilitated ion transfer (FIT), while also being an indicator of hydrophobicity [7, 26]. One of the great successful applications of ILs is found in two-phase solvent extraction procedures where they have elicited high distribution ratios [19] for metal complexes like Sr²⁺ extraction with dibenzo-18-crown-6. However, recent data, using imidazolium based ILs [18], has shown that at mild pH (low HNO₃ concentration) a cationic exchange mechanism predominates whereby the cationic component leaches into the aqueous phase and is replaced by the charged metal-complex in the IL phase. In order to inhibit this leaching effect, more hydrophobic ILs have been sought. For the past decade Kakiuchi et al. [10, 29] have studied the w|IL interface demonstrating that the width of the PPW is proportional to the ILs solubility through the following relationship[28]:
\[
\ln K_{wp}^w = -\frac{(\Delta G_{\text{cation}}^{R_{IL\rightarrow w}} + \Delta G_{\text{anion}}^{R_{IL\rightarrow w}})}{RT}
\]  

(4.1.7)

where \( \Delta G_{i}^{R_{IL\rightarrow w}} \) is the Gibbs free energy of transfer of the anionic or cation component of the IL and \( \Delta G_{i}^{R_{IL\rightarrow w}} = z_i F \Delta_{i}^w \phi_i^{w} \). \( \Delta_{i}^w \phi_i^{w} \) is the standard transfer potential of the IL component, estimated here using the return peak potential obtained from the CV in Figure 4.1.7. The transfer potentials of the cation and anion species were estimated to be \(-0.600\) and \(0.200\) V respectively eliciting a \( K_{wp}^w = 8.9 \times 10^{-7} \). Relative to imidazolium-based ILs, which have a solubility factor averaging \(10^{-3}\), the P_{66614}TB IL prepared here is exceptionally hydrophobic.

Figure 4.1.8: CVs obtained using Cells 3 and 4 for curves A and B respectively. For curve A the following calibrated instrument parameters were used: initial potential equal to \(0.000\) V; upper and lower potentials equal to \(0.391\) and \(-0.430\) V respectively; and with a scan rate of \(0.020\) V\(\cdot\)s\(^{-1}\). The following parameters were used for Curve B: initial potential equal to \(0.400\) V; upper and lower potentials equal to \(0.490\) and \(-0.430\) V respectively; and with a scan rate of \(0.020\) V\(\cdot\)s\(^{-1}\).
Liquid|liquid electrochemistry allows the direct measurement of the Gibbs free energy of transfer; however, when this is performed conventionally at an ITIES between water and a molecular solvent the tetraphenylarsonium-tetraphenylborate (TATB), non-thermodynamic assumption is used [26, 63]. The TATB assumption states that the standard Gibbs energy of transfer of tetraphenylarsonium and tetraphenylborate are equal but of opposite sign and, therefore, the potential between the simple IT of these two ions would be the point of zero charge [26, 63]. To calibrate the potential window at the w|P66614TB interface using the TATB assumption, Cells 4.1.2 and 4.1.3 were employed with 1.5 mM of tetraphenylarsronium chloride (TPAsCl) and sodium tetraphenylborate (NaTPB) dissolved in the aqueous phase; Figures 4.1.8A and B show the respective CVs obtained from these two cells. Using the transfer potentials, $E_{1/2}$, for TPAs and TPB of –0.706 and –0.083 V, respectively, the point of zero charge (PZC) was estimated and the CVs in Figure 4.1.8 have been adjusted to reflect this with 0.000 V at the mid-point between the two ion transfers. The calculated $\Delta E_p$ values for IT are equal to 0.121 and 0.150 V for TPAs$^+$ and TPB$^-$, respectively.

Figure 4.1.9: Experimental (—) and simulated (○) CVs obtained using Cell 4.1.4; initial potential of –0.100 V and a potential range from –0.100 to 0.360 V with 0.020 V·s$^{-1}$. Simulation parameters: $k^o = 5 \times 10^{-3}$ cm·s$^{-1}$, $D_{TMA^+,w} = 2.0 \times 10^{-5}$ cm$^2$·s$^{-1}$, and $D_{TMA^+,IL} = 5.0 \times 10^{-10}$ cm$^2$·s$^{-1}$. 
The Butler-Volmer simulation at the micro-ITIES was used to examine the kinetics of ion transfer and the results overlaid onto the experimental CV data obtained for TMA⁺ IT using Cell 4.1.4 in Figure 4.1.9 (red curve); the overlaid simulated curve (○) used the following parameters: \( \alpha = 0.5, \ k^0 = 5 \times 10^{-4} \ \text{cm} \cdot \text{s}^{-1}, \ D_{TMA^+,w} = 2 \times 10^{-5} \ \text{cm}^2 \cdot \text{s}^{-1}, \ D_{TMA^+,IL} = 5 \times 10^{-10} \ \text{cm}^2 \cdot \text{s}^{-1}, \ \nu = 0.020 \ \text{V} \cdot \text{s}^{-1}, \ [TMA^+]_{aq} = 1.1 \ \text{mM}, \ \text{and} \ T = 333.15 \ \text{K}. \) These CVs have excellent overlap and the \( k^0 \) value used in the liquid|liquid simulations is very similar to that used in the solid Pt-UME simulations. This similarity is encouraging with wider implications towards the application of these simulation models. The low diffusion of TMA⁺ in the IL phase could be the result of extensive ion-pair formation and should be regarded as an effective or apparent diffusion coefficient.

**Figure 4.1.10:** Cyclic voltammogram obtained using Cell 4.1.4 and the following instrument parameters: initial potential equal to 0.000 V; upper and lower potentials equal to 0.402 and −0.442 V respectively; and with a scan rate of 0.020 V⋅s⁻¹.

Figure 4.1.10 illustrates a CV taken using Cell 4.1.4 with 1.1 mM of TMANO₃ dissolved in the aqueous phase. The scan was initiated at −0.200 V and scanned in the forward direction at 0.020 V⋅s⁻¹ towards more positive potentials. At 0.343 V, an anodic peak current was observed, which is indicative of TMA⁺ transfer from w to IL. The upper potential is reached at 0.402 V at which point the potential was switched in the reverse direction until −0.442 V. During this portion of the scan, two cathodic peak
currents at 0.247 and −0.361 V can be observed and correspond to the back transfer of TMA$^+$ from IL→w and the transfer of NO$_3^−$ from w→IL, respectively. The final portion of the CV potential sweep was taken from −0.442 to 0.000 V revealing one anodic peak current at −0.239 V representing the back transfer of NO$_3^−$ from IL→w. ΔE$_p$ for the TMA$^+$ and NO$_3^−$ transfer is 0.096 and 0.122 V, respectively. Large peak-to-peak separations for IT (>0.066 V for a reversible system at 60°C) has been observed previously at the w|IL interface [7, 9, 25, 26, 29, 30] and is analogous to that observed at the solid UME; similarly, IL viscosity and uncompensated resistance [7, 10] have been used to explain this difference. Unlike the anodic and cathodic peak current differences observed at the UME using the Fc/Fc$^+$ redox couple, the change of intensity between the w→IL and IL→w transfer peak currents can be explained by virtue of the difference in diffusion coefficients between each phase; with magnitudes of $1 \times 10^{-5}$ and $1 \times 10^{-8}$ cm$^2$·s$^{-1}$ in the aqueous and IL phases respectively. One of the interesting features of micro-ITIES cyclic voltammetry at the w|DCE interface is the asymmetric diffusion regime [38, 39], which generates a peak current for IT coming out of the pipette, where the system is diffusion controlled, and a steady state wave for ion transfer coming into the pipette (only for systems with low viscosity) from the external solution where the system is consumption controlled. By convention, the transfer of a positive ion from w→DCE elicits a positive peak current and a negative peak current from a negative ion [38, 39]. It is interesting to note that ion transfer at the w|IL interface is somewhat different. IT from w→IL of NO$_3^−$ and TMA$^+$ in Figure 4B are similarly biased and this agrees well with the theory of IT at the micro-ITIES [38, 39]. Because of the low diffusion coefficients in the IL phase; however, the back transfers of the ions from the IL to aqueous phase also demonstrate a peak shape.

Table 4.1.3: Ion transfer data at the w|P$_{66614}$TB micro-ITIES.

<table>
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<th>E$_{1/2}$ / V</th>
<th>Δϕ$^x$ / V</th>
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<td>0.293</td>
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<tr>
<td>TPA$^+$</td>
<td>0.121</td>
<td>-0.698</td>
<td>-0.303</td>
</tr>
<tr>
<td>NO$_3^−$</td>
<td>0.096</td>
<td>-0.461</td>
<td>-0.305</td>
</tr>
<tr>
<td>TPB</td>
<td>0.150</td>
<td>-0.071</td>
<td>-0.323</td>
</tr>
</tbody>
</table>
The simple IT of TPB$^+$, TBA$^+$, TMA$^+$, and NO$_3^-$ assures a TATB scale at the w|$P_{66614}$TB ITIES; these values are listed in Table 4.1.3. These transfer potentials are similar to those obtained by Samec et al. [25] and Kakiuchi et al. [7, 24], supporting the same trends in ion hydrophilicity observed at the w|$DCE$ ITIES; with decreasing hydrophilicity: TMA$^+$>TPA$^+$ and NO$_3^->TPB^-$.

4.1.5 - Conclusions

Herein, the facile preparation of a hydrophobic phosphonium IL has been described. This IL possessed a high viscosity when compared to other hydrophobic ILs, 17993.8 and 1206.2 mPa∙s at 25 and 60°C, respectively.

Conductivity results indicate that the peak-to-peak separations observed in homogeneous $P_{66614}$TB IL electrochemistry are not simply the result of uncompensated $iR$ drop but a consequence of slow ET kinetics. The examination of the Fc/Fc$^+$ redox couple at a solid disk Pt-UME revealed a shift in the $i_{p,c}/i_{p,a}$ from 1:1 to 1.4:1 at higher temperatures. This may be explained with ion pairing-like or coordination-like chemistry between the components of the IL and the redox species. Simulation results showed good overlap with Fc/Fc$^+$ experimental CVs using $D_{Fc}$, $D_{Fc^+}$, and $k^o$ equal to $3.2 \times 10^{-8}$ cm$^2$∙s$^{-1}$, $0.5 \times 10^{-8}$ cm$^2$∙s$^{-1}$, and $5 \times 10^{-4}$ cm∙s$^{-1}$ corroborating the hypothesis that low $D_{Fc^+}$ results in the Fc$^+$ remaining closely associated with the electrode surface eliciting a disproportionate cathodic peak current response.

Investigations at the micro-ITIES demonstrated a large w|IL PPW, 0.8 V. Simple IT behaviour was observed in a similar manner to that at other w|IL interfaces in the literature [7, 25]. The PPW of the w|IL interface was calibrated, using the TATB assumption, allowing quantitative analysis of IT and FIT, while the wide PPW lends itself to applications in the solvent extraction of metal ions in nuclear waste.

Simulations at the micro-ITIES showed significant overlap as well, and both solid-liquid and liquid|liquid simulations used a $k^o$ of $5 \times 10^{-4}$ cm∙s$^{-1}$. This indicates the general success of these simulations and signals a small step forward towards a greater understanding of ET/IT IL kinetics.

4.1.6 - References

Chapter 4.2 - Tetraoctylphosphonium tetrakis(pentafluorophenyl)borate room temperature ionic liquid towards enhanced physicochemical properties for electrochemistry

4.2.1 - Introduction

While room temperature ionic liquids (ILs) are very attractive in conventional electrochemistry, due to their chemical inertness and increased redox potential windows [1], their applications at the interface between two immiscible electrolytic solutions (ITIES) have been limited because their hydphilicity leads to very narrow polarizable potential windows (PPWs) [1, 2] and high-cost reagents [3, 4]. Currently, groups are motivated towards the preparation of low-cost ILs that have enhanced physicochemical properties for electrochemistry.

Since requirements for electrolytes in conventional electrochemistry are very straightforward, only electrochemical aspects at the ITIES will be emphasized. ITIES has been used to study ion transfer (IT) reactions between water and 1,2-dichloroethane [2, 5-9] (DCE), nitrobenzene (NB) [10, 11], as well as trifluorotoluene (TFT) [12]; simple ion transfer (IT) can be described using equation 1.4, where ion \( i \) with charge \( z_i \) transfers from aqueous, w, to organic, o. This ion partitioning can be controlled through the application of a potential so that ions can be pushed or pulled across the interface. This facile principle has expanded, resulting in advances towards applications such as sensors [13, 14], ion-selective membranes [15], metal ion extraction processes [16-18], along with garnering an improved understanding of ion partitioning and aspects of fundamental electrochemistry [19-21].

New biphasic solvent combinations are constantly being sought to fulfill the requirements of these burgeoning applications including gels [13, 14] and ILs [1, 2, 4, 8, 15, 17, 18, 22-25]. ILs are large organic salts often composed of a quaternary alkylammonium/alklyphosphonium or imidazolium cations paired with an asymmetric anion such as bis(trifluoromethyl-sulfonyl)imide (\( \text{NTf}_2 \)) [2, 26]; these salts are defined by their low melting point – below 100°C or around room temperature. ILs have a number of unique properties including low vapour pressure, inherent conductivity, and over the past decade have been shown to be superior solvents versus traditional organic solvents in biphasic, metal ion extraction processes [17, 26]. Of particular importance is the extraction of uranium and useful isotopic fission byproducts found in spent nuclear
fuel (SNF) [16, 17, 27, 28]. These procedures employ a ligand, like tributylphosphate (TBP) used in the Plutonium Uranium Extraction (PUREX) [16] process, dissolved in the organic (or in this case IL) phase to coordinate to the metal of interest making it more miscible towards the organic phase. Unfortunately, some of ILs tested have demonstrated a disturbing tendency to leach cations through an exchange process during metal extraction [26]; an example, using 1-butyl-3-methylimidazolium (C₄mim⁺) cation, is detailed below:

\[
\text{UO}_2^{2+} + \text{NO}_3^- + \text{TBP}_{(IL)} + \text{C}_4\text{mim}^+ \rightleftharpoons 2\text{TBP}_{(IL)}^+ + \text{C}_4\text{mim}^+ (\text{aq})
\]  

(4.2.1)

In previous methods employing organic solvents, the uranyl ion coordinates with two nitrate anions forming a neutral species, thus preserving charge neutrality as it partitions to the organic phase [29]. The reaction shown in equation 4.2.1 occurs at low aqueous nitric acid concentrations, neutral pH, which is the typical conditions for reclaiming the metal at the end of the extraction procedure [26].

Nevertheless, while ILs have improved extraction efficiency, the leaching of IL components during an industrial-scale procedure, negating any advantage gained through their non-volatility, is undesirable for multiple reasons. For example, the possible toxicity of these reagents could pose an environmental hazard and health risk, should they be leaked into the environment. Additionally, the primary aim is to recycle these designer solvents during industrial scale use, so loosing the cationic component to the aqueous phase is potentially catastrophic for their application.

There are several ways to approach the solution to this problem. One method could be to embrace this deficiency and incorporate a ‘sacrificial’ cation or anion component such that the IL could be regenerated during a separate stage at the end of the process [30]. Alternatively, another aqueous ion could be employed to ensure a neutral metal species was formed, as was recently demonstrated by Dietz et al. [31] in their extraction of the pertechnetate anion through the use of a sodium counter ion. Lastly, the leaching of cationic or anionic components could be mitigated by simply increasing the hydrophobicity of the IL phase [2, 8, 26].

This final option is made feasible by augmenting the hydrophobicity of both cations and anions. It is evident that tetrakis(pentafluorophenyl)borate should be an
excellent candidate because of its hydrophobicity and chemical inertness [32, 33]. While long-chain alkylphosphonium cation IT was not observed at a w/DCE micro-ITIES [2, 8], tuning physicochemical properties for a better electrochemical performance still needs to be considered. For instance, a cationic/anionic combination should have the most favourable characteristics of low viscosity, high conductivity, low melting point, in addition to being extremely hydrophobic. Low cost components are preferred. With these in mind, an extremely hydrophobic IL, tetraoctylphosphonium tetrakis(pentafluorophenyl)borate (P8888TB), was synthesized and the physicochemical properties such as density, viscosity, and conductivity were analyzed at various temperatures. Electron transfer (ET) and simple ion transfer (IT) reactions at metal|IL and liquid|liquid interfaces were explored using a Pt-disc ultramicroelectrode (UME) and micro-ITIES housed at the tip of a micropipette (both interfaces were 25 μm in diameter), respectively. Additionally, the kinetics of ET and IT were examined through the use of finite element analysis, which is a computational method for solving non-linear equations, such as those describing Fick’s laws of diffusion and Butler-Volmer equations for charge transfer. The software suite also incorporates the development of two and even three dimensional geometries which can be tailored to mirror precisely the experimental apparatus.

4.2.2 - Theory

Simulations of electrochemical phenomena have garnered insight into the processes occurring at metal electrode|electrolyte [8, 23] and liquid|liquid interfaces [2, 3, 7, 8, 34-36]. In particular, finite element analysis can be used to account for the physical geometry of an apparatus as well as reaction kinetics, exploring their attributes as well as more closely approximating the actual experiment [2, 37]. Two simulations for electrochemistry at a ultramicroelectrode (UME) and a water|IL (w|IL) micro-interface hosted by a micropipette were carried out, and their geometries are illustrated in Figures 4.2.1A and B, respectively. The simulation runtime can be greatly reduced by converting the simulation into its 2D cross section and even further by recognizing the axis of symmetry that still remains.
The UME geometry (Figure 4.2.1A) was composed of 5 boundaries. The rectangular area framed by these boundaries constitutes the IL solution with mass transfer within this area described by Fick’s laws of diffusion through equation 2.1.

**Figure 4.2.1:** Simulation geometry for (A) the ultramicroelectrode with 2D boundaries (red dashed line) 1, 2, 3, 4, and 5 designated as axial symmetry, flux, concentration, insulator, and concentration, respectively; (B) the micropipette with the 2D simulation geometry (black arrows) describing the boundary conditions: 1, 3, 4, 6, and 7, axial symmetry; 9-14, insulator (glass surface); 2, 8, 15, 16, and 17, concentration.
The simple one electron oxidation/reduction reaction, as defined by equation 4.1.2. A full description of the UME Butler-Volmer theory can be found in section 2.2, while a microITIES theory is described in detail in section 3.2.

4.2.3 - Experimental

4.2.3.1 Chemicals.
All reagents were purchased at the highest quality available and utilized as received without further purification. Trioctylphosphonium, 1-bromoocctane, tetramethylammonium sulfate \((TMA_2SO_4)\), tetraethylammonium hydrogen sulfate \((TEAHSO_4)\), tetrpropylammonium hydrogen sulfate \((TPrAHSO_4)\), tetrabutylammonium hydrogen sulfate \((TBAHSO_4)\), lithium sulfate \((Li_2SO_4)\), trioctylphosphine, 1-bromoocctane, ferrocene \((Fc)\), bis(pentamethylcyclopentadienyl)iron(II) (or decamethylerrocene, DMFc), 7,7,8,8-tetracyanoquinodimethane \((TCNQ)\), and dichloromethane \((DCM)\) were obtained from Sigma-Aldrich Canada (Mississauga, ON). Potassium tetrakis(pentafluorophenyl)borate was bought from Boulder Scientific Inc. (Longmont, CO). All aqueous solutions were prepared using ultrapure water \((18.2\ M\Omega)\) processed using a Barnstead water filtration system (Thermo Scientific, Asheville, NC).

4.2.3.2 Instrumentation

\(\text{NMR}\). \(^1\text{H}\) and \(^{31}\text{P}\) NMR were acquired by dissolution of ~7 mg of IL sample in CDCl\(_3\) and using a 400 MHz Varian Mercury Nuclear Magnetic Resonance Spectrometer.

\(\text{Conductivity}\). A Solartron Analytical 1260 Impedance/gain Analyzer (Ametek Advanced Measurement Technology, Farnborough, Hampshire, United Kingdom), along with an electrochemical cell consisting of two disc shaped glassy-carbon electrodes, was employed for the determination of conductivity through the complex impedance method. This method involved scanning the frequency from typically \(1\ M\Omega\) to \(300\ k\Omega\) while monitoring the impedance. A graph of \(\log|Z'|\) versus \(\log(f)\), where \(Z'\) is the real component of the impedance and \(f\) is the frequency, reveals an initial plateau followed by a gradual increase; this initial plateau was taken to be a measure of the solution resistance, \(R_s\). A series of KCl solutions of concentrations with known conductivities were prepared and measured. Graphing the known conductivities of these solutions versus \(1/R_s\) gave a
linear response, that, when fitted using linear regression, had a slope of 11.959 cm$^{-1}$; this slope constitutes the cell constant, $l/A_e$ where $l$ is the distance between the two electrodes and $A_e$ is the electrode area. Using the cell constant, $R_s$ from the IL sample was measured and translated into conductivity. Temperature within the electrochemical cell was controlled using a water circulator (VWR, Mississauga, ON) while the applied AC voltage amplitude was 0.100 and 1.000 V for the KCl and IL solutions, respectively.

Rheometry. The viscosity of P$_{8888}$TB was determined for various temperatures (controlled by a water circulator) by plotting the shear stress versus shear rate as measured by an AR1500ex Rheometer from TA Instruments (Grimsby, ON); the upper plate diameter and plate gap were 40 mm and 800 μm, respectively.

Density. A DMA4500 Density Meter (Anton Paar, Saint Laurent, Quebec) was used to perform temperature controlled density measurements.

Electrochemistry. Unless otherwise stated, electrochemistry measurements were performed using the Modulab System from Solartron Analytical (Ametek Advanced Measurement Technology, Farnborough, Hampshire, United Kingdom) equipped with a Femto ammeter. All experiments were temperature-controlled using a water circulator (VWR, Mississauga, ON) operating at 60°C unless indicated. Liquid/liquid interfacial experiments utilized a specially prepared micropipette hosted in a modified pipette holder which contained the aqueous phase such that the micropipette was immersed into the IL phase, which was kept in a small vial; the interface was maintained at the tip of the capillary and continuously monitored using a CCD camera (Motic Inc., Richmond, BC) with an attached 12× variable zoom lens assembly (Navitar, Rochester, NY). UME and Micropipette fabrication has been described in sections 2.3.2 and 2.3.3, respectively, and elsewhere [2, 8, 16, 17, 38].

The following electrochemical cells were used:

\[
\begin{array}{c|c|c|c}
\text{Ag} & \text{Ag}_2\text{SO}_4 & 10 \text{mM Li}_2\text{SO}_4 & \text{P}_{8888}\text{TB} \\
(aq) & & (IL) & \text{AgTB} \\
\text{Ag} & & & \text{Ag}
\end{array}
\] (Cell 4.2.1)
### 4.2.4 - Results and Discussion

#### 4.2.4.1 - $P_{ssss}TB$ Preparation and Structural Elucidation.

In a glovebox under inert atmospheric conditions, 20 mL (0.045 mol) of trioctylphosphine and 10 mL (0.056 mol) of 1-bromooctane were added to a pressure tube (ACE Glass Inc., Vineland, NJ) along with a magnetic stirrer; the tube was sealed, removed from the glovebox, and stirred for 4 days at room temperature. Subsequently, the pressure tube was opened and charged with 33.2614 g of potassium tetrakis(pentafluorophenyl)borate (KTB) along with 50 mL of dichloromethane (DCM). It is important to note that KTB shows little solubility in DCM; however, its implementation versus a water/methanol mixture ensures that the majority of KBr metathesis product can be removed through filtration; this ultimately results in fewer aqueous-organic extractions during purification. The mixture was stirred for 72 hours, after which a white solid was suspended in solution. This solid was removed via Büchner vacuum filtration using #42 ashless filter paper (55 mm in diameter, Little Chalfont, Buckinghamshire, UK) beneath a ~1.5 cm thick layer of activated charcoal; DCM was removed under reduced pressure in a rotoevaporator. At this stage the sample appeared
as a viscous, slightly yellow liquid, which was dissolved in 125 mL of DCM and extracted 5 times using 125 mL aliquots of ultrapure water.

After removing the DCM, and in order to ensure any un-reacted trioctylphosphine was removed, the IL was recrystallized in pentane (m.p. −129°C) through immersion in a dry-ice/acetone bath (−78°C). In this procedure a 1:1 volume of pentane to IL was combined in a vial and stirred with a glass rod to ensure thorough mixing. This mixture was then placed in the dry-ice/acetone bath for 10-15 minutes at which point the IL formed a solid phase at the bottom and the organic solvent could be decanted off the top. This recrystallization was repeated 3 times; the product appeared as a soft white solid with a final yield of ~93%.

P_{8888}TB was characterized by proton and phosphorus NMR; these are available online within the supplementary material of reference [39].

4.2.4.2 - Physicochemical characterization of P_{8888}TB

In order to elucidate its physical properties, the novel IL, P_{8888}TB, was characterized using a variety of analytical and electrochemical techniques. Figure 4.2.2A depicts the cyclic voltammogram (CV) acquired at a scan rate of 0.050 V∙s⁻¹ and at 60°C using a Pt-disc ultramicroelectrode (UME), 25 μm in diameter. The initial potential was 0.000 V and the potential range was between −1.000 and 2.480 V. P_{8888}TB presents a relatively wide metal|IL potential window, ~3.5 V, which is similar to our previous ionic liquid, trihexyltetradecylphosphonium tetrakis(pentafluorophenyl)borate (P_{66614}TB) [8], and typical of most ILs in the literature [40].

The CV shown in Figure 4.2.2A indicates the purity of the final IL product; the current-potential response is flat within the potential range and free of any peaks caused by impurities. The potential window might be extended to more negative potentials if the IL was degassed (i.e. dissolved O₂ was removed). Subsequently, three electroactive species including 7,7,8,8-tetracyanoquinodimethane (TCNQ), bis(pentamethylpentadienyl)-iron(II) (DMFc), and ferrocene (Fc) were dissolved in separate samples of the IL and analyzed using CVs.

Figure 4.2.2B illustrates the CV obtained with 5 mM of TCNQ in P_{8888}TB; the scan was initiated at 1.000 V and scanned towards negative potentials at a rate of 0.050 V∙s⁻¹ until −1.000 V was reached. Two cathodic peaks were observed at 0.461 and
−0.160 V corresponding to the reduction of TCNQ to TCNQ\(^{-}\) and, subsequently, TCNQ\(^{-}\) to TCNQ\(^{2-}\), respectively. The CV was then scanned into the positive direction from −1.000 to 2.480 V, during which two anodic peaks were observed at −0.070 and 0.524 V, which are related to the oxidation of TCNQ\(^{2-}\) to TCNQ\(^{-}\) and then TCNQ\(^{-}\) to TCNQ. Owing to the high viscosity in the IL, diffusion is slow and, therefore, electroactive species directly associated with the electrode surface are rapidly consumed while the system must then wait for material to diffuse towards the electrode surface; this occurs even when employing UMEs [1, 8, 23, 24, 41, 42].

![Cyclic voltammograms acquired using a 25 μm Pt-disc ultramicroelectrode with an Ag-wire quasi-reference/counter electrode in P\(_{8888}\)TB with (A) no electroactive species, (B) 5 mM TCNQ, (C) 10 mM DMFc, and (D) 17 mM Fc; a scan rate of 0.050 V·s\(^{-1}\) was used throughout.](image)

**Figure 4.2.2:** Cyclic voltammograms acquired using a 25 μm Pt-disc ultramicroelectrode with an Ag-wire quasi-reference/counter electrode in P\(_{8888}\)TB with (A) no electroactive species, (B) 5 mM TCNQ, (C) 10 mM DMFc, and (D) 17 mM Fc; a scan rate of 0.050 V·s\(^{-1}\) was used throughout.

Interestingly, these two redox-couples have quasi-reversible CV character in that the peak-to-peak separations, \(\Delta E_p\), for TCNQ→ TCNQ\(^{-}\) and TCNQ\(^{-}\)→ TCNQ\(^{2-}\) are
0.063 and 0.060 V while the ratio of the cathodic to anodic peak currents, \( i_{p,c}/i_{p,a} \), are 1.17 and 0.36, respectively; at 60°C \( \Delta E_p = 0.066 \) V and \( i_{p,c}/i_{p,a} = 1 \), for a reversible system [43]. It is common that the anodic peak current is different from the cathodic one in ILs [8, 44] owing to a difference in diffusion coefficients [8, 41] between the oxidized and reduced state as well as possible solvent relaxation effects [23]. DMFc and Fc were similarly analyzed using P_{8888}TB solutions of 10 and 17 mM and are shown in Figures 4.2C and 4.2D, respectively. The DMFc anodic and cathodic peaks appear at 0.244 and 0.163 V generating a \( \Delta E_p \) of 0.081 V with a \( i_{p,c}/i_{p,a} = 1.00 \); the Fc redox couple was observed at \( 1.011/0.866 \) V giving values for \( \Delta E_p \) and \( i_{p,c}/i_{p,a} \) of 0.144 V and 1.14, respectively. The response for all three electroactive species show improved reversibility versus the previous IL with peak-to-peak separations at or near the desired 0.066 V. Interestingly, the peak current ratio’s for all species are close to 1, which seems to indicate that the IL environment has the same affinity, or degree of intermolecular interaction, for both the reduced and oxidized forms. The TNCQ\(^{-}\)/TCNQ\(^{2-}\) couple is the only exception \( (i_{p,c}/i_{p,a} = 0.36) \); however, this may be owing to an increased charge localization and therefore an increase in the level of interaction. Through a facile scan rate experiment [43], the diffusion coefficients were determined for TCNQ/TCNQ\(^{-}\), DMFc/DMFc\(^{+}\), and Fc/Fc\(^{+}\) to be 2.7, 6.1, and \( 10.9 \times 10^{-8} \) cm\(^2\) s\(^{-1}\), respectively.

In order to evaluate further the kinetics of electron transfer (ET), simulated CVs were generated through COMSOL 3.5a Multiphysics software employing finite element analysis and overlaid onto experimental curves. These simulations were performed using the geometry depicted in Figure 4.2.1A along with Fick’s laws of diffusion to govern the mass transfer of species while Butler-Volmer kinetics, at the electrode surface, were used to describe the oxidation/reduction of the species of interest. Figure 4.2.2 illustrates the first redox couple for each of the three electroactive species with the experimental curves (solid line) and simulated curves (○) overlaid. Unlike in conventional electrolyte solutions, ILs seem to induce a change in the effective diffusion coefficients between two different charge states within a species. This disparity between the oxidized and reduced states has been recognized by Hapiot’s group [42, 45] using the redox species such as \( \text{O}_2/\text{O}_2^- \) and by Compton et al. through their work with ferrocene and arenes [23, 41].
The disparity between the two peak current values can result in a ratio of \( \frac{D_{\text{red}}}{D_{\text{ox}}} \) of 1000 [42]. Therefore, for the electroactive species studied here, three parameters were of primary importance for optimization: the standard rate constant, \( k^0 \) and the diffusion coefficient of species \( i \) in the IL phase, \( D_{i,\text{IL}} \) for the oxidized and reduced forms.

Thus, for the TCNQ/TCNQ\(^{-}\) couple these parameters were optimized at \( 5 \times 10^{-3} \) cm\( \cdot \)s\(^{-1} \) for \( k^0 \) while both \( D_{\text{TCNQ,IL}} \) and \( D_{\text{TCNQ }^{-},\text{IL}} \) were set equal to \( 1.25 \times 10^{-8} \) cm\(^2\)\( \cdot \)s\(^{-1} \). Similarly, for DMFc/DMFc\(^{+}\), \( k^0 \) was \( 5 \times 10^{-3} \) cm\( \cdot \)s\(^{-1} \) while both \( D_{\text{DMFc}^{+},\text{IL}} \) and \( D_{\text{DMFc}_{\text{IL}} D^{+}} \) were \( 5.6 \times 10^{-8} \) and \( 4 \times 10^{-8} \) cm\(^2\)\( \cdot \)s\(^{-1} \). The Fc/Fc\(^{+}\) couple showed slightly different characteristics with a smaller \( k^0 \) value of \( 5 \times 10^{-4} \) cm\( \cdot \)s\(^{-1} \) and with a much larger disparity in diffusion coefficients having \( D_{\text{Fc}^{+},\text{IL}} \) and \( D_{\text{Fc}_{\text{IL}} D^{+}} \) equal to \( 9 \times 10^{-8} \) and \( 4 \times 10^{-8} \) cm\(^2\)\( \cdot \)s\(^{-1} \). For TCNQ/TCNQ\(^{-}\) and DMFc/DMFc\(^{+}\) the simulation overlay demonstrates excellent agreement with the experimental CV, while that shown for Fc/Fc\(^{+}\) is relatively good; this indicates the suitability of the chosen parameters. Interestingly, the ratio of \( \frac{D_{\text{Fc}_{\text{IL}} D^{+}}}{D_{\text{Fc}^{+},\text{IL}}} \) and \( \frac{D_{\text{DMFc}^{+},\text{IL}}}{D_{\text{DMFc}_{\text{IL}} D^{+}}} \) was 0.44 and 0.70 which is in reasonable agreement with those reported by Compton’s group; using a Fc redox couple, they detailed a ratio of 1 to 2 for the majority of ILs they examined, however they also reported a value of 7.80 for the IL trihexyltetradecylphosphonium trifluorotri(pentafluoroethyl)phosphate (P\(_{66614}\)FAP) [41]. Additionally, our previous IL, P\(_{66614}\)TB showed a similar result compared to Compton et al. [41] with a value of 6.4 [8]. It’s possible that, because both the cation and anion in P\(_{8888}\)TB are highly symmetrical, this reduces the influence of the IL environment towards the electroactive species and thus the diffusion coefficients in the present case are close to 1.

Table 4.2.1 lists some of the physical properties (density, viscosity, and conductivity) of P\(_{8888}\)TB measured over a series of temperatures. As expected, the viscosity and density decreased with increasing temperature. The viscosity was high when compared to imidazolium and quaternary ammonium/phosphonium cations [8, 24, 25] coupled with bis(trifluoromethylsulfonyl)imide (NTf\(_2\)) as an anion; however, it shows a modest decrease relative to a previous IL, P\(_{66614}\)TB. This is especially true at 60°C where P\(_{66614}\)TB [8] and P\(_{8888}\)TB 1206 and 727 mPa\( \cdot \)s, respectively. A low viscosity is
advantageous for ILs in terms of pour-ability and thus its ease of use. However, in terms of liquid|liquid electrochemistry, a viscous organic phase has been shown to improve the stability of the interface. Similarly, the conductivity of $P_{8888}$TB is relatively good compared other ionic liquids [44] and shows a slight improvement over $P_{66614}$TB [8].

**Table 4.2.1**: The density, viscosity, and conductivity relative to temperature for the pure $P_{8888}$TB IL.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Density (g cm$^{-3}$)</th>
<th>Viscosity (mPa s)</th>
<th>Conductivity ($\mu$S cm$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>25</td>
<td>1.248</td>
<td>7101.11</td>
<td>157.5</td>
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<tr>
<td>35</td>
<td>1.239</td>
<td>3480.17</td>
<td>157.4</td>
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<tr>
<td>90</td>
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**4.2.4.3 - Biphasic, water|$P_{8888}$TB, characterization at a micro-ITIES**

**Figure 4.2.3**: Cyclic voltammogram taken at a w|$P_{8888}$TB micro-interface using Cell 4.2.1 with an initial potential of $-0.121$ V, a scan rate of 0.020 V·s$^{-1}$, and a potential range from $-0.470$ to 0.476.

Figure 4.2.3 shows a CV acquired using Cell 4.2.1, or a ‘blank’ CV, at a micro-ITIES housed at the tip of a micropipette with an initial potential of $-0.121$ V, a potential range from $-0.470$ to 0.476 V, and a scan rate of 0.020 V·s$^{-1}$. This CV shows the wide
polarizable potential window (PPW) available at a w|IL interface using P
8888 TB. The positive end of the PPW is limited by the transfer of the anionic component of the IL phase, TB−, from IL to w and Li+ from w to IL. Similarly, the negative end is limited by the transfer of SO4 2− from w to IL and the cationic component of the IL, P
8888 + , from IL to w. In this way, the total size of the PPW is ~0.9 V, which is comparable to other w|IL systems [3, 8, 22], but shows marked improvement over ILs that incorporate the NTf2 anion; these are typically limited to a PPW no larger than ~0.4 V [2].

Analogous to redox chemistry at a UME, IT at a w|IL micro-interface reveals symmetric character; i.e. linear diffusion, or a peak-shaped current-potential response, in both the forward and reverse directions. At traditional water|organic solvent micropipette interfaces this is not usually the case. For example, at a w|DCE micropipette ITIES the CV result is typically asymmetric such that ions crossing from inside to outside the pipette are rapidly consumed owing to the small volume of solution within the microchannel associated with the interface generating a peak shaped wave. Those crossing from outside to inside display a sigmoidal or ‘S’ shaped wave owing to the relatively large hemispherical volume directly surrounding the ITIES; this provides a sufficient amount of ions to elicit and maintain a steady state current. Because the IL phase was kept outside the capillary and owing to the high viscosity (i.e. low rate of diffusion) the effective volume of material associated with the ITIES was greatly reduced and hence a peak shaped wave was the result. This is also why, at the edge of the PPW there was a return peak directly after the switching potential.

Liquid|liquid electrochemistry can be used to measure directly the formal IT potential, Δ
w→IL Φ′, of a charged species such that the formal transfer potential is related to the Gibbs free energy of transfer, analogous to metal|electrolyte interfaces, as ΔG
w→IL = zFΔ
w→IL Φ′. In this way, using the potentials at the edge of the CV shown in Figure 4.2.3 to estimate Δ
w→IL Φ′ of the cationic and anionic components of the ILs.

Substituting these values into equation 4.1.7 [22], the solubility constant, K
w→sp , was approximated as 5.0 × 10−15. Therefore, P
8888 TB is an extremely hydrophobic IL, which is critical since the larger the PPW the more electrochemical phenomena can be observed and recorded. This increase in hydrophobicity translates directly into a decreased
propensity to undergo cationic exchange during biphasic, water-IL, metal ion extraction procedures [26]. Dietz et al. [26] discovered that ILs composed of short chain dialkylimidazolium cations undergo a cationic exchange mechanism at low concentrations of nitric acid in the aqueous phase. This results in the transfer of a charged metal complex, e.g. UO$_2$NO$_3$TBP$^+$ (where TBP is the ligand tributylphosphate), into the IL phase and, in order to maintain charge neutrality, an imidazolium cation transfers into the aqueous phase; at high nitric acid concentrations (low pH) two nitrate molecules coordinate to the metal center and generate a neutral complex [26]. They also found that an increase in the alkyl chain length on the imidazolium could eliminate this from happening – i.e. make the IL more hydrophobic. Based on the low $K_{sp}^w$ estimated herein for P$_{8888}$TB, it is reasonable to conclude that cationic exchange would be negligible.

**Figure 4.2.4:** Cyclic voltammograms recorded using Cell 4.2.2 (●) and Cell 4.2.3 (●); instrument parameters are similar to those detailed for Figure 4.2.3.

It is important to mention that NTf$_2^-$ based ILs, while having favourable physical characteristics like low viscosity and high conductivity, experience PPWs that are too small to be of use in liquid|liquid electrochemistry [2]; therefore, TB$^-$ based ILs are preferred because they are more hydrophobic, giving access to a much wider liquid|liquid potential range.

Unlike metal|electrolyte interfaces, whose potential range can be calibrated using a reference electrode, in liquid|liquid chemistry the potential is often calibrated with an internal standard according to a non-thermodynamic assumption; the
tetraphenylarsonium-tetraphenylborate (TATB) or Parker's assumption [46]. Parker's assumption states that the Gibbs free energy of transfer for tetraphenylarsonium (TPAs⁺) and tetraphenylborate (TPB⁻) are equal since they are of opposite charge, similar size, and experimentally their IT appears at opposite ends of the PPW. Therefore, the midpoint between their IT, captured via CV, is defined as the point of zero charge (PZC) [46]. This calibration has been utilized for the interface between water and traditional molecular solvents such as DCE and NB over the past 30 years [4, 47-49] and recently for the w|TFT interface [12].

Therefore, employing Cells 4.2.2 and 4.2.3, the CVs of TPB⁻ and TPAs⁺ simple IT were recorded and are displayed as an overlay in Figure 4.2.4. By using the edge of the PPW to align the CVs, the PZC and ultimately the formal transfer potential of these two ions was estimated; \( \Delta_{\text{PPW}}^{\text{w}} \phi_{\text{TPB}}^{\circ} \) and \( \Delta_{\text{PPW}}^{\text{w}} \phi_{\text{TPAs}}^{\circ} \) were determined to be 0.288 and −0.288 V, respectively. An attempt was made to record a CV with both TPB⁻ and TPAs⁺ dissolved in the aqueous phase; however, despite hours of sonication, not enough of the TPAsTPB salt was dissolved to appear on a CV. Similarly, dissolving TPAsTPB in P8888TB was problematic as it seems to undergo metathesis with the IL, altering its physical properties.

Simultaneously, the IT of NO₃⁻ and TMA⁺ were also performed, as shown in Figure 4.2.4 with formal transfer potentials determined to be −0.352 and 0.270 V, so that these ions could then be used to calibrate other species IT. Figure 4.2.5 demonstrates this using Cell 4.2.4 for TMA⁺ IT as well as Cell 4.2.5 with X equal to tetraethylammonium (TEA⁺), tetrapropylammonium (TPrA⁺), and tetrabutylammonium (TBA⁺), which were all calibrated after addition of 0.8 mM of TMA⁺ to the Cell, and determined to have formal IT potentials of 0.100, −0.044, and −0.179 V, respectively. The trend in formal IT potentials agree well with that shown at the w|DCE [5, 6], w|NB [6], and w|TFT [12], which were similar to those demonstrated recently for an w|IL ITIES [18]. That is, with increasing hydrophobicity of the ion, correlated to increasing alkyl chain length in the case of the alkylammonium cations, the formal IT potentials shift to more negative values; i.e. TMA⁺>TEA⁺>TPrA⁺>TBA⁺. The formal IT potentials of these ions are listed in Table 4.2.2.
Figure 4.2.5: Cyclic Voltammograms acquired using Cell 4.2.4 (▬) and Cell 4.2.5 with X = TBA$^+$ (▬), TPrA$^+$ (▬), and TEA$^+$ (▬); the peak currents associated with the simple IT for each species have been labelled correspondingly. Each formal IT potential has been calibrated using TMA$^+$ IT according to the TATB assumption.

Table 4.2.2: Formal ion transfer potentials for ions at the $w|P_{8888}TB$ interface based on the TATB assumption.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\Delta^w_{\text{IL}}\phi^{\infty}/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPAs$^+$</td>
<td>-0.288</td>
</tr>
<tr>
<td>TMA$^+$</td>
<td>0.270</td>
</tr>
<tr>
<td>TEA$^+$</td>
<td>0.100</td>
</tr>
<tr>
<td>TPrA$^+$</td>
<td>-0.044</td>
</tr>
<tr>
<td>TBA$^+$</td>
<td>-0.179</td>
</tr>
<tr>
<td>TPB$^-$</td>
<td>0.288</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-0.352</td>
</tr>
</tbody>
</table>

Similar to the ET case, IT was explored through simulations and the geometry shown in Figure 4.2.1B. Figure 4.2.6 depicts the CV obtained using Cell 4.2.4 for TMA$^+$ transfer (solid line) and with the simulated curve overlaid (○). The key kinetic parameters used to generate the latter were $k^0$, $D_w$, $D_{\text{IL}}$, and $\Delta^w_{\text{IL}}\phi^{\infty}_{\text{TMA}^+}$ with optimized values of $2 \times 10^{-3}$ cm$^2$s$^{-1}$, $1.8 \times 10^{-5}$ cm$^2$s$^{-1}$, $1.5 \times 10^{-5}$ cm$^2$s$^{-1}$, and 0.175 V. Interestingly, based on these values, the kinetics of IT at the $w|P_{8888}TB$ interface are 4
times faster than that shown previously for w|P_{66614}TB where $k^0$ was found to be $5 \times 10^{-4}$ cm$\cdot$s$^{-1}$.

**Figure 4.2.6:** Cyclic voltammograms recorded using Cell 4.2.4 (solid line) showing TMA$^+$ ion transfer along with a simulated curve (○) generated using the geometry shown in Figure 4.2.1B.

**Figure 4.2.7:** Simulated cyclic voltammograms generated using the $k^0 > 1 \times 10^{-2}$ (○) along with $1 \times 10^{-3}$ (—) and $1 \times 10^{-4}$ cm$^2$·s$^{-1}$ (–).

Using this simulation code, the general effect of varying the standard rate constant was also explored and is illustrated in Figure 4.2.7. $k^0$ was varied from, at its highest, $1 \times 10^5$ to $1 \times 10^{-4}$ cm$\cdot$s$^{-1}$, at the low end; any standard rate constant above
$1 \times 10^{-2}$ cm$\cdot$s$^{-1}$ elicits overlapping traces that are consistent with the Butler-Volmer kinetics reaching a Nernstian, or completely reversible, state. This facile exercise also illustrates that as the standard rate constant is reduced the peak-to-peak separation increases and the system trends towards a quasi-reversible state. The $k^0$ optimized herein is almost an order of magnitude greater than that found for P$_{6614}$TB; therefore, IT at the w/$P_{8888}$TB interface shows more reversible character.

4.2.5 - Conclusions

Through a facile synthetic process a hydrophobic IL, $P_{8888}$TB, was prepared using relatively cost-effective starting materials and purified through a simple recrystallization technique. Critically, this IL possesses a series of modest improvements over previous ILs including a reduced viscosity, higher conductivity, and more reversible ET and IT kinetics. The characterization of the IL was performed through a variety of analytical techniques, while the ET and IT kinetics were developed using a well established finite element analysis or simulation program; this program allows for the development of 2D and 3D geometric models to better approximate experimental conditions.

It is important to note that other ILs based on imidazolium cations or bis(trifluoromethylsulfonyl)imide anions are not sufficiently hydrophobic as to offer a wide PPW at liquid|liquid interfaces. Therefore, while these ILs may have more favourable physical characteristics, like conductivity, they are not suitable for ITIES electrochemistry and thus cannot readily be used to investigate IT or ligand assisted ion transfer.

Finally, while the many improvements $P_{8888}$TB shows over previous ILs [8] may be minor when examined individually, taken together they amount to a significant enhancement.

4.2.6 - References

Chapter 5 - Hydrophobicity evaluation of alkylphosphonium ionic liquids for polymer additives

5.1 - Introduction

Ionic liquids (ILs), often composed of alkylammonium/alkylphosphonium or imidazolium cations with melting points below 100°C, have been used in applications as alternative solvents/solid state support in lithium batteries [1-5], for micelle formation [6], solar cells [4, 7], as surfactants [8], and in polymerizable coatings [9-11]. Their properties include negligible vapour pressure, good conductivity, and high thermal stability. The unique aspect of ILs is their tunability; that is significant changes in physicochemical properties can be achieved through minor changes to substituents or by pairing different anions and cations together.

One property of particular interest is hydrophobicity [12-14], which influences an ILs suitability towards various coating applications [9-11] and in biphasic, water|IL (w|IL), metal ion extraction [15, 16]. Solid-fluid-vapour (so-called three phase) contact angles have been used to probe the surface characteristic (wet-ability or ‘non-stick’ properties) of solids [17, 18], while a variation of this technique, water contact angles (WCA) measurement, has recently been adapted to estimate or quantify surface (e.g. coating) hydrophobicity [10, 19]. The WCA method involves either coating a suitable material (e.g. cloth) with the IL [10] or preparing the finished fully polymerized coating or self-assembled monolayer (SAM) [19]. A water droplet is mechanically dispensed onto the surface and the contact angle is then measured using a CCD or equivalent camera and accompanying software. This methodology has many advantages as it inherently describes surface effects, such as roughness, which are often synergistic towards creating water repellent materials. However, it has a significant disadvantage in gaining molecular information specifically: hydrophobicity/hydrophilicity information obtained through WCA measurements is a function of the surface morphology, environmental conditions, and packing of the polymers/molecules at the interface. To gain quantitative information about the molecular species independently, an alternative technique must be used.

Electrochemistry at the interface between two immiscible electrolytic solutions (ITIES), typically water|1,2-dichloroethane (w/o or w/DCE) [20, 21], offers a
complimentary technique to WCA and presents a unique opportunity to measure quantitatively the hydrophobicity of charged monomers or polymer additives early on. This technique has two critical advantages. First, it requires only a small amount of material – on the milligram scale or lower. Second, because it can be employed in the initial, developmental stages it can have a powerful predictive aspect that can aid decision-making and illuminate avenues to direct successful synthetic efforts. In this way, a facile electrochemical technique can save a great deal of resources, time, and energy.

ITIES electrochemistry at a micro-interface utilizes an electrode placed in each phase, aqueous and organic, with a potential difference applied to the two electrodes, therefore to the interface in the presence of enough electrolytes in the two phases. The potential difference is termed the Galvani potential difference, $\phi_w - \phi_o = \Delta^w_o \phi$, across the w/o interface that becomes the driving force for ion transfer (IT). The potential required to elicit IT is referred to as the formal ion transfer potential (for species $i$), $\Delta^w_o \phi_i^{o'}$, which is a constant unique to each ion and biphasic system. This is related to Gibbs free energy, $\Delta G_{i}^{o'} = zF\Delta^w_o \phi_i^{o'}$, which is analogous to the traditional metal-electrolyte electrochemistry such that $\Delta G_{i}^{o'} = -zFE_i^{o'}$, whereby $E_i^{o'}$ is the formal redox potential. The Gibbs free energy of IT provides access to the key thermodynamic relationship in this study, $K_{sp}$: $\Delta G_{salt}^{o'} = RT\ln K_{sp}$ such that $\Delta G_{salt}^{o'} = \Delta G_{cation}^{o'} + \Delta G_{union}^{o'}$. Thus, through one facile measurement, the quantitative assessment of ion hydrophobicity can be obtained and comparisons can be made. Developments in biphasic electrochemistry are continuously being reviewed and a few contemporary examples have been included [20-22].

Table 5.1 lists the ILs evaluated. Phosphonium ILs were chosen as the focus owing to their high electrochemical and thermal stability [23, 24]. This technique has been utilized to investigate ILs of moderate hydrophobicity [12], including imidazolium based ILs. Cations of high hydrophobicity are examined and direct comparisons between one pair of fluorinated and non-fluorinated ILs are made.

Additionally, the hydrophobic performance of a variety of highly fluorinated polymerizable phosphonium salts used in photopolymeric systems had been evaluated [25]. In the initial attempts to characterize their IT potentials, it was found that they were
too hydrophobic for our experimental setup. This led to analysis of a suite of phosphonium ILs (Table 5.1) with varying molecular architecture to understand the limits of this technique, and provide a deeper understanding between molecular structure of phosphonium ILs, and their hydrophobicity/hydrophilicity.

**Table 5.1**: Structural list of quaternized phosphonium ionic liquids (ILs) tested for hydrophobicity; the first six ILs have been divided into two groups R-tributylphosphonium and R-tris(1-hydroxypropyl)phosphonium with anions \( \text{B(C}_6\text{F}_5)_4 \) and \( \text{I}^- \), respectively unless otherwise noted. The R groups are given on the left most column.

<table>
<thead>
<tr>
<th>R group</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C4H9</td>
<td>1a</td>
<td>1b</td>
</tr>
<tr>
<td>C3F9</td>
<td>2a</td>
<td>2b</td>
</tr>
<tr>
<td>C22H7</td>
<td>3a</td>
<td>3b</td>
</tr>
<tr>
<td>HO</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>( \text{B(C}_6\text{F}_5)_4 )</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>( \text{I}^- )</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

### 5.2 - Experimental

**Chemicals.** All reagents were used as purchased without further purification, unless otherwise noted. All compounds were synthesized under a \( \text{N}_2 \) atmosphere or prepared in a nitrogen-filled MBraun Labmaster 130 glove box. Solvents were purchased from Caledon and dried using an MBraun Solvent Purification System. Lithium chloride, lithium iodide, lithium bromide, lithium nitrate, lithium sulfate monohydrate, 1,2-dichloroethane (DCE), dichloromethane, tetramethyl-ammonium chloride (TMACl), tetramethylylammonium
iodide (TMAI), and were purchased from Sigma-Aldrich Canada (Mississauga, ON). Iododecane, and iodoheptane were purchased from Alfa Aesar, and 1H,1H,2H,2H-perfluorohexyl iodide was purchased from Fluoroflash. Tetraoctylphosphonium chloride (P$_{888}$Cl), tributylphosphate, and tris(3-hydroxy-propyl)phosphine were generous gifts from Cytec Industries Inc. (Niagara Falls, ON). Potassium tetrakis(pentafluorophenyl)borate (K(B(C$_6$F$_5$)$_4$)) was purchased from Boulder Scientific Company (Longmont, CO). The ionic liquid, tetraoctylphosphonium tetrakis(tetrafluorophenyl)borate (P$_{888}$TB) was prepared by facile metathesis in dichloromethane as has been described elsewhere [14]. Nuclear Magnetic Resonance (NMR) spectroscopy was conducted on a Varian INOVA 400 MHz spectrometer (¹H 400.09 MHz, ³¹P{¹H} 161.82 MHz, ¹⁹F 376.15 MHz). All ¹H spectra were referenced relative to tetramethyl silane (CDCl$_3$; ¹H δ$_H$ = 7.26 ppm and CO(CD$_3$)$_2$; ¹H δ$_H$ = 2.04). The chemical shifts for ³¹P{¹H} NMR spectroscopy were referenced using an external standard (85% H$_3$PO$_4$; δ$_p$ = 0). The chemical shifts for ¹⁹F{¹H} NMR spectroscopy were also referenced using an external standard (trifluorotoluene; δ$_F$=-63.9 ppm). Mass spectrometry for the phosphonium salts was recorded in both positive and negative ion modes using electrospray ionization (ESI) Micromass LCT spectrometer. Phosphonium salts 1-6 were synthesized using either tributylphosphate or tri(hydroxypropyl)phosphine and a stoichiometric excess of the alkyl halide in either acetonitrile or DMF. The solution was stirred for 24 hours before purification and isolation. Ion-exchange reactions were performed by adding solid potassium tetrakis(pentafluorophenyl) borate to a solution containing a phosphonium salt in DCM. The mixture was stirred for 24 hours prior to purification. Purity of the ion-exchange product was determined by silver nitrate tests and by mass spectrometry (absence of (2M+I)$^-$ clusters in TOF-MS-ES+ spectra). Synthesis of the phosphonium salts 4, 5, and 6 is described elsewhere [9, 26]; all characterization data are available upon request.

**Micropipettes.** Micropipettes were fabricated in-house using a facile method described in section 2.3.3 as well as elsewhere [12-14, 16, 27-29].

**Electrochemical Instrumentation.** Measurements were carried out using a Modulab System (Ametek Advanced Measurement Technology, Farnborough, UK) that is
equipped with a femto ammeter. A micro-interface was employed that required only a two-electrode system; no ohmic compensation was necessary; however, the Modulab does possess a positive feedback loop for signal correction. The following electrochemical cells were used:

\[
\begin{array}{c|c|c|c|c}
\text{Ag} & 2.5 \text{ mM IL} & 5 \text{ mM } \text{P}_{\text{soss}} \text{B(C,F}_3)_4 & \text{AgB(C}_6\text{F}_5)_4 & \text{Ag} \\
& (aq) & (DCE) & & \\
\text{AgCl} & 2.5 \text{ mM LiI} & & & \\
\text{(aq)} & & & & \\
\end{array}
\]

(Cell 5.1)

\[
\begin{array}{c|c|c|c|c}
\text{Ag} & 2.5 \text{ mM N(CH}_3)_4\text{I} & 5 \text{ mM IL} & \text{AgB(C}_6\text{F}_5)_4 & \text{Ag} \\
& (aq) & (DCE) & & \\
\text{AgI} & 2.5 \text{ mM LiI} & & & \\
& (aq) & & & \\
\end{array}
\]

(Cell 5.2)

\[
\begin{array}{c|c|c|c|c}
\text{Ag} & 3.4 \text{ mM N(CH}_3)_4\text{Cl} & 5 \text{ mM IL} & \text{AgB(C}_6\text{F}_5)_4 & \text{Ag} \\
& (aq) & (DCE) & & \\
\text{AgCl} & 2.5 \text{ mM LiCl} & & & \\
& (aq) & & & \\
\end{array}
\]

(Cell 5.3)

**5.3 - Results and Discussion**

Two main groups of phosphonium ionic liquids (ILs) were synthesized, including tributyl- and tris(3-hydroxypropyl)phosphonium with the fourth substituent varied as detailed in Table 5.1. The ILs featuring the tris(3-hydroxypropyl) groups exhibited favourable solubility in water and were tested using biphasic electrochemistry by dissolution in the aqueous phase. Figure 5.1 illustrates the cyclic voltammogram (CV) obtained using Cell 5.1 containing the IL 1b, 2b, and 3b with an initial Galvani potential difference between the water (w) and organic (o) phases of −0.100 V. In case of 1b, the CV was first swept in the forward direction, towards positive potentials, at a rate of 0.020 V·s⁻¹. A peak shaped wave was observed with a peak maximum at 0.215 V; this is indicative of the cation transfer, in this case tris(3-hydroxypropyl)hexylphosphonium from w to o, *i.e.* from inside the capillary to the outside.

The scan was continued to a switching potential of 0.434 V and then proceeded in the negative direction to −0.300 V. During the backward scan a sigmoidal-shaped wave can be seen with a half-wave potential at approximately 0.178 V; this is representative of a cation transfer from o to w [21, 30].

The peak shaped wave is a result of the micropipette internal geometry; *i.e.* the microchannel. Species closely associated with the interface rapidly transfer, generating a
sharp increase in the current signal, which ultimately peaks with a subsequent exponential decay in current. During the reverse scan, the sigmoidal wave is analogous to metal-electrolyte electrochemistry at a disk shaped ultramicroelectrode; species in the surrounding solution diffuse from a large – relative to the electrode size – hemispherical volume surrounding the micro-ITIES [21]. This generates a rise in current followed by a steady state and is sometimes referred to as hemispherical diffusion or diffusion-controlled. These data are in good agreement with voltammetry at a liquid|liquid micro-interface held at the tip of a pulled pipette as first published by Girault et al. [30].

The sharp rise in current at the switching potential of 0.434 V is indicative of the transfer of the supporting electrolyte; in this instance Li⁺ from w to o and B(C₆F₅)₄⁻ from o to w. Similarly, at −0.300 V a sharp decrease in current was observed (not shown), which is indicative of I⁻ transferring from w to o, along with P₈₈₈₈⁺ from o to w.

![Cyclic voltammograms](image)

**Figure 5.1:** Cyclic voltammograms acquired at 0.020 V·s⁻¹ with a potential range from approximately −0.300 to 0.500 V using Cell 5.1 with compounds 1b, 2b, and 3b.
CVs obtained using Cell 5.1, shown in Figure 5.1, for ILs 2b and 3b, both utilized a potential range of approximately −0.300 to 0.500 V with a scan rate of 0.020 V∙s⁻¹. The potential scale in each CV experiment was calibrated using the TATB [31], or Parker’s assumption and addition of tetramethylammonium iodide (TMAI) to the aqueous phase. The transfer of TMA⁺ was employed as an internal standard, with a formal transfer potential of 0.160 V [32], using equation 2.9. The half-wave potential, Δωφ₁/₂, for each IT was determined from the peak shaped wave and the potential at the peak maximum, Δωφₓ, within the CV through equation 3.4 [33, 34]. Equation 3.4 was developed for a large (millimeter) sized metal-electrolyte interface, therefore its implementation here is a convenient estimation. To the best of my knowledge, at the time of publication, a similar numerical treatment of the CV profile, as that performed by Nicholson and Shain [33, 34] for large interfaces, has not been presented for IT at a micro-ITIES housed at the tip of a pulled pipette.

Based on this calibration, the formal IT potentials for the IL cations, Δωφ₀,₁IL, 1b, 2b, and 3b, were determined to be 0.189, 0.138, and 0.032 V, respectively. The amount of applied Galvanic potential difference across the w|DCE interface required to elicit IT is related to the energy barrier that must be overcome; the higher the amount of applied potential necessary, the greater the energy barrier. In this case, a high energy barrier signifies a greater hydrophilicity.

In standard redox chemistry, the formal redox potential can be related to the Gibbs free energy via ΔG = −zFE₀ and an analogous relationship can be developed for the IT case utilizing the formal transfer potential; i.e. ΔGᵣᵣ,₀→w = zFΔωφ₀ [20, 35, 36]. This in turn can be employed to estimate the aqueous solubility of the ion of interest through its Kₛᵣ via, ΔGᵣᵣ,₀→w = RT ln Kₛᵣ [20, 35, 36]. In this way the Kₛᵣ for 1b, 2b, and 3b were estimated to be 1.3 × 10⁸, 1.7 × 10⁷, and 2.8 × 10⁵, respectively. This demonstrates a trend of increasing hydrophobicity with the varied R-group according to 1b < 2b < 3b. This is in good agreement with the IL structure; that is, longer alkyl chains elicit greater hydrophobicity. Likewise, fluorination has been used to increase the hydrophobicity of molecular, organic solvents and ILs [37].
Moving forward, the R-tributylphosphonium series, including 1a, 2a, and 3a, along with tetraoctylphosphonium, 7 (see Table 5.1) were investigated. The cations were paired with the tetrakis(pentafluorophenyl)borate anion \((\text{B(C}_6\text{F}_5)_4^−)\) and dissolved in the DCE phase as detailed in Cell 5.2. No IL cation transfer was observed within the polarizable potential window (PPW), as it limited by the transfer of the aqueous phases supporting electrolytes \(\text{Li}^+\) and \(\Gamma\), from w to o, at positive and negative potentials, respectively.

Taking advantage of the high stability of the micro-ITIES electrolytic cell and the low current required by a micro-interface, the region beyond the typical PPW was probed, as was recently demonstrated [27, 28]. Figure 5.2 illustrates the CV obtained using Cell 5.2 with the IL 3a dissolved in the organic phase. During the forward scan, from the initial potential of 0.000 V to 0.487 V, the transfer peak of TMA\(^+\) was visible with a peak potential at 0.188 V. During the reverse scan, a large peak-shaped wave with a peak potential of approximately −0.416 V has been attributed to iodide transfer from w to o.

Figure 5.2: Cyclic voltammogram acquired using Cell 5.2 with 3a as the IL. Instrument parameters included a scan rate of 0.020 V·s\(^−1\), an initial potential of 0.000 V, and a potential range from 0.487 to −0.602 V.

However, in order to elucidate this system further and discern if other ions may be transferring, differential pulse voltammetry (DPV) was employed with the following instrument parameters: 4 mV, +/-50 mV, 0.1 s, and 0.05 s step, pulse amplitude, pulse period, and pulse width, respectively, along with a potential range between 0.000 V and −0.800 V, approximately. Figure 5.3 illustrates overlaid DPV curves obtained for separate experiments such that the IL in Cell 5.2 has been varied such that 7, 1a, 2a, and
are represented by black, red, purple, and green traces, respectively. The potential scale was again calibrated using TMA$^+$ transfer as an internal standard and equation 2.5; however, the half-wave potential was calculated through the following [38, 39]:

\[
\Delta^w \phi_{max} = \Delta^w \phi_{1/2} + \frac{RT}{zF} \sqrt{\frac{D_w}{D_o}} - \frac{\Delta E}{2}
\]  

(5.1)

where $\Delta^w \phi_{max}$ is the potential at the peak maximum, $D_a$ is the diffusion coefficient in phase $a$, and $\Delta E$ is the pulse amplitude. If the diffusion coefficient is assumed to be equal in each phase, equation 5.3 can be reduced to a simple relation.

In all four cases, the sweep was initiated at 0.000 V as shown; a negative peak current was subsequently observed at $-0.265$ V and has been attributed to the transfer of $\Gamma$ from w to o. This provides a formal transfer potential for $\Gamma$ of $-0.290$ V, which is in fair agreement with that determined by Abraham and Danil De Namor [40] ($-0.254$ V) and Samec et al. [41] ($-0.342$ V). The former was calculated based on solubility data whilst the latter was determined through a rigorous numerical approach based on the CV edge of the PPW scan profile [41]. $\Delta^w \phi'_{f'}$ is also in fair agreement with that reported by Girault et al. [42] demonstrated a range of formal ion transfer values for $\Gamma$, from $-0.320$ to $-0.340$ V, dependent on which supporting electrolyte was present in the organic phase, using a microhole experiment with no supporting electrolyte. To the best of my knowledge, this is the first time the IT of $\Gamma$ has been observed through voltammetric techniques at conventional, supporting electrolyte concentrations. Little variation, $\pm 10$ mV, in $\Delta^w \phi'_{f'}$ was observed, which is in good agreement with Giraults group’s results [42].

After $\Gamma$ transfer, a second peak was observed. The peak potential at current maximum varied from $-0.534$ to $-0.490$, $-0.526$, and $-0.639$ V for curves 7, 1a, 2a, and 3a, respectively, which were taken to be the IL cation transfer from o to w. Using these peak maxima, the formal transfer potentials were calculated to be $-0.559$, $-0.515$, $-0.551$, and $-0.664$ V for the cations of ILS 7, 1a, 2a, and 3a, respectively. Similar to the previous case, proceeding to negative potentials attracts the cation (this time dissolved in the DCE phase) and causes it to transfer from o to w. The less applied potential required
the more hydrophilic the ion; therefore, a trend of increasing cation hydrophilicity can be deduced such that $3a < 2a < 1a$ and have calculated $K_{sp}$ values estimated as $5.9 \times 10^{-12}$, $3.5 \times 10^{-10}$, $4.8 \times 10^{-10}$, and $2.0 \times 10^{-9}$, respectively.

**Figure 5.3:** Differential pulse voltammograms recorded using Cell 5.2 with ILs 7, 1a, 2a, and 3a for Instrument parameters included a step, pulse amplitude, pulse period, and pulse width of 4 mV, $+/-50$ mV, 0.1 s, and 0.05 s, respectively with a potential range from approximately 0.000 and $-0.750$ V.

This indicates that the asymmetric cation $3a$ ($P_{44410}^+$) has a greater hydrophobicity than the symmetric tetraoctylphosphonium ($P_{8888}^+$) cation. Compound $3a$ may behave as a surfactant, and this difference in IT potentials may be the result of ion pairing at the interface or increased ion-ion interaction between $P_{44410}^+$ and its counter ion $B(C_6F_5)_4^-$. It is possible that the reduced alkyl chain length translates to greater access to the positively
charged center of $P_{44410}^+$ that, in turn, means more ion-ion interaction between $P_{44410}^+$ and $\Gamma^-$ or $B(C_6F_5)_4^-$. The increased density of ILs compared to molecular solvents has been attributed to the strong interaction between the cation and anion [43], which may lead to greater charge-charge interaction in solution; particularly at the liquid|liquid interface. This interaction is greater with smaller anion components and generates reduced diffusion coefficients of redox species [43]. The symmetric $P_{8888}^+$ cation has its charge shielded by the long alkyl chains and is thus likely to coordinate weakly to either small or large anions in solution.

Alternatively, this disparity between $P_{8888}^+$ and $P_{44410}^+$ transfer potentials may be owing to a surfactant effect. The single longer chain on $P_{44410}^+$ could extend into the organic phase and provide more sites for dispersion interactions. Nonetheless, these findings show the intimate behaviour between ion-pairs at interfaces may be elucidated that using these electrochemical techniques.

The difference in hydrophilicity between 1a and 2a – between the non-fluorinated and fluorinated form, respectively – is slightly more than 4 times. However, taken strictly from a water solubility perspective, this is most likely not an appreciable difference and therefore, the R group -(CH$_2$)$_2$(C$_4$H$_9$) would be as effective as -(CH$_2$)$_2$(C$_4$F$_9$) for water repellent applications. The difference between 1b and 2b is similar to the difference shown between 1a and 2a and serves to corroborate the results for the hydrophobic IL case; 1b is approximately 7 times more hydrophilic than 2b.

Subsequently, the system was swept in the positive direction from $-0.800$ to $0.000$ V and two peaks were observed and demonstrate fair correspondence to those revealed in the negative scan. However, the negative scan direction was employed as the peaks showed greater current maxima and thus were more readily identified/resolved.

Other aqueous phase supporting electrolytes were investigated including LiBr, LiCl, LiNO$_3$, and Li$_2$SO$_4$. Figure 5.4 illustrates a comparison between the DPV curves obtained using Cells 5.2 and 5.3 with the aqueous phase electrolytes LiI and LiCl, respectively; the same instrument parameters employed in Figure 5.3 were used here with the exception of an expanded potential range – from approximately $0.500$ to $-0.800$ V.

Within Curve A of Figure 5.4, 3 peaks can be discerned including the transfer of TMA$^+$ (N(CH$_3$)$_4^+$) followed by $\Gamma^-$ both from w to o at $0.185$ and $-0.240$ V, respectively, whilst
the third, at $-0.639 \text{ V}$ is that of the cation from 3a transferring from o to w. Curve B, however, demonstrates that Cl$^-$ transfer, at roughly $-0.550 \text{ V}$, essentially obscures the DPV and does not allow for the observation of the IL cation transfer; similar results were obtained for the other lithium salts tested. $\Gamma^-$ is sufficiently hydrophilic that its IT potential is shifted so that the more hydrophobic IL cations can be resolved.

**Figure 5.4:** Differential pulse voltammograms recorded using Cell 5.2 and 5.3 for curves A and B, respectively, with IL equal to 3a. Ion transfer peaks of interest have been labelled; note that P$_{44410}$ is the cation for IL 3a. Instrument parameters are the same as those used in Figure 3.

Using the formal IT potential and Gibbs free energy relationship, $\Delta G_i^{\circ'} = zF\Delta \phi^{\circ'}$, the Gibbs free energy of the salt could be determined, $\Delta G_{\text{salt}}^{\circ'} = \Delta G_{\text{cation}}^{\circ'} + \Delta G_{\text{anion}}^{\circ'}$, which was then used to calculate its $K_{sp}$ via $\Delta G_{\text{salt}}^{\circ'} = -RT \ln K_{sp}$.

Table 5.2 summarizes the formal IT potentials for each cation as well as their respective calculated Gibbs free energy of IT and $K_{sp}$. The cations of ILs 4, 5, and 6 were all visible within the PPW and thus analyzed using CV (data not shown). 5 represents the modification of 4 to an acrylate that generates close to a 20 times increase in hydrophobicity that is likely owing to reduced hydrogen bond interactions within the aqueous phase; resonance between the two oxygens in the acrylate would constitute charge delocalization and thus reduced potential for hydrogen bonding between water and 6. Not surprisingly 6 shows still more hydrophobic character than 5, since 6 has no oxygens but with only $\pi$-H interactions from the allyl and aromatic groups along with dispersive forces. Both are possible monomers or polymer additives and while their
changes in hydrophobicity may be obvious, discriminating quantitatively between other more specialized subunits utilizing this technique could be of considerable value.

Table 5.2: List of each cation formal ion transfer potential along with its calculated Gibbs free energy of transfer and water solubility product equilibrium, $K_{sp}$, constant;* $K_{sp}$ was calculated for the IL salt using the standard ion transfer potentials of $\Gamma^-$ and $\text{B(C}_6\text{F}_5\text{)}_4^-$ of $-0.290$ and $0.709$ V [42], respectively.

<table>
<thead>
<tr>
<th>IL</th>
<th>$\Delta_{\phi}^w\phi_{cation}^{(i)}$</th>
<th>$\Delta G_{cation}^{(i)}$</th>
<th>$K_{SP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-0.515</td>
<td>-49661</td>
<td>$2.1 \times 10^{-21}$</td>
</tr>
<tr>
<td>2a</td>
<td>-0.551</td>
<td>-53196</td>
<td>$5.0 \times 10^{-22}$</td>
</tr>
<tr>
<td>3a</td>
<td>-0.664</td>
<td>-64112</td>
<td>$6.1 \times 10^{-24}$</td>
</tr>
<tr>
<td>1b</td>
<td>0.189</td>
<td>18236</td>
<td>$1.3 \times 10^{8}$</td>
</tr>
<tr>
<td>2b</td>
<td>0.138</td>
<td>13340</td>
<td>$1.7 \times 10^{7}$</td>
</tr>
<tr>
<td>3b</td>
<td>0.032</td>
<td>3088</td>
<td>$2.8 \times 10^{5}$</td>
</tr>
<tr>
<td>4</td>
<td>-0.127</td>
<td>-12237</td>
<td>$7.4 \times 10^{-15}$</td>
</tr>
<tr>
<td>5</td>
<td>-0.266</td>
<td>-25665</td>
<td>$3.3 \times 10^{-17}$</td>
</tr>
<tr>
<td>6</td>
<td>-0.34</td>
<td>-32805</td>
<td>$1.9 \times 10^{-18}$</td>
</tr>
<tr>
<td>7</td>
<td>-0.559</td>
<td>-53953</td>
<td>$3.6 \times 10^{-22}$</td>
</tr>
</tbody>
</table>

5.4 - Conclusions

To the best of my knowledge, for the first time the IT of hydrophobic cations have been observed at conventional supporting electrolyte concentrations at an w|DCE micro-
ITIES. The IT potentials are beyond the PPW. This was made possible by utilizing LiI as the aqueous phase supporting electrolyte along with the improved sensitivity of DPV. Two main groups of quaternized phosphonium ILs were examined. The first group consisted of three hydroxypropyl groups with the fourth R group varied; these cations were paired with the iodide anion and dissolved in the aqueous phase for electrochemical analysis. The second set was possessed of 3 butyl substituents with the fourth arm analogous to those found in group one and paired with the $\text{B(C}_6\text{F}_5\text{)}_4^-$ anion; by making the varied R groups identical between the two subsets it was then possible to make comparisons between their trends in hydrophobicity. Significantly, similar trends were
observed between the first and second group whose transfer occurred within and outside the PPW, respectively, therefore offering validation for this technique of operating outside the PPW.

This chapter hopefully serves to demonstrate the complementary utility of liquid-liquid electrochemistry used in conjunction with WCA and other surface techniques, towards the evaluation of ionized polymer components. This electrochemical method can be used early on in the development stages to distinguish compounds of interest, in this way, focusing synthetic efforts.

5.5 - References

Chapter 6.1 - Determination of alkali metal ion transfers at liquid|liquid interfaces stabilized by a micropipette

6.1.1 - Introduction

Ion transfer (IT) at an immiscible interface between two electrolytic solutions (ITIES), often using biphasic systems like water|1,2-dichloroethane (w|DCE) [1-16] or water|nitrobenzene (w|NB) [1, 17-20], has been described as useful biomimetics for cell membranes [21], employed as ion-selective electrodes in sensor applications [22-25], and rationalized as having implications towards metal ion extraction processes [11, 12, 21, 26]. IT can be described using equation 1.4. This can be instigated through a polarized interface, whereby one ion in a dissolved salt is miscible in either phase such that a potential difference, \( \phi_w - \phi_o = \Delta_o^w \phi \), develops across the ITIES [17-19, 27]; where \( \phi_o \) is the potential in phase \( \alpha \). Alternatively, the application of an external potential, through the use of electrodes immersed in both phases, can also cause IT through a push/pull mechanism; as the potential is made more positive in the aqueous phase cations are repelled (pushed) across the ITIES while anions are attracted (pulled) from the organic phase. In either case, the potential at which ions transfer in any single biphasic system, is referred to as the standard transfer potential, \( \Delta_o^w \phi^o \), when considering only activity coefficients (\( a_{i,\alpha} \)), or formal transfer potential, \( \Delta_o^w \phi^{o'} \), when concentrations (\( c_{i,\alpha} \)) are used in approximation at high dilution. This is expressed mathematically in the following Nernst relationship:

\[
\Delta_o^\beta \phi_l = \Delta_o^\beta \phi_l^o + \frac{RT}{z_i F} \ln \left( \frac{a_{i,\alpha}}{a_{i,\beta}} \right) = \Delta_o^\beta \phi_l^o + \frac{RT}{z_i F} \ln \left( \frac{\gamma_{i,\alpha}}{\gamma_{i,\beta}} \right) + \frac{RT}{z_i F} \ln \left( \frac{c_{i,\alpha}}{c_{i,\beta}} \right) = \Delta_o^\beta \phi_l^o + \frac{RT}{z_i F} \ln \left( \frac{c_{i,\alpha}}{c_{i,\beta}} \right) \tag{6.1.1}
\]

where \( F, R, \) and \( T \) are Faraday’s constant, the gas constant, and temperature in Kelvin, respectively. The thermodynamics diagram for the IT is illustrated in Figure 1.2, where the formal ion transfer potential is linked with the Gibbs free energy. If particularly hydrophobic and hydrophilic supporting electrolyte salts are dissolved in the organic and aqueous phases, respectively, such that ion partitioning across the ITIES is negligible, then it is said to be polarizable [27, 28]. The formal IT potentials of these salts then
dictate the size of the polarizable potential window (PPW); that is the applied potential range that can be scanned or swept using a potentiostat and a triangular waveform, while the measured current is plotted versus the applied potential to generate a cyclic voltammogram (CV). In this way, the CV is limited by the IT of the supporting electrolyte, which appears as an exponential increase in current at the positive end, as a result of the metal cation transferring from w to o and the large organic anion from o to w. Alkali metal salts are typically used owing to their high hydrophilicity that, in turn, means a larger PPW and translates into an increased ability to characterize other electrochemical phenomena occurring at lower potentials [3, 6, 9, 29].

However, since these ions limit the PPW, their formal transfer potentials are not readily determined. Free metal formal IT potentials are valuable constants when evaluating the effectiveness of ligand assisted or facilitated ion transfer (FIT); this process is shown in equation 1.6. Figure 1.2 illustrates how ligands can be used to lower the Gibbs free energy of transfer and how this relates to hydration and solvation. Equation 1.6 shows one possible mechanism in which the ligand is considered to be extremely hydrophobic and remains in the organic phase; this is referred to as ‘transfer through interfacial complexation’ (TIC) in the forward direction and ‘transfer through interfacial decomplexation’ (TID) if the reaction is reversed [14, 15]. It should be noted that two other mechanisms are recognized and include transfer of the metal species followed by organic phase complexation (TOC) or, if the ligand has some hydrophilicity, aqueous phase complexation and transfer (ACT) [14, 15]; these mechanisms are illustrated in Figure 1.3. The electrochemistry of FIT has been the focus of much research [15, 20, 30] and is an excellent resource to evaluate various ligands and biphasic solvent systems for metal extraction. Girault et al. [15] developed a facile series of equations that have been used as the basis of a diagnostic tool for the evaluation of biphasic metal extraction [11, 12]; of particular interest is one describing TIC/TID shown below:

\[
-\frac{zF}{RT} \left( \Delta^w_\phi \phi^*_{L,o} - \Delta^w_\phi \phi^*_{o,L} \right) = n \ln \left( c^*_{L,o} \right) + \ln \beta + \ln \xi \quad (6.1.2)
\]

\( \Delta^w_\phi \phi^*_{L,o} \) is the formal IT potential of the metal ion-ligand complex and varies depending on the initial ligand concentration, \( c^*_{L,o} \). \( \xi \) is equal to \( \sqrt{D_o/D_w} \); where \( D_o \) and \( D_w \) are the
diffusion coefficients in the organic solvent and water phases, respectively. In this way, a linear relationship can be developed such that the slope and y-intercept are the stoichiometry, \( n \), and overall complexation constant, \( \beta \). These constants are then used to discriminate between biphasic and ligand systems generating a quantitative description of metal ion extraction efficiency.

However, a serious problem exists in the determination of \( \Delta_e^w \phi^o \); since the metal species typically limit the PPW, this constant is difficult to determine. Early attempts towards estimating them used numerical calculations surrounding the limiting current profile at the edge of the PPW utilizing a large-ITIES (centimeter scale) [3, 6, 7]. Recently, the theoretical model developed by Oldham [29] for little or no supporting electrolyte at an ultramicroelectrode (UME) was translated for use at a microhole ITIES by Wilke [8], and was used to determine multiple formal IT potentials through a curve fitting technique [9]. The strategy, therein [8], arose from the idea that reducing the Faradaic current at the edge of PPW by means of the micro-interface and minimum electrolyte concentrations would allow the observation of these elusive species. The interface is often supported through a microhole drilled in a polyimide film using UV-photoablation [9, 16]; however, it is difficult to achieve a consistent, uniform hole geometry and the film has a limited number of uses as it will become deformed by the organic solvent. A pulled, silanized glass pipette with the micro-ITIES supported at the tip and held in a specialized micropipette holder offers another method for reaching alkali metal IT [2]. This apparatus has been further developed by utilizing a syringe that greatly stabilizes the ITIES [10-13]. The micropipette fabrication method generates a microchannel that is of uniform, consistent diameter, and constructing it out of glass means the apparatus can be used almost indefinitely. By virtue of the ITIES stability, the simple IT of alkali metals traditionally limiting the PPW at typical supporting electrolyte concentrations (~5 mM) have been observed. Herein is described the evaluation of their IT and formal IT potentials using CVs and differential pulse voltammograms (DPVs).

Several excellent liquid|liquid electrochemical reviews have been published and were invaluable in preparing this report; a couple of these are provided [27, 28].
6.1.2 – Experimental

6.1.2.1 Chemicals
All chemicals were of reagent grade, having been used as purchased without further purification. Lithium nitrate (LiNO$_3$), sodium nitrate (NaNO$_3$), potassium nitrate (KNO$_3$), rubidium nitrate (RbNO$_3$), cesium nitrate (CsNO$_3$), 1,2-dichloroethane (DCE), dichloromethane (DCM), and trimethylchlorosilane were bought from Sigma-Aldrich Canada Ltd. (Mississauga, ON). Trihexyltetradecylphosphonium chloride (P$_{66614}$Cl) and potassium tetrakis(pentafluorophenyl)borate (KTB) were obtained from Strem Chemicals Inc. (Newburyport, MA) and Boulder Scientific Company (Longmont, CO), respectively. All aqueous solutions were prepared using ultrapure, Milli-Q, water (18.2 MΩ). The organic phase supporting electrolyte P$_{66614}$TB was prepared through a simple metathesis reaction between the P$_{66614}$Cl and KTB salts in dichloromethane in a procedure described elsewhere [13].

6.1.2.2 Micropipette
Micropipette fabrication has been described in a few recent publications [10-13], as well as in section 2.3.3.

6.1.2.3 Instrumentation
CVs and DPVs were obtained using a Modulab System (Ametek Advanced Measurement Technology, Farnborough, New Hampshire, United Kingdom) equipped with a femto ammeter. The working electrode lead of the potentiostat was attached to the micropipette holder through a BNC connector that in turn was connected to an integrated silver wire mounted within the aqueous phase; the counter and reference electrodes were coupled to a single silver wire immersed in the organic phase. Because of the small current employed at a micro-ITIES, the system only requires two electrodes. The following electrochemical cells were used:

\[
\begin{array}{c|c|c|c|c}
\text{Ag} & \text{AgNO}_3 & 5 \text{ mM XNO}_3 & 5 \text{ mM P}_{66614} \text{TB} & \text{AgTB} & \text{Ag} \\
\text{(aq)} & \text{(aq)} & \text{(DCE)} & & & \\
\end{array}
\]  
(Cell 6.1.2)

\[
\begin{array}{c|c|c|c|c}
\text{Ag} & \text{AgCl} & 5 \text{ mM TEACL} & 5 \text{ mM P}_{66614} \text{TB} & \text{AgTB} & \text{Ag} \\
\text{(aq)} & \text{(aq)} & \text{(DCE)} & & & \\
\end{array}
\]  
(Cell 6.1.3)
To ensure the ITIES remained at the tip of the capillary, it was continuously monitored during electrochemical experimentation using a CCD camera (Motic Inc., Richmond, BC) fixed to a variable 12× magnification lens assembly (Navitar, Rochester, NY).

6.1.3 - Results and Discussion

6.1.3.1 Cyclic voltammetry
The CV obtained using Cell 6.1.1 with X equal to Cs⁺ is shown in Figure 6.1.1A with an initial potential of 0.000 V, from which the potential was swept at a rate of 0.020 V·s⁻¹ in the forward direction towards more positive potentials until 0.900 V was reached. During this initial segment a peak-shaped wave can be observed at approximately 0.600 V which is attributed to the simple ion transfer (IT) of Cs⁺ from w to o.

The CV was subsequently scanned in the reverse direction from 0.900 to −0.450 V, during which two curve features were observed; a sigmoidal shaped wave with a half-wave potential of 0.480 V and a peak-shaped wave at −0.400 V. These have been attributed to the return transfer of Cs⁺ from o to w and the IT of NO₃⁻ from w to o, respectively. Finally the potential was swept from −0.450 to 0.000 V and a sigmoidal shaped wave was observed with a half-wave potential of −0.311 V, which is indicative of NO₃⁻ IT from o to w. The potential scale has been calibrated, and the formal transfer potential, \( \Delta_{o}^{w} \phi \), was determined, using the tetraphenylarsonium-tetraphenylborate (TATB), or Parker’s assumption [18, 31]. This is possible by taking advantage of the nitrate IT as an internal reference, which was taken to be −0.380 V, and using equation 2.9. The formal transfer potential of nitrate was determined through calibration with the well established formal transfer potential of tetramethylammonium (TMA⁺), 0.160 V [5, 6]. While the half-wave potentials, \( \Delta_{o}^{w} \phi_{1/2} \), were obtained from the CVs using the peak potential, \( \Delta_{o}^{w} \phi_{p} \), and equation 3.4 [32]. Equation 3.4 was developed based on a reversible Nernstian system without considerations for migration effects [32]; while it is unclear as to whether migration is present, the use of equation 3.4 is done as an approximation.

The shapes of the CVs shown in Figure 6.1.1A for Cs⁺ and NO₃⁻ are in good agreement with simple IT at an ITIES housed at the tip of a micropipette [2, 33]. Such that an ion is transferred from w to o, a peak-shaped wave is observed owning to the
pipette geometry; the limited volume of the aqueous phase in the microchannel means that there is a small amount of ions near the ITIES and, as such, they are consumed rapidly generating a sharp rise in the current response followed quickly by an exponential decay (*i.e.* peak-shaped) [33]. In this initial scenario the system is said to be under consumption control. During the return scan, the sigmoidal wave is a product of the system under diffusion control. The relatively large hemispherical volume directly surrounding the ITIES, on the organic side, means that material can freely diffuse to the interface faster than it is consumed. This results in a sharp rise followed by a plateau in the current-potential response (*i.e.* a steady state current) [33].

Figure 6.1.1: A. CV obtained with an initial/final potential of 0.000 V, a potential range from approximately −0.450 to 0.900 V, and a scan rate of 0.020 V·s⁻¹, using Cell 6.1.1 with X equal to Cs⁺; B. DPV of the same cell acquired with a potential range from −0.450 to 0.900 V, with a step, pulse amplitude, period, and pulse width of 4 mV, 50 mV, 0.1 s, and 0.05 s, respectively.

The formal transfer potential of free Cs⁺ has long been established [6, 9], but at the metal ion concentrations shown in Cell 6.1.1, Cs⁺ IT would typically limit the PPW; this is seen as a continuous rise in current, which was not observed. However, a plateau
in the current response can be seen during the forward scan. This was believed to be the transfer of the anionic component of the supporting electrolyte in the organic phase, tetrakis(pentafluorophenyl)borate (TB⁻), from o to w, which would generate a sigmoidal shaped wave with a steady state current; because TB⁻ IT signal is merged, or occurs almost simultaneously with Cs⁺ IT, only the steady state portion of the curve can be seen. Similarly a possible peak-shaped wave can be discerned at 0.700 V, for the reverse scan, which would indicate the transfer of TB⁻ back across the ITIES from w to o.

6.1.3.2 Differential pulse voltammetry

In order to explore this phenomenon further and possibly resolve Cs⁺ and TB⁻ IT, DPVs were acquired using Cell 6.1.1 with the following instrument parameters: a potential range from −0.450 to 0.900 V with a step, pulse amplitude, period, and pulse width of 4 mV, 50 mV, 0.1 s, and 0.05 s, respectively. Figure 6.1.1B depicts the DPV obtained with CsNO₃ in the aqueous phase; two peaks can be observed at approximately −0.380 and 0.455 V, which are ascribed to the IT of NO₃⁻ and Cs⁺, respectively. Interestingly, after the peak at 0.455 V, there is a shoulder in the current response, which, when compared to the CV experiment is associated with the proposed TB⁻ IT. Therefore, in order to elucidate Cs⁺ and TB⁻ IT, a Gaussian curve fitting approach was employed using Igor Pro 6.22a software (Wavemetrics, Portland, OR); the multi-peak curve fitting is shown overlaid on to the DPV in Figure 6.1.1B with each IT fit separately for NO₃⁻ (blue), Cs⁺ (green), TB⁻ (dotted), and a composite of all three (red); the individual peak fittings are displayed without the incorporation of the baseline correction factor used in the composite curve. Using this method, the formal IT potential, Δ⁰", of Cs⁺ and TB⁻ was determined to be 0.466 and 0.854 V, respectively.

In order to determine the influence of TB⁻ and the alkali metal cations on the peak intensity of the DPV curves, a simple concentration experiment was conducted with the results displayed in Figure 6.1.2. In Figure 6.1.2 curves A, B, C, and D correspond to LiNO₃ concentrations in the aqueous phase of 5, 5, 2, and 2 mM where as P₆₆₆₁₄TB in the DCE phase was 5, 1, 5, and 1 mM, respectively. Thus, between traces A and B, when the amount of P₆₆₆₁₄TB is dropped significantly, the peak maximum drops from 1.7 to 1.4 nA; however, if LiNO₃ is shifted from 5 to 2 mM, then this generates a dramatic drop, as seen between curves A and C, from 1.7 to 0.8 nA. Additionally, the final DPV, D in
Figure 6.1.2, shows the system with a limited amount of analyte/supporting electrolyte. From this facile experiment it can be concluded that TB$^-$ is a small contributor to the IT signal and simultaneously gave a current range with which to target during curve fitting. It is interesting to note that the peak maxima for these various concentrations are very consistent, ranging from 0.708 to 0.705, 0.692 and 0.689 V; this indicates that this method is reasonably concentration-independent.

![Graph](image)

**Figure 6.1.2:** DPVs acquired using Cell 6.1.1 with X = Li$^+$, initial and final potentials of 0.000 to 1.250 V as well as step, pulse amplitude, pulse period, and pulse width of 4 mV, 50 mV, 0.1 s, and 0.05 s, respectively. The concentrations of LiNO$_3$ in water and P$_{66614}$TB in DCE were varied such that contain (A) 5 and 5 mM; (B) 5 and 1 mM; (C) 2 and 5 mM; and (D) 2 and 1 mM of the solutions, respectively.

It is important to note that the w|DCE interface was monitored continuously throughout each electrochemical experiment and no movement, on a microscopic level, was observed. This is in contrast to an excellent report by Dale and Unwin [34] in which they observed the movement of an w|DCE interface held in a pulled capillary using confocal scanning laser microscopy. In that report [34] the DCE phase was maintained within the capillary and the interfacial diameter was 44 $\mu$m. In order to mitigate the movement of the ITIES the DCE phase was held externally with the pipette mounted and immersed in a vertical position; DCE has a higher density so putting it inside a vertically mounted pipette would favour droplet formation and would be a force working against
maintaining a static surface tension. Furthermore, in the present chapter a smaller interface was also employed, 25 μm, in order to aid stability. Lastly, the syringe incorporated into the experimental design was integral to maintaining the ITIES; no mention to a similar implementation within the experimental set up could be found in the article by Dale and Unwin [34].

It should also be noted that the DCE phase was considered to be water-saturated. It has recently been discovered that the water concentration within the organic phase can affect the formal transfer potentials of ions across the w/o interface [35], essentially facilitating their transfer (i.e. reducing the applied potential required to elicit IT). Water saturated organic phases are typical during metal extraction techniques and are essentially unavoidable; therefore, the experimental conditions reflect those experienced during conventional reprocessing at larger interfaces.

6.1.3.3 IT of other alkali metal ions
Owing to the stability of the system using Cs\(^+\), other alkali metal ions were similarly tested such that X in Cell 6.1.1 was substituted with Li\(^+\), Na\(^+\), K\(^+\), and Rb\(^+\) in turn with formal IT potentials determined using the Gaussian curve fitting as 0.696, 0.710, 0.638, and 0.562 V, respectively. Both CV (data not shown) and DPV experiments were conducted with the DPV traces overlaid in Figure 6.1.3. The formal transfer potential results, obtained from the DPV curve fitting, are listed in Table 6.1.1 along with estimations towards the TB\(^-\) formal transfer potential for each associated metal ion.

Also included in Table 6.1.1 are formal transfer potentials gleaned from published values [3, 6, 7, 9]. The first set was reported by Girault et al. [6] in 1991, in which the formal transfer potentials of all the alkali metal ions but Cs\(^+\) were estimated through a working curve developed numerically and based on the ratio of the edge of scan and return peak current, at the edge of the PPW, for a large w/DCE interface. Cesium was distributed in concentrations such that it did not limit the PPW, thus appearing within it; Cs\(^+\) and tetraphenylborate were then used to validate their method by increasing their concentrations to a point where they did limit the PPW [6]. These formal IT potentials were also estimated by Samec et al. [3, 7] using a rigorous numerical approach incorporating partition and activity coefficients; however, this method again used a large-ITIES and the current at the edge of the PPW. In both these cases, complete IT was not
strictly observed and their values should be considered as estimates. The trend in hydrophilicity shown by these previous publications, \( \text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+ \) \([3, 6, 7]\), is reproduced herein and can be linked to the increasing atomic radius. As the van der Waals radius increases (Table 6.1.1) \([36]\), the hydrophilicity decreases with the only exception to this trend being lithium. This can possibly be explained by its smaller hydration sphere \([37]\); lithium is proposed to have 4 water molecules coordinated within its primary hydration sphere while the other alkali metal ions have between 5 and 8. This smaller hydration sphere may result in a decrease in the amount of energy required to elicit IT.

![Graph showing the trend in hydrophilicity](image)

**Figure 6.1.3:** DPVs acquired using Cell 6.1.1 (alkali metal ions) with initial and final potentials of \(-0.500\) to \(1.250\) V and step, pulse amplitude, pulse period, and pulse width of \(4\) mV, \(50\) mV, \(0.1\) s, and \(0.05\) s, respectively.

Almost twenty years later, Girault *et al.* \([9]\), using the microhole curve fitting technique mentioned previously, determined \(\Delta_{\text{o}}^w \phi_{\text{Li}^+}^{\phi'} \) and \(\Delta_{\text{o}}^w \phi_{\text{Cs}^+}^{\phi'} \) to be \(0.650\) and \(0.480\) V, respectively. This technique requires limited supporting electrolyte, implementing a curve fitting approach applied directly to the experimental CVs or linear sweep voltammograms (LSVs). The mathematical treatment surrounding the current response in a system with minimal to no supporting electrolyte at an ultramicroelectrode was pioneered by Oldham \([29]\) and later adapted for use at a micro-ITIES by Wilke \([8]\). The metal ion formal transfer potentials are in excellent agreement with this previous report;
however, the value obtained for $\Delta^w_{o} \phi^{TF}$ shows poor agreement: 0.710 [9] versus 0.904 V for $X = Cs^{+}$. TB$^{-}$ was examined for each of the alkali metal ions and are listed in Table 6.1.1 with all showing similar formal transfer potentials of approximately 0.9 to 1.0 V.

**Table 6.1.1**: Formal ion transfer potentials of metal ions traditionally limiting the PPW obtained from the literature along with the CV and DPV experiments reported herein.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\Delta^w_{o} \phi^{TF}$ (large-ITIES$^{a}$)</th>
<th>$\Delta^w_{o} \phi^{TF}$ (large-ITIES$^{b}$)</th>
<th>$\Delta^w_{o} \phi^{TF}$ (microhole$^{c}$)</th>
<th>$M^{+}$</th>
<th>TB$^{-}$</th>
<th>$\text{Radii}_{\text{vdW}} \AA$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>0.576</td>
<td>0.590$^{b}$</td>
<td>0.650</td>
<td>0.696</td>
<td>1.041</td>
<td>1.82</td>
</tr>
<tr>
<td>Na$^{+}$</td>
<td>0.579</td>
<td>0.590$^{b}$</td>
<td>0.679</td>
<td>1.063</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.538</td>
<td>0.518$^{b}$</td>
<td>0.638</td>
<td>1.061</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>0.475</td>
<td>0.435$^{c}$</td>
<td>0.562</td>
<td>1.000</td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>0.386</td>
<td>0.363$^{c}$</td>
<td>0.516</td>
<td>0.904</td>
<td>3.43</td>
<td></td>
</tr>
</tbody>
</table>

\[a \text{ is ref } [6]
\[b \text{ is ref } [7]
\[c \text{ is ref } [3]
\[d \text{ is ref } [9]
\[e \text{ is this work}
\[f \text{ is ref } [36]
\[vdW \text{ is van der Waals radii}]

The $\Delta^w_{o} \phi^{TF}$ values listed should be treated as effective formal ion transfer potentials since, at the edge of the PPW, migration and double layer capacitative effects begin to increase [4, 7, 17]. Because of the nature of this experiment, the use of a two-electrode system and pushing the boundaries of the PPW, some uncompensated $iR$-drop may also be present; however, this is mitigated by using a DPV technique versus strictly CV. Additionally, the large amount of ion flux taking place at the ITIES during the alkali metal ion transfer may result in a delay in the onset of TB$^{-}$ IT. The massive injection of alkali metal ions into the organic phase would, in and of itself, generate a localized electric field which, in turn, may retard the movement of TB$^{-}$, impeding its IT.

### 6.1.3.4 Verification of TB$^{-}$ transfer

To confirm the presence of TB$^{-}$ transfer, Cell 6.1.1 with $X$ equal to TMA$^{+}$ was utilized since it transfers well within the PPW and well before TB$^{-}$. Figure 6.1.4 illustrates the DPV experiment performed using the same instrument parameters as described for the alkali metal ions except for the potential range, which was from $-0.100$ to $0.800$ V. Peaks associated with TMA$^{+}$ and TB$^{-}$ IT were characterized at 0.135 and 0.590 V,
respectively; the DPV was also subjected to the same multi-peak, Gaussian curve fitting as was performed for Cs$^+$ and the other alkali metal ions. The DPV, illustrated in Figure 6.1.4, was calibrated using the formal ion transfer potential of TMA$^+$; 0.160 V [5, 6]. Interestingly, the formal ion transfer potential for TB$^-$ was found to be 0.615 V.

![Differential pulse voltammogram](image)

Figure 6.1.4: Differential pulse voltammogram acquired using Cell 6.1.1 with X equal to TMA$^+$, a potential range from −0.100 to 0.800 V, a step, pulse amplitude, period, and pulse width of 4 mV, 50 mV, 0.1 s, and 0.05 s, respectively.

Analogous experiments were conducted using Cell 6.1.2 and tetraethylammonium chloride (TEACl); just as in the TMA$^+$ experiments, the PPW was calibrated using the known formal transfer potential for TEA$^+$, 0.019 V [5]. The DPV curve fitting (data not shown) determined a similar $\Delta w_o \phi_{TB}^w$ to that found using TMA$^+$; 0.610 V. It is plausible that TMA$^+$ and TEA$^+$ would have little ion-ion interaction at the interface due to their transfer potentials occurring far away from the TB$^-$ IT, whereas the massive flux of alkali metal ions at the interface may exert a considerable influence on the determination of TB$^-$ transfer potential. Admittedly, the formal ion transfer potential of TB$^-$ is an estimate and the IT may occur simultaneously with the alkali metal ion transfer. Interestingly, Girault et al. [9] performed a thorough verification of their microhole technique where they analyzed $\Delta w_o \phi_{TB}^w$ in association with various counterions and in relation to different metal salts in the aqueous phase; they showed that the TB$^-$ formal transfer potential could vary from 0.670 to 0.700 to 0.710 V. The $\Delta w_o \phi_{TB}^w$ value in the presence of TMA$^+$ and TEA$^+$
agrees well with those previously reported by Girault et al. [9]. Li$^+$ and Cs$^+$ were present in their study, however, at a lower concentration.

Based on the reduced peak current intensity of the TB$^-$ IT, it should be noted that the major signal contributors, in the alkali ion case, are these ions themselves. While the micropipette technique may be poor for the determination of TB$^-$ formal transfer potential, owing to the simultaneous and overwhelming IT signal for the cation from w to o, it is certainly an excellent method for obtaining the formal ion transfer potential of many hydrophilic ions originating inside the pipette.

6.1.4 - Conclusions

The observed simple IT of all alkali metal ions and the characterization of their formal ion transfer potentials at a micro w/DCE interface, using CV and DPV, have been performed for the first time. Using Gaussian curve fitting of the experimentally acquired DPV, the formal transfer potentials were determined to be 0.696, 0.710, 0.638, 0.562, and 0.516 V for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$, respectively.

Using a micro liquid|liquid interface housed at the tip of a micropipette, equipping it with a modified pipette holder incorporating a syringe, and silanization of the pipette all contributed to the greatly improved stability of the interface able to observe alkali metal ion transfer. The use of a micro-ITIES reduced the amount of Faradaic current at the PPW edge and thus allowed access to potentials never before achieved using conventional electrolyte concentrations at a liquid|liquid interface.

The simultaneous transfer of TB$^-$ was also discussed with evidence towards migration and increased flux at the interface contributing to a delay in its transfer and therefore, resulting in the observed apparent formal ion transfer potentials of higher than 0.900 V.

6.1.5 - References

Chapter 6.2 - Formal transfer potentials of strontium and uranyl ions at water|1,2-dichloroethane interfaces

6.2.1 - Introduction

With the imminent depletion of the world’s fossil fuel supply and the long recognized environmental issues surrounding anthropogenic CO\textsubscript{2} emission [1], alternative energy sources are being sought; front runners include solar and nuclear power generation. Nuclear power plants, unlike solar, are not an intermittent energy source [1] and, therefore, are considered more reliable. Implementing a closed loop fuel cycle, in which spent nuclear fuel (SNF) is recycled instead of – as in the present model – prepared for permanent geologic disposal, can extend the life of the nuclear industry for hundreds of years [1].

Indeed, the majority of SNF, approximately 95%, is UO\textsubscript{2} suitable for energy production; the other 5% is fission decay products (e.g. \textsuperscript{90}Sr and \textsuperscript{137}Cs), which can behave as neutron absorbers, disrupting the fission process and lowering the fuel rod efficiency [2]. These metals have isotopes that are valuable in-and-of-themselves for use in nuclear medicine or radioimmunotherapy (RIT) [3-7]. \textsuperscript{90}Y, combined with monoclonal antibodies (mAb), has been used in targeting and treating cancer [3, 4, 6, 7]. Similarly, \textsuperscript{82}Rb is used for myocardial perfusion imaging, a diagnostic technique examining the heart and circulatory system [8]. The advantage of \textsuperscript{90}Y and \textsuperscript{82}Rb is that they are short lived isotopes ($t_{1/2} = 64$ hours and 76 seconds respectively), which is useful since it means less radiolytic toxicity to patients, but also means on-site clinical generators are required for these isotopes to be effective [7, 9-11]. These in-house generators use a parent/daughter strategy and, from the above examples, take the form of \textsuperscript{90}Sr/\textsuperscript{90}Y and \textsuperscript{82}Sr/\textsuperscript{82}Rb [7, 9-11]. Strontium is a major component of SNF [2] and, thus could be a source for parent isotopes.

The take home message is that SNF should not be viewed simply as waste but as a potential resource. This begs the question: how to selectively and effectively isolate these materials? \textsuperscript{90}Sr has been separated from the nuclear waste stream almost since the inception of the civilian nuclear program owing to its use in other applications [12]. However, its recent incorporation into the medicinal field has sparked interest towards improving the purity of \textsuperscript{90}Sr extraction.
Contemporary methods of metal ion separation involve the use of aqueous/organic biphasic systems with processes like Plutonium/URanium Extraction (PUREX) and TRans-Uranic Extraction (TRUEX) [13-15]. In either case, a ligand, dissolved in the organic phase, coordinates to the metal center causing it to partition into the organic phase.

Ion partitioning or ion transfer of metals has been analyzed through a facile electrochemical technique at the interface between two immiscible electrolytic solutions (ITIES), often between water and 1,2-dichloroethane (w|DCE) [16-21] or water and nitrobenzene (w|NB) [22, 23]. In this method ions are pushed or pulled across the ITIES by an applied potential. Should a potential be administered to either phase, a potential drop or difference would develop across the ITIES, such that $\Delta \phi = \phi_w - \phi_o$, where $\phi$ is the potential in phase w or o. A positive potential, administered to the aqueous phase, will repel cations prompting them to cross the interface while attracting anions from the organic phase. If applied to free metal species this is termed simple ion transfer (IT) and is shown in equation 1.4. However, if a ligand, $L$, is dissolved in the organic phase and used to assist ion transfer, the mechanism is called facilitated ion transfer (FIT) and equation 6.1.3 is used. Just as in conventional electrochemistry at a solid electrode where $\Delta G = -zFE^o$, the Gibbs free energy can be related to the potential difference developed across the ITIES in the same manner, $\Delta G = zF\Delta \phi^o$. Where $E^o$ is the formal redox potential at a solid electrode, $\Delta \phi^o$ is the formal IT potential at an aqueous|organic solvent interface, $z$ is the charge, and $F$ is Faraday’s constant.

The theory of FIT at a w|o interface, using cyclic voltammetry (CV), has been developed thoroughly [18, 19, 24, 25]. Equation 6.1.2 forms the basis of a diagnostic method for evaluating various ligands and biphasic systems, if we assume that diffusion processes are equal in both phases. Equation 6.1.2 differentiates between the formal IT potential of the metal ion-ligand complex, $\Delta \phi^o_{L,o}$, and that of the free metal ion species, $\Delta \phi^o_{o}$; where the latter is a constant and behaves like a point of reference, whereby, with increasing initial ligand concentration, $c_{L,o}^*$, the metal ions transfer more easily. Thus, the formal transfer potential of the metal ion-ligand complex is linearly dependent on the
ligand concentration. The $n$ and $\beta$ terms are the overall stoichiometry of the interfacial complexation reaction (equation 1.6) and its associated, overall complexation constant, respectively. In this way, by varying the ligand concentration in the organic phase and measuring $\Delta \phi^{\text{ITIES}}_{\Delta \mu}$ through CV experiments, $n$ and $\beta$ can be determined and used as a quantitative measure towards the fitness of various ligand and solvent combinations.

Unfortunately, this is complicated by the fact that most free metal ionic species transfer outside the polarized potential window (PPW) and their formal transfer potential constants are difficult to determine, due to their high hydrophilicity. At first, Girault et al. [26, 27], working at a large (centimeter scale) ITIES, used the ratio between the current at the edge of scan and the return peak current ($I_{\text{cos}}/I_{\text{rp}}$) along with working curves generated through numerical calculations to estimate the transfer of alkali ions and other multiply charged metals. Similarly, Samec et al. [28, 29] implemented sophisticated numerical calculations compared to the profile of the PPW edge to estimate the formal IT potentials.

Later, with improvements towards the micro-ITIES apparatus, a microhole interface was utilized [30-32]. This technique was based on the principle of minimal supporting electrolyte first developed for solid ultramicroelectrodes by Oldham [33], but later extended to the micro liquid|liquid interface by Wilke [32]. Girault et al. [30] examined several cations and anions through direct curve fitting of the experimentally acquired CVs. However, this micro-ITIES is typically supported at a hole formed in a polyimide sheet (25 μm thick) via UV photoablation. It is difficult to ensure a consistent microhole size and geometry while, additionally, the polyimide film can become deformed by absorption of the organic solvent, limiting the number of times it can be used. This approach focused on reducing the interfacial size and the amount of electrolyte in solution in order to limit the Faradaic current in the hopes of observing simple IT at higher potentials.

Herein, is described the facile observation of IT of metal ion species at a micro-ITIES, housed at the tip of a 25 μm diameter silanized borosilicate glass capillary, with the formal IT potential being obtained directly from differential pulse voltammograms (DPVs). This is made possible by the use of a custom-modified micropipette holder, intended for physiological applications, which is equipped with a syringe greatly
stabilizing the ITIES at the capillary tip. This apparatus was used to observe the IT of Sr\(^{2+}\) and UO\(_2^{2+}\) directly, at conventional concentrations, for the first time; in this way determining their formal transfer potential. Additionally, a glass capillary can be used almost indefinitely and the fabrication method ensures a consistent micro-ITIES size of 25 μm in diameter.

6.2.2 - Experimental

6.2.2.1 - Chemicals
All chemicals were of reagent grade and utilized without further purification. Uranium nitrate hexahydrate (UO\(_2\)(NO\(_3\))\(_2\)·6H\(_2\)O) and strontium nitrate (Sr(NO\(_3\))\(_2\)) were purchased from Fisher Scientific (ThermoFisher Scientific, Ottawa ON) and Sigma-Aldrich Canada Ltd. (Mississauga, ON), respectively. Trihexyltetradecylphosphonium chloride (P\(_{66614}\)Cl) and potassium tetrakis(pentafluorophenyl)borate (KTB) were obtained from Strem Chemicals Inc. (Newburyport, MA) and Boulder Scientific Company (Longmont, CO), respectively. Aqueous solutions were made up using ultrapure, Milli-Q, water (18.2 MΩ). The organic phase supporting electrolyte P\(_{66614}\)TB was prepared through a simple metathesis reaction between the P\(_{66614}\)Cl and KTB salts in dichloromethane in a procedure described elsewhere [34].

6.2.2.2 - Micropipette
A few recent publications describe the micropipette fabrication [20, 21, 34, 35], with a detailed description available in section 2.3.2.

6.2.2.3 - Instrumentation
The Modulab System (Ametek Advanced Measurement Technology, Farnborough, New Hampshire, United Kingdom) equipped with a femto-ammeter was utilized for all electrochemical experiments. Owing to the reduced current required at a micro-ITIES, a two-electrode system was employed with the working electrode (WE) lead attached to a BNC connector that was subsequently fixed to the micropipette holder. The holder is designed with an incorporated/internal silver wire that is sealed within the aqueous phase; the BNC connector provides the external contact. The counter (CE) and reference electrode (RE) leads were coupled together with a standard alligator clip on the end gripping another silver wire immersed in the organic phase. Figure 6.2.1A and B
illustrate the assembled and disassembled micropipette holder, respectively, highlighting its components. The following electrochemical cell was used:

\[
\begin{array}{c|c|c|c|c}
\text{Ag} & \text{AgNO}_3 & 3 \text{ mM X(NO}_3)_2 & 5 \text{ mM P}_{6614}^\text{(aq)} & \text{AgTB} & \text{Ag} \\
\hline
\text{(aq)} & \text{(aq)} & \text{(DCE)} & \text{(aq)} & \\
\end{array}
\]

(Cell 6.2.1)

A CCD camera (Motic Inc., Richmond, BC) fixed to a variable 12× magnification lens assembly (Navitar, Rochester, NY) was used to monitor the ITIES continuously, ensuring it did not fluctuate during experimentation.

Curve fitting was performed using Igor Pro 6.22a (Wavemetric Inc., Portland, OR) on an Acer Aspire laptop (Acer America Corporation (Canada), Mississauga ON) with a 1.66 GHz Intel Core 2 Duo processor and 2 GB of DDR2 RAM.

Figure 6.2.1: (A) Micropipette plus holder with perspective view of micro-ITIES; (B) Component diagram of the micropipette holder.
6.2.3 - Results and Discussion

Figure 6.2.2A shows the CV obtained with Cell 6.2.1 and X equal to Sr$^{2+}$; the trace was acquired utilizing an initial potential of 0.210 V and scanning in the forward direction to a final potential of approximately 1.200 V, at which point the CV was scanned in the reverse direction towards negative potentials. During this first segment a peak-shaped wave can be seen at roughly 0.780 V.

![Figure 6.2.2](image_url)

Figure 6.2.2: Using Cell 6.2.1 with X equal to Sr$^{2+}$; A: cyclic voltammogram obtained with an initial/final potential of 0.210 V, a potential range from approximately −0.590 to 1.200 V, and a scan rate of 0.020 V·s$^{-1}$. B: differential pulse voltammogram acquired with a potential range from −0.590 to 1.200 V, a step, pulse amplitude, period, and pulse width of 4 mV, 50 mV, 0.1 s, and 0.05 s, respectively. Curve fitting for each proposed IT using Igor 6.3A software; NO$_3^-$ (blue), Sr$^{2+}$ (green), TB$^-$ (purple), and the three combined (red).

The sigmoidal wave in Figure 6.2.2 is difficult to discern; however, an inflection in the current-potential response of the return sweep at ~0.9 V was deemed to coincide with the limiting or steady state current ($i_{ss}$) for the return transfer of Sr$^{2+}$; thus the half-wave
potential was evaluated by plotting \( \ln \left( \frac{i_{ss} - i}{i} \right) \) versus \( E \) and determining the potential at the x-intercept, as described in Bard and Faulkner [36]. These two curve features were attributed to the IT of \( \text{Sr}^{2+} \) from w to o and back, displaying the peak and sigmoidal shaped waves, respectively. The asymmetry of ion transfer is a direct result of the pipette geometry [37, 38]. Using \( \text{Sr}^{2+} \) IT as an example, during the forward scan ions in the pipette transfer from w to o; however, the volume of material near the interface was small and rapidly consumed, the current-potential response rises exponentially but was then followed by an exponential decay as ions diffused towards the ITIES from higher up in the microchannel. During the reverse scan, material that has crossed the ITIES occupied a relatively large (compared to the volume within the microchannel) hemispherical volume surrounding the micro-ITIES; thus, mass transfer of material towards the interface appears to be faster than its rate of consumption, generating a rise in current followed by a plateau or steady state.

The asymmetric shape of the forward and reverse curves is in good agreement with simple ion transfer (IT) of a cation across a w\|o interface as described in the literature for a micro-ITIES housed at the tip of a micropipette [37, 38]. By convention, the transfer of a cation from w to o elicits a positive current response.

The scan was continued to the second switching potential of approximately \(-0.590 \text{ V}\) and another peak-shaped curve feature can be observed in this segment at \(-0.400 \text{ V}\); this has been attributed to the IT of nitrate from w to o. The scan direction was subsequently changed towards increasing potential and progressed until \(0.410 \text{ V}\) was reached, completing one cycle by returning to the initial potential. For this final portion, a sigmoidal wave can be observed with a half-wave potential of \(-0.307 \text{ V}\).

This observation concerning peak and sigmoidal waves is expected based on diffusion regimes for simple IT at a micropipette [37, 38]. Nitrate IT was used to calibrate the polarized potential window (PPW), operating as an internal standard; based on the TATB assumption [39], or scale, the formal transfer potential of nitrate, \( \Delta_{\text{f}}^{\Phi_{\text{NO}_3}} \), was taken to be \(-0.380 \text{ V}\) [40]. The TATB assumption [39] leads to equation 2.9, where the half-wave potentials were obtained from the CV using the peak potentials and equation 3.4 [36, 41]. It is critical to reiterate that the ITIES was monitored continuously.
and microscopically throughout each experiment for any change in its shape or position; none was observed.

Additionally, the theoretical peak current as described by the diffusion coefficients obtained from the literature for nitrate [42] and strontium [43] of 1.4 and $1.2 \times 10^{-5}$ cm$^2$s$^{-1}$, respectively, and using equation 2.7 [36]. The expected peak current values for nitrate and strontium were calculated to be 4.2 and 5.9 nA; the nitrate peak at 4.5 nA demonstrates good agreement with the calculated value, however, the strontium peak is 3 times higher than the theoretical at 17.3 nA. The higher strontium value may be owning to ion-pair formation at the interface between strontium and nitrate or strontium and TB$^-$. The simple IT of metal species typically limits the PPW generating a ‘linear ramp’ in the current-potential response. The ability to observe the $\text{Sr}^{2+}$ IT of these metals in this case is attributed to the great reduction in the interfacial size (to 25 µm), significant improvement surrounding the experimental set up by means of a syringe to back-fill the capillary, along with silanization of the outside of the capillary tip, all of which contribute to a highly stable ITIES. From the calibrated CV, the formal transfer potential of $\text{Sr}^{2+}$ was estimated to be 0.768 V.

Similarly, dioxouranium was also studied using Cell 6.2.1 ($X = \text{UO}_2^{2+}$) as shown in Figure 6.2.3A; however, during the forward scan, a familiar exponential increase in current and typical of metals limiting the PPW was observed. Examining the $\text{UO}_2^{2+}$ CV closely, an inflection can be discerned at 0.820 V separating two possible curve features; considering the first to be $\text{UO}_2^{2+}$ IT with a peak potential of 0.757 V, $\Delta_w^{\text{IT}}$ was estimated to be 0.743 V.

Alkali and other metal ion formal transfer potentials limiting the PPW were estimated by Girault et al. [26, 27] using a large (centimeter scale) w|DCE interface along with the ratio of the current at the edge of scan to the return peak current ($I_{eos}/I_{rp}$), which they compared to a working curve derived through numerical calculations. It is important to note that, with the exception of $\text{Cs}^+$, Girault et al. [26, 27] did not strictly observe the IT of these metal ions. Later, using a microhole apparatus with minimal supporting
electrolyte in either phase and a curve fitting technique [32, 33], IT of Li⁺ and Cs⁺ were observed [30], along with UO₂²⁺ [31]; ΔwφCO₃⁻ was estimated to be 0.865 V.

**Figure 6.2.3:** Using Cell 6.2.1 with X equal to UO₂²⁺, A: CV obtained with an initial/final potential of −0.100 V, a potential range from approximately −0.600 to 1.200 V, and a scan rate of 0.020 V∙s⁻¹. B: DPV acquired with a potential range from −0.600 to 1.200 V, a step, pulse amplitude, period, and pulse width of 4 mV, 50 mV, 0.1 s, and 0.05 s, respectively.

The present CV results are similar to those shown previously for alkali metals and dioxouranium [26, 30, 31], and both are complicated by the possible simultaneous transfer of the anionic component of the supporting electrolyte in the organic phase, in this case TB⁻. Further to this is the question of sufficient electrolyte concentration since the metal species behaves as both supporting electrolyte and analyte. In the microhole experiment [30-33], the lack of supporting electrolyte leads to a predictable distortion of the current-potential response, which can mean up to a 3-fold increase in the observed steady state current; in the present case, higher electrolyte concentrations are thought to mitigate this phenomenon; however, some uncompensated iR-drop may still be present.
In order to confirm the formal transfer potentials obtain using CV, differential pulse voltammograms (DPVs) were also implemented, as illustrated in Figures 6.2.2B and 6.2.3B for Cell 6.2.1 with X equal to Sr\(^{2+}\) and UO\(_2\)\(^{2+}\), respectively. The instrument parameters included initial and final potentials of approximately −0.590 and 1.250 V, respectively, along with step, pulse amplitude, pulse period, and pulse width of 4 mV, 50 mV, 0.1 s, and 0.05 s, respectively. Examining the DPVs in Figure 6.2.2B and 6.2.3B, only two peaks are observed in each curve. Moving in the forward direction, the first peak, at −0.398 V, is associated with simple nitrate IT, whilst the second peak, at approximately 0.582 and 631 V (for Sr\(^{2+}\) and UO\(_2\)\(^{2+}\) respectively), is the metal and/or TB\(^-\) IT. Nitrate IT was again employed to calibrate the potential scale, using equation 2.9 along with equation 5.3 from Girault’s book [44]. In equation 5.3, \(D_w\) and \(D_o\) are the diffusion coefficients in the aqueous and organic phases respectively; these were taken to be equal and, thus, equation 6.2.2 reduces to a simple relation.

In the positive potential region, a transfer peak and a shoulder were observed for both DPVs with Sr(NO\(_3\))\(_2\) and UO\(_2\)(NO\(_3\))\(_2\) in aqueous phase, respectively (Figures 6.2.2B and 6.2.3B). It is plausible that the shoulder is at the same Galvani potential difference in these Figures. While the peak potential values are very close to those for the transfer of the two ions obtained from the CVs in Figures 6.2.2A and 6.2.3A, the shoulder was proposed to represent the TB\(^-\) transfer from o to w. To elucidate between strontium/dioxouranium and TB\(^-\) IT, a multi-peak Gaussian curve fitting was applied directly to the DPVs for each ion; nitrate (blue), metal ion (green), TB\(^-\) (purple), and a composite of the three (red). From the curve fitting, the formal IT potential for the strontium and dioxouranium cations was found to be 0.654 and 0.699 V, respectively. While the respective \(\Delta_o^w \phi_{TB}^o\) for Cell 6.2.1 with X equal to Sr\(^{2+}\) and UO\(_2\)\(^{2+}\) was found to be 1.161 and 1.131 V, respectively. The formal IT potential of TB\(^-\) found here is in good agreement with each other and agrees with our recent data using alkali metal ions in place of Sr\(^{2+}\) and UO\(_2\)\(^{2+}\) [40].

The difference in formal transfer potentials observed between the two methods is thought to arise from uncompensated \(iR\)-drop present in the CV case, which is mitigated through the DPV experiment. The two cations have a charge of 2+ that might introduce
more experimental error in determining the formal transfer potential. Therefore, the values obtained from the DPVs are considered to be better estimates.

The formal transfer potential discovered using DPV for \( \text{Sr}^{2+} \), 0.654, is similar to that shown recently for \( \text{Rb}^+ \) of 0.562 V [40]. It has been shown, through the alkali metal ions, travelling down the periodic table with increasing atomic radius there is a decrease in the formal transfer potential [40]. Strontium has a van der Waals radius of 2.49 Å compared to that for rubidium of 3.03 Å [45]; however, the increased formal transfer potential is a consequence of increased charge density (1+ versus 2+ on the metal center). Additionally, these two metals should possess similar hydration spheres since \( \text{Rb}^+ \) and \( \text{Cs}^+ \) are proposed to both have 8 water molecules coordinated to them in solution; therefore, when comparing \( \text{Sr}^{2+} \) and \( \text{Rb}^+ \), this should not play a significant role. Additionally, when Mähler et al. [46] examined the hydration spheres of the alkali metals using large angle X-ray scattering and double difference infrared they showed that rubidium and cesium were only weakly coordinated; by extension, strontium should also be weakly coordinated.

6.2.4 - Conclusions

The simple IT of strontium and uranium, which typically limits the PPW, was observed for the first time utilizing a micro-interface hosted by a 25 μm diameter micropipette. The determination of the formal IT potentials for these free metal ions were characterized through the facile use of DPV and CV. \( \Delta_{o}^{w} \phi_{\text{Sr}^{2+}}^{\text{e}} \) and \( \Delta_{o}^{w} \phi_{\text{UO}^{2+}}^{\text{e}} \) were determined to be 0.768 and 0.743 V using CV and 0.654 and 0.699 V from DPV, which were resolved from TB\(^{-}\) transfer using a Gaussian multi-peak curve fitting approach.

The observation of simple IT of these heavy metal ions was made possible by the reduction of the micropipette diameter to 25 μm along with the significant improvement of the experimental set-up such as the unique design of micropipette holder and capillary fabrication. This set-up offers a facile approach to micropipette fabrication which generates a consistent, uniform micro-interface that can be used repeatedly. The philosophy behind this approach, analogous to the microhole technique [30], is to decrease the amount of Faradaic current by reducing the interfacial surface area and thus
allowing simple IT of metals limiting the PPW to be observed. Interestingly, owing to the improved interfacial stability, conventional electrolyte concentrations can be used.

6.2.5 - References


Chapter 6.3 - Evaluation of Gibbs free energy of dioxouranium transfer at an electrified liquid|liquid interface supported on a microhole

6.3.1 - Introduction

Dioxouranium or uranyl (UO$_{2}^{2+}$) is the most common oxidation and chemical state of uranium in nuclear waste recycling [1, 2]. After removal from the nuclear fuel chamber the spent fuel pellets are dissolved into an aqueous solution via concentrated nitric acid [1, 2] for the purpose of separating the uranium from its neutron-absorbing fission byproducts via solvent extraction. The PUREX (Plutonium Uranium Extraction) process of solvent extraction, between water and a paraffinic organic solvent like n-dodecane, utilizes an organic ligand, or complexing agent, like tributylphosphate (TBP) [1, 2] and has been described by the following chemical reaction of UO$_{2}^{2+}$ with TBP:

$$\text{UO}_{2}^{2+} + 2\text{NO}_3^{-} + 2\text{TBP} \rightleftharpoons \text{UO}_2(\text{NO}_3)_2\text{TBP}$$

(6.3.1)

Of particular interest is the measurement and evaluation of the effectiveness of ligands towards metal ion species for the purpose of determining their selectivity. One possible avenue, such that direct thermodynamic data concerning complexation reactions can be obtained is through the facile use of voltammetric techniques at the interface between two immiscible electrolytic solutions (ITIES) [3-6]. A typical ITIES is the interface between water and 1,2-dichloroethane (DCE) [3, 4, 7-13]. A potential can be applied across the interface where ions are transferred across the ITIES through a push/pull mechanism. This process can be generalized as in equation 1.4 [14, 15]. This process is referred to as simple ion transfer (IT) and each ionic species has a unique standard IT potential, $\Delta_w^{0}\phi'$, analogous to the standard redox potential, $E^{0}$, found in conventional electrochemistry, and is described, for a general case at the ITIES, w|o, by equation 6.1.2. The formal IT, $\Delta_w^{0}\phi'$, (shown on the right of equation 6.1.2) is achieved if the concentrations of the charged species are used. Several comprehensive reviews on electrochemistry at the ITIES are available[14-17]. Analogous to conventional solvent metal extraction, ligands, $L$, can be used to facilitated ion transfer (FIT) processes through the equation 1.6.

If $i^*$ and $L$ are replaced with UO$_{2}^{2+}$ and TBP, respectively, then this would be the electrochemical equivalent of the PUREX process shown in equation 6.3.1. The
conventional PUREX process is made possible by the formation of a neutral metal-
nitrato[18, 19] species. Through the use of an applied electric field, ion transfer, from w
to o, is achieved and, applied on an industrial scale, may elicit a new method of metal
extraction. The use of ligands in FIT causes ion transfer to occur more readily and thus
reduces the required amount of applied potential, the driving force. The theory of FIT has
been described by the pioneering work of Homolka et al.[20], Samec et al.[21], and
Girault et al.[3, 4], and based on this work the stoichiometry, n, and the overall
complexation constant, \( \beta \), can be determined for equation 6.3.4. However, integral to this
evaluation is the degree of potential shift between the free metal formal transfer potential
and the ligand assisted transfer potential. Determination of the formal transfer potential of
dioxouranium is therefore necessary in order to evaluate these important thermodynamic
parameters. Yet, not many formal IT potentials of metal ions are available.

Metal ions, soluble predominately in the aqueous phase, tend to transfer at the
limit of the polarized potential window (PPW) and their \( \Delta^n\phi^o \) have been extrapolated
using working curves [8, 22], however, this estimate is complicated by the simultaneous
transfer of supporting electrolyte ions and can generate erroneous results. It is therefore
advantageous to study the transfer of these metal ions in the absence of supporting
electrolyte.

In the late 1980’s and early 1990’s, Oldham [23, 24] developed a mathematical
treatment to describe the effects on the voltammetric response of little or no supporting
electrolyte at a solid-liquid ultramicro-electrode (UME) interface. Oldham[24] showed
that the limiting current response was three times higher in the unsupported case relative
to an experiment performed using excess supporting electrolyte owing to migrational
effects and the appearance of a ‘linear ramp’ in current; thus, the standard half-wave
potential, determined using conventional data treatment techniques, would also suffer
from this exaggeration; however, corrected standard potentials could be obtained if these
effects were taken into account. Cyclic voltammetry (CV) and linear sweep voltammetry
(LSV) conducted at ITIES hosted by microholes have been shown to be analogous to
voltammetry at recessed disc UME [9, 12, 25] and, thus, the adaptation of Oldham’s
theory towards the ITIES was performed by Wilke [25] and shown recently through curve
fitting [12]. The mathematical treatment described by Wilke [25] was greatly simplified
if the magnitude of the charge on the two components of the salt is equal; \( z_i = -z_j \).

However, this is not true for the current study using dioxouranium acetate dihydrate (UO\(_2\)Ac\(_2\)\cdot2H\(_2\)O) salt, where dioxouranium is 2\(^+\) and acetate is 1\(^-\). Therefore a new curve fitting approach is described herein, which is applicable to any charge ratio.

The Gibbs free energy of UO\(_2\)\(^{2+}\) transfer was evaluated at the aqueous|nitrobenzene (w|NB) interface\([26]\), based on ion pair extraction of the metal ion from an acidic aqueous phase. However, this technique is complex and requires sensitive measurements of the concentration distribution between the two phases. The present method is facile and constitutes a direct, single measurement of the formal transfer potential, and thus, Gibbs free energy of ion transfer.

Finite element analysis was also employed via COMSOL Multiphysics 3.5a software to describe the kinetics of IT using Butler-Volmer formalism.

**6.3.2 Simulation**

![Simulation Geometry](image)

*Figure 6.3.1: Simulation Geometry*

Simulations were conducted utilizing finite element analysis software COMSOL 3.5a and a Butler-Volmer kinetic model described by Fick’s Laws of diffusion.

Finite element analysis has proven to be effective towards describing liquid|liquid electrochemical phenomena [5, 11, 13, 27] and including Nernstian systems using Fluxpert software [27]. The simulation geometry, as shown in Figure 6.3.1, was designed
to mimic the microhole ITIES experiments more closely by incorporating the conical shape of the microhole. As described previously [12], the microhole is generated through UV-photoablation, which leaves a slightly larger radius on the side subjected to the laser beam; the microhole used in the experiment had radii of 11.2 and 13.1 μm on the back and front of the film, respectively – these dimensions were incorporated into the simulation. In general, the geometry consisted of two rectangular areas termed Subdomains 1 and 2, representing the aqueous and DCE phases, respectively. These two Subdomains are separated by a narrow channel that constitutes the microhole with a boundary flush to Subdomain 2 (organic phase, o) hosting the ITIES. The location of the phase boundary, either on the side of the aqueous or organic phase or in between, can influence the voltammetry as has been shown [9, 12, 27]. Thus, its position was chosen to reflect the experimental – flush with the organic phase; in this way IT from w to o will be analogous to redox chemistry performed at a recessed microdisc electrode [9, 25].

Under investigation is simple ion transfer (IT), as shown in equation 1.4. A full description the theory is found in section 3.2.

6.3.2.1 Computations.

All curve fittings in the Oldham’s regime were achieved within 40 iterations and performed using Igor Pro 6.12a (Wavemetrics Inc., Portland, OR). Igor procedures and COMSOL code is available in the supplementary material of reference [28].

6.3.3 - Experimental

6.3.3.1 Chemicals.

All chemicals were of reagent grade and used as purchased without further purification. Bis(triphenylphosphoranylidine)ammonium chloride (BACl) and lithium tetrakis(pentafluorophenyl) borate ethyl etherate (LiTB purum) were purchased from Acros Organics (Thermo Fisher Scientific, Geel, Belgium). Lithium chloride, and tetramethylammonium bromide (TMABr) were purchased from Sigma-Aldrich Chemie GmbH (Buchs, Switzerland). BATB was prepared as has been previously described [12] through a facile metathesis reaction in a methanol:water solution (2:1, V:V); the salt was purified through recrystallization in acetone. Uranium acetate dihydrate (UO₂Ac₂·2H₂O) was generously provided by another research group at EPFL.
Figure 6.3.2: Schematic of two-electrode experimental apparatus fabricated using Teflon. The w|DCE interface was supported by a microhole drilled in a 25 μm thick film of polyimide (Kapton) that was held by the two blocks tightly connected by four screws running along the y-axis.

6.3.3.2 Micro-ITIES

The micro-hole ITIES experimental apparatus consisted of two Teflon blocks with chambers fabricated into each block which housed the aqueous phase and the organic phase plus aqueous reference phase, respectively [12], as shown in Figure 6.3.2. Owing to the low current utilized in this setup, only two-electrodes were necessary: one positioned in the aqueous phase and attached to the working electrode (WE) lead of the potentiostat, and the other placed in the aqueous reference phase and attached to the reference/counter (RE/CE) potentiostat leads. Both electrodes functioned as quasi-reference electrodes. The aqueous and organic phases were separated by a 25 μm thick polyimide film (Kapton, Dupont; purchased from Goodfellow, U.K.). Microholes were fabricated in the polyimide film using UV-photoablation and a metal mask. This technique utilizes a 193 nm ArF excimer laser beam (Lambda Physik, Göttingen, Germany, fluence = 0.2 J, frequency = 50 Hz), which generates a conical hole in the film. The two diameters at either ends of the hole were determined to be 22.4 and 26.1 μm using an optical microscope. In this way, the ratio of the diameter to the length of the channel was approximately equal, d/L≈ 1, and has been shown to generate reproducible results [9]. The two compartments were screwed in place with the polyamide film and a rubber o-ring in between and at the center of the two chambers; the o-ring was positioned
in a circular groove fabricated into the Teflon wall, which ensured a tight seal and no movement of the polyimide film. During experimental preparation the aqueous chamber was filled first with the larger diameter positioned in this phase; thus, the aqueous phase fills the microhole and the ITIES was flush with the organic phase and its behaviour was analogous to a solid inlaid microelectrode [9]. The electrochemical cell examined is detailed below:

\[
\begin{align*}
\text{Ag} & \quad \text{AgAc} & 0.5 \text{ mM } \text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O} & 0.5 \text{ mM } \text{BATB} & 10 \text{ mM } \text{LiCl} & \text{AgCl} & \text{Ag} \\
& & (aq) & (DCE) & (aq \sim \text{ref.}) & & \\
& & & & & & \\
\end{align*}
\]

(Cell 6.3.1)

DCE was used as the organic solvent instead of the typical PUREX solvent n-dodecane [1, 2], owing to its lower viscosity and since IT at the w|DCE interface is well established [3, 4, 7-13].

6.3.3.3 Electrochemical instrumentation.
All electrochemical measurements were obtained using an Autolab potentiostat (Metrohm, Utrecht, Netherlands).

6.3.4 - Results and Discussion

Figure 6.3.3: Linear sweep voltammogram obtained using Cell 6.3.1 and curve fitting obtained using equation 6.3.3; the following experimental parameters were used: scan rate equal to 0.020 V·s\(^{-1}\) with a potential range from 0.030 to 1.550 V.

Figure 6.3.3 shows the experimental linear sweep voltammetry (LSV) curve (red) acquired during a scan from 0.030 to 1.550 V at a scan rate of 0.020 V·s\(^{-1}\), after the
addition of approximately 0.5 mM TMABr, in Cell 6.3.1. The steady increase in current with a half-wave potential observed at 0.160 V, and plateau at approximately 0.410 V, corresponds to the transfer of the TMA$^+$ cation from the aqueous to organic phase, w to o. This was quickly followed by another current increase beginning at 0.450 V, which can be attributed to TB$^-$ transfer, o to w. A final current increase was observed from approximately 0.686 to 1.200 V and is ascribed to UO$_2^{2+}$ transfer, w to o. The transfer of TB$^-$ and UO$_2^{2+}$ are difficult to distinguish; however, the conclusion to separate the seemingly large sigmoidal wave from 0.450 to 1.200 V into two IT waves was brought about by three mitigating factors.

The first is based on the concentration of the analytes and the radius, $r_d$, of the ITIES, since the steady state current for each IT can be approximated through the equation 3.1 for the limiting current at a planar micro-disc electrode [25]. The diffusion coefficient of uranium [29] has been determined for acidic solutions as $0.4 \times 10^{-5}$ cm$^2$·s$^{-1}$ and was used here to determine an approximate steady state current response value: $2.16 \times 10^{-9}$ A. The value of the limiting current suggests that dioxouranium itself cannot be the sole contributor and, therefore, points to the participation of another ion. The steady state current value in and of itself is not wholly significant by virtue of its approximation; however, a change in the slope of the current-potential response in Figure 6.3.3 at 0.800 V also points to a change in the ion being transferred. Finally, and most convincingly, TB$^-$ is present in the organic phase and its formal transfer potential is well established, at 0.709 V [12], and undoubtedly transfers within the ascribed 0.450 to 1.200 V potential range. Therefore, the large sigmoidal wave was separated into two sections with the first being used to describe TB$^-$ IT and the second for UO$_2^{2+}$ IT.

Conventional evaluation of LSVs or cyclic voltammograms (CVs) obtained from liquid|liquid systems begins with calibrating the potential scale using the TATB assumption [30, 31] and with known IT potentials; this technique is analogous to an internal standard method. In the present case TMA$^+$ IT was used as the internal standard, $\Delta_o^{\phi_o^\prime} = 0.160$ V [32]. First the electrochemical cell is scanned, then a known concentration of internal standard is added, and the system is scanned again. In systems with an abundance of supporting electrolyte, the observed half-wave potential, $\Delta_o^{\phi_{1/2}}$, is
often considered equivalent to the formal transfer potential, \( \Delta_o \psi' \), through equation 2.9. The addition of supporting electrolyte, however, reduces the size of the polarizable potential window (PPW) making the IT of extremely hydrophilic species unobservable \([10, 12]\). In systems where little or no supporting electrolyte is added, it has been demonstrated that the relationship \( \Delta_o \psi_{1/2} = \Delta_o \psi' \) does not hold \([7, 10, 12, 23-25]\).

Examination of these solutions was made accessible by the pioneering work of Oldham\([23, 24]\), who derived the theory to describe voltammetric response in unsupported systems at the solid ultramicroelectrodes (UME). Oldham’s theory describes the voltammetric response as one in which steady state is never actually achieved but the current continues to increase linearly with potential \([24]\). This model has been adapted for use at the liquid|liquid micro-interface by the work of Wilke \([25]\) by taking into account migration along with diffusion effects. In the liquid|liquid case, the continuous linear increase in current, or “linear ramp” that Oldham describes \([24]\), is owing the migration of the counterion of the ion being transferred undergoing mass transport in each phase away from the ITIES and towards the reference electrode or bulk solution. This migration causes a charge separation or concentration polarization within each phase between the bulk and surface concentrations at the interface\([24]\). Therefore, an increase in effective resistivity also contributed to the observed “linear ramp” \([24]\) in the current response. According to this theory \([23-25]\), the actual half-wave potential, \( \Delta_o \psi_{1/2,i} \), was augmented, becoming a sum of the observed half-wave potential, \( \Delta_o \psi_{1/2,i} \), and a unit describing migration \([25]\):

\[
\Delta_o \psi_{1/2,i} = \Delta_o \psi_{1/2,i} + \frac{RT}{z_i F} \ln \left( 2^{-z_i/z_j} \left( 1 - \frac{z_i}{z_j} \right) \right) \quad (6.3.1)
\]

where \( i \) and \( j \) are the anionic and cationic components of the salt under investigation. The potential, is defined as a function of the current is \([25]\):

\[
\Delta_o \psi = \Delta_o \psi_{1/2} + \frac{RT}{z_i F} \ln \left( 1 - \frac{z_i}{z_j} \right) \left( \frac{I}{I_{\lim} - I} \right) \left( \frac{I_{\lim}}{I_{\lim} - I} \right)^{-z_i/z_j} \quad (6.3.2)
\]
If the charge ratio of the salt components is 1 \((z_i = -z_j)\) than the analysis is greatly simplified and equation 6.3.2 can be rearranged to current as a function of potential [25]:

\[
I = I_{\text{lim}} \left[ 1 + \exp \left( \frac{z_iF}{RT} \left( \Delta_u^w \phi - \Delta_u^w \phi_{1/2} \right) \right) - \sqrt{-1 + \exp \left( \frac{z_iF}{RT} \left( \Delta_u^w \phi - \Delta_u^w \phi_{1/2} \right) \right)^2} \right] \]  
(6.3.3)

As has been shown recently [12], the steady state IT component (the linear rise before achieving the plateau current) of the experimental curve can be fit using equation 6.3.3, whereby \(z_iF/RT, \Delta_u^w \phi_{1/2}, \text{and } I_{\text{lim}}\) were determined. However, the dioxouranium acetate salt fails this criterion and thus curve fitting using equation 6.3.3 would be erroneous. Figure 6.3.3 shows the curve fitting results (dashed curve) obtained using equation 6.3.3 and is shown here in order to illustrate more clearly the segregation between TB\(^-\) and UO\(_2^{2+}\) IT. Additionally, since \(z_i \neq -z_j\), rearranging equation 6.3.2 in terms of current becomes a tedious mathematical procedure; therefore it was chosen to use equation 6.3.2 and invert the axis of our experimental curves. In this new curve fitting method, four coefficients were used: \(RT/z_iF, \Delta_u^w \phi_{1/2}, -z_i/z_j, \text{and } I_{\text{lim}}\).

Figure 6.3.4 shows the experimental LSV (○) divided into segments A, B, and C for the transfer waves of UO\(_2^{2+}\), TB\(^-\), and TMA\(^+\), respectively, which have been baseline-corrected for each IT in order to facilitate curve fitting (-----) achieved using equation 6.3.2. This excellent match illustrates the effectiveness of this technique for the determination of extremely hydrophilic species like dioxouranium; the highest \(\chi^2\) (curve fitting parameter) was observed during TB\(^-\) IT curve fitting with a result of 0.0355 – this is most likely owing to its poor resolution from the UO\(_2^{2+}\) IT. In each curve fitting the charge ratio was held constant, e.g. for UO\(_2^{2+}\) \(-z_i/z_j = 2\), while the \(I_{\text{lim}}, \Delta_u^w \phi_{1/2}, \text{and } RT/z_iF\) terms were allowed to vary; the latter term corresponds to the slope of the associated current increase during IT and is calculated to be 0.0257 and 0.0128 for \(z_i = 1\) and 2, respectively. After the fitting was obtained the values of \(RT/z_iF\) for UO\(_2^{2+}\), TB\(^-\), and TMA\(^+\) transfer were determined to be 0.04945, 0.05453, and 0.0588, respectively. This deviation is similar to the one noted by Girault et al. [12] using equation 6.3.3 with the analogous term \(z_iF/RT\), and may be owing to a lack of separation between the ITs along with the high resistivity.
brought about by the extreme hydrophilicity of dioxouranium. The best half-wave potential separation between the internal reference and the ion of interest to achieve optimal results has been reported to be between 0.350 and 0.450 V[12].

Figure 6.3.4: Experimental (---) LSV described in Figure 6.3.3 after axis inversion and baseline corrected in A, B, and C for UO$_2$$^{2+}$, TB$^-$, and TMA$^+$ transfer, respectively; each includes curve fitting (▬) results obtained using equation 6.3.2.

The formal transfer potential of UO$_2$$^{2+}$, $\Delta^w\phi_{UO_2}^o$, and TB$^-$, $\Delta^w\phi_{TB}^o$, were determined to be 0.865 and 0.600 V, respectively, at the w|DCE interface using TMA$^+$ IT as the internal standard. The TB$^-$ result is in fair agreement with recently published results, 0.709 V [12]; the difference is probably owing to its poor resolution, but may also be the result of ion pair formation, which has been shown to increase with increasing hydrophilicity [12] (i.e. TB’s interaction/adsorption at the interface with UO$_2$$^{2+}$). The
dioxouranium cation shows extreme hydrophilicity to the extent that it is one of the most
hydrophilic ions yet measured \[12, 22\] with a \(\Delta_w^o \phi_{\alpha}^o\) greater than lithium, \(\text{Li}^+\); \(\Delta_w^o \phi_{\alpha}^o\) = 0.650 V \[12\]. The transfer potential is related to the Gibbs free energy of transfer via
\(\Delta G_{tr, w \rightarrow o} = z_i F \Delta_w^o \phi_{\alpha}^o\) such that \(\Delta G_{tr, UO_2^{2+}} = 167 \text{kJ} \cdot \text{mol}^{-1}\); compared to \(\text{Li}^+\), which is 62.7 \text{kJ} \cdot \text{mol}^{-1}\) with perchlorate as a counter ion \[12\]. The formal IT potential of dioxouranium was also approximated using equation 6.3.3 and determined to be 0.850 V; this curve fitting result is illustrated in Figure 6.3.3. \(\Delta_w^o \phi_{UO_2^{2+}}\) obtained using equation 6.3.2 and 6.3.3, are in good agreement; however, both results should be considered as estimations owing to the poor resolution of UO\(_2^{2+}\) and TB\(^{-}\) IT, and it may be the case that these ions are, in fact, transferring simultaneously.

The Gibbs free energy of transfer determined by Yoshida et al. \[26\] at the w|NB interface was 72 \text{kJ} \cdot \text{mol}^{-1}, giving a formal transfer potential of 0.373 V. This value was obtained through analytical determination of several constants and the following equation \[26\]:

\[
\log \left( \frac{D_M^{1/2}}{D_H} \right) = \frac{\Delta G_{tr, H}^o - \Delta G_{tr, M}^o}{2.303RT} + \log \left[ \frac{\gamma_{H,o}^o / \gamma_{H,w}^o}{\left( \gamma_{M,o}^o / \gamma_{M,w}^o \right)^{1/2}} \right] \\
+ \log \left[ \frac{1 + \sum K_{i,p,MY_o,o} \times \left( \gamma_{MY_o,o}^o / \gamma_{MY_w,o}^o \right)(\gamma_{Y,o} c_{Y,o})^{1/2}}{1 + K_{i,p,HY_o,o} \gamma_{HY_o,o} \gamma_{Y,o} c_{Y,o}} \right] \quad (6.3.4)
\]

where \(D_i\), for equation 6.3.4 only, refers to the distribution ratio of species \(i\) and was measured using analytical techniques such as Inductively Coupled Plasma Atomic Emission Spectrometry \[26\]. Species \(Y\) in equation 6.3.4 is the anionic component of the metal salt being evaluated, in that this methodology takes into account the ion pair formation of the metal with its counter ion in the organic phase as well as with \(\text{H}^+\); the \(K\) terms in equation 6.3.4 represent the equilibrium constants of these two reactions and were determined electrochemically by the Yoshida et al. \[26\]. The activity coefficients, \(\gamma_{i,\alpha}\) of species \(i\) in phase \(\alpha\) were calculated by an extended Debye-Hückel equation in conjunction with an additional relationship formulated by Yoshida et al. \[26\]. The final term to be described, \(c_{Y,o}\), is the concentration of the metal species counterion in the organic phase and was estimated by Yoshida and co-workers via the same formulation.
used to evaluate the activity coefficients [26]. This approach [26] requires the use of multiple analytical techniques and draws on a deep understanding of thermodynamics. However, the Gibbs free energy of transfer obtained for UO$_2^{2+}$ is only applicable to the w|NB interface since the solvation environment, and hence formal IT potential, will be particular to that solvent system [14]. Thus, while accurate, the $\Delta_w^{\text{NB}} \phi_{\text{UO}_2^{2+}}$ determined by Yoshida et al. [26] cannot be used at the w|DCE interface and, therefore, what is presented herein is a facile, unidisciplinary approach for the determination of the formal IT potential of dioxouranium. It should be stressed that the formal IT potential UO$_2^{2+}$ at the w|NB[26] interface is much lower than that determined here at a w|DCE interface. While this translates to less applied potential required to elicit uranyl IT, it also means that the w|NB ITIES will have a narrower PPW than that experienced at a w|DCE interface. A narrower PPW also means that less IT and FIT can be observed and quantified; hence, this is why DCE is a valuable organic solvent for studying FIT.

**Figure 6.3.2:** Simulated LSVs obtained using the microhole geometry depicted in Figure 6.3.1, with $z_i = 1$ and 2 for A and B, respectively. The following parameters were used in both: $\alpha = 0.5$, $c_i^w = 1.0$ mM, $c_{i,o} = 0.0$ mM, $\nu = 0.020$ V·s$^{-1}$, $\Delta_w^{\text{NB}} \phi_i^o = 0.250$ V, and varying $k^o$ as indicated in the legend.
To garner more insight into the kinetics of IT at a microhole interface, this system
was studied using finite element analysis with the geometry shown in Figure 6.3.1. The
boundary condition at the interface was set to follow Butler-Volmer (BV) formalism. And
the UO$_2^{2+}$ diffusion in the two domains obey Fick’s laws of diffusion.

Figures 6.3.5A and 6.3.5B show simulation LSV curves obtained using $z_i = 1$ and
$z_j = 2$, along with $a = 0.5$, $c_{i,w} = 1.0$ mM, $c_{i,o} = 0.0$ mM, $v = 0.020$ V·s$^{-1}$, $\Delta_{o} w f(o) = 0.250$ V, and with $k^0$ values of 1, 0.1, 0.01, and 0.001 cm·s$^{-1}$. The diffusion coefficients for both
phases were held at $1 \times 10^{-5}$ cm$^2$·s$^{-1}$. When $k^0 = 1.0$ cm·s$^{-1}$ the curves shown in Figure
6.3.5A and 6.3.5B are in good agreement with those calculated by Wilke [25] and
obtained by Josserand et al. [27] using a Nernstian model. By augmenting the standard
rate constant, the overall kinetics of the reaction can be changed, which alters the slope of
linear approach to the steady state current. As shown in Figure 6.3.5, with smaller values
of $k^0$ the slope of the linear portion of the curve, before the current plateaus, decreases
and the half-wave potential shifts; this resembles the change predicted by Oldham’s theory of
redox chemistry performed in the absence of supporting electrolyte [23, 24]. Figure
6.3.5B indicates that, with increased charge, slower reaction kinetics have a reduced
effect on the slope of the IT curve. Therefore, migration effects associated with IT in
systems with little or no supporting electrolyte was approximated using slow BV kinetics.

Each IT was examined individually and compared versus the LSVs obtained
experimentally with an initial concentration of 0.5 mM, where UO$_2^{2+}$ and TMA$^+$ were
present only in the aqueous phase (Subdomain 1 in Figure 6.3.1) and TB$^-$ was only
present in the organic phase. The diffusion coefficient, standard rate constant, and
transfer coefficient were varied until a good overlap was achieved; the final standard rate
constant, $k^0$, and transfer coefficient for each ion was maintained at $1 \times 10^{-3}$ cm·s$^{-1}$ and
0.5, while the diffusion coefficients, $D_{i,w} = D_{i,o}$, for, TB$^-$, and TMA$^+$ were equal to 2.6,
and $1.4 \times 10^{-5}$ cm$^2$·s$^{-1}$, respectively. Two diffusion coefficients for UO$_2^{2+}$ were used:
1.0 and $7.5 \times 10^{-5}$ cm$^2$·s$^{-1}$ as shown in Figure 6.3.6B as (△) and (○) curves, respectively.
The first value was obtained by using the limiting current value generated during curve
fitting via equation 6.3.2; this value was then used to solve for $D$ in equation 3.2 and is in
fair agreement with that demonstrated previously [29]. The latter UO$_2^{2+}$ diffusion
coefficient was determined through iterative simulations to best approximate the steady
state current obtained experimentally. The formal IT potentials used in the simulation were also varied, for \( \text{TMA}^+ \), \( \text{TB}^- \), and \( \text{UO}_2^{2+} \) IT the final values were 0.143, 0.490, and 0.983 V, respectively and these are in fair agreement with those obtained from the curve fitting results.

*Figure 6.3.6:* (A) contains the experimental results as described in Figure 6.3.3 with an overlay of the TMA\(^+\) and TB\(^-\) simulated IT. (B), (C), and (D) illustrate the individual, baseline corrected experimental LSVs overlaid with the simulated IT for \( \text{UO}_2^{2+} \) (w to o), TMA\(^+\) (w to o), and TB\(^-\) (o to w), respectively. The simulation parameters were as follows: \( \alpha = 0.5 \), \( k^0 = 1 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1} \), \( c_{i, \alpha} = 0.5 \text{ mM} \), with \( D_{i,w} = D_{i,o} = 7.5, 2.6 \), and \( 1.4 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1} \) and \( \Delta_i \phi' \) = 1.400, 0.941, and 0.593 V for \( \text{UO}_2^{2+} \), TB\(^-\), and TMA\(^+\), respectively.

Figure 6.3.6B, C, and D contain the individual overlaid simulation curves (○) obtained for the respective ITs of \( \text{UO}_2^{2+} \), TB\(^-\), and TMA\(^+\) with the experimental (—) data under baseline correction. Figure 6.3.6C and 6.3.6D demonstrate the effective overlap of
the simulation results to the experimental while indicating that IT in the absence of supporting electrolyte can be successfully approximated using a BV model; augmenting only the diffusion coefficient and the standard rate constant can achieve a reasonable approximation of migration effects. Figure 6.3.6A includes a simulation curve such that both TMA$^+$ and TB$^-$ ions are considered simultaneously and overlaid on the experimental results generating a good overlap.

However, in Figure 6.3.6B, showing the curve obtained for UO$_2^{2+}$ IT, which constitutes the edge of the PPW, is poor. This situation remained despite utilizing a range of different $k^o$ values from $1 \times 10^{-3}$ to $1 \times 10^{-10}$ cm·s$^{-1}$ for both diffusion coefficients and is most likely owing to the high ohmic polarization induced at the ITIES combined with total ion depletion near the interface. The experimental curve and the simulation curve, obtained with $D_{UO_2^{2+}}$ equal to $1.0 \times 10^{-5}$ cm$^2$·s$^{-1}$, in Figure 6.3.6B are similar to Fig. 10 shown in Oldham’s previous work [24], where he describes an analogous redox scenario as follows:

$$R^{2-} \rightarrow 2e^- + P \quad (6.3.5)$$

In this scenario, the electroactive species, R$^{2-}$, is oxidized to the product, P, liberating two electrons; not shown is the counter ion, C, which has a charge of 1$^+$ [24]. As the reaction shown in equation 6.3.15 proceeds, the concentration profiles of R$^{2-}$ and C$^+$ decrease at similar rates with distance from the electrode surface [24]; this results in a large ohmic polarization. Oldham [24] compared the theoretical LSVs and showed that, in the above example, the curve without supporting electrolyte has a steady state current three times higher than that with supporting electrolyte. Within the present simulation parameters only two terms exist which can increase the steady state current: the initial concentration of the ion being transferred and the diffusion coefficient. Therefore, an effective diffusion coefficient was used to approximate the ohmic polarization and this value is much higher than the uranyl diffusion coefficient given in the literature [29]. While this does show excellent agreement with the experimental steady state value, it does not overlap well with the linear rise in the current response. Additionally, curve ($\triangle$) in Figure 6.3.6B shows the simulation response using a smaller diffusion coefficient; this is what would be expected should the system have adequate supporting electrolyte.
Therefore, the BV model can be used to describe most IT. But in extreme cases, as with UO$_2$^{2+} IT, where the ion demonstrates extreme hydrophilicity, the simulation result indicates there is a limitation to the BV kinetic model and a more complex strategy must be broached.

A mixed diffusive and migrational model considers the current density at the interface as a linear combination of the diffusion, $i_d$, and migration, $i_m$, components such that[33]:

$$i = i_d + i_m$$  \hspace{1cm} (6.3.6)

And the flux of charged species, in a solution without convection, can be described by the Nernst-Planck equation [33]:

$$J_i(x) = -D_{i,\alpha} \nabla c_{i,\alpha} - \frac{z_i F}{RT} D_{i,\alpha} c_{i,\alpha} \nabla \phi$$  \hspace{1cm} (6.3.7)

TMA$^+$ and TB$^-$ ions transfer at relatively low applied potential compared to dioxouranium, and, since the migration effect is proportional to the magnitude of the applied electric field [23-25, 33], it follows that the migrational component of the flux of these ions across the interface is minimal. Thus TMA$^+$ and TB$^-$ ITs can be easily predicted by BV kinetics and Fick’s Laws of diffusion, while UO$_2$^{2+} cannot since the applied potential (hence migration) is much greater. A more complex simulation incorporating the Nernst-Planck equation and described in detail in chapter 6.4.

6.3.5 - Conclusions

Herein was described the IT of UO$_2$^{2+} across a w/DCE ITIES supported by a 25 µm diameter microhole, without supporting electrolyte. Using the theory developed by Oldham[23, 24] and Wilke[25] the formal transfer potential, $\Delta^w_{\alpha} \phi_{UO_2^{2+}}$, for dioxouranium was determined to be 0.865 V.

Ion transfer was studied, with COMSOL Multiphysics 3.5a, to describe the kinetics of IT using a BV model. The LSV obtained utilized the following parameters: $\alpha = 0.5$, $k^o = 1 \times 10^{-3}$ cm·s$^{-1}$, and $D_{i,\alpha}$ for UO$_2$^{2+}, TB$^-$, and TMA$^+$ equal 7.5, 2.6, and $1.4 \times 10^{-5}$ cm$^2$·s$^{-1}$, respectively, to obtain good overlap with the simulation versus the
experimental results for all but dioxouranium. Since this BV model considered only the
diffusive component, the simulation might be improved by augmenting the flux of the
electroactive species through the utilization of the Nernst-Planck equation.

6.3.4 - References

6.4 - Nernst-Planck model used to explore liquid|liquid interfacial ion transfer with no supporting electrolyte

6.4.1 – Introduction

Measurement of the applied Galvani potential difference (i.e. formal ion transfer potential, $\Delta_{\text{F}}^{\text{f}} \phi^i$) required to elicit ion transfer (IT) of highly hydrophilic metal species from an aqueous to organic solution at the interface between two immiscible electrolytic solutions (ITIES) is difficult. This is owing to metal ion transfer occurring at the limit of, or outside, the polarized potential window (PPW) as observed during cyclic or linear sweep voltammetry (CV or LSV) [1-5]. Simple IT can be described by equation 4.1.1. The formal IT potential of each metal ion is a constant unique to that species and biphasic system. If a ligand is used to assist the metal ion transfer through interfacial complexation this process is commonly called facilitated ion transfer (FIT). Interestingly, the formal transfer potential of the metal ion-ligand complex is dependent on the concentration of the metal ion and ligand species; FIT is shown in equation 1.6.

Additionally, employing a ligand greatly reduces the value of applied potential required to elicit IT [2, 6-10]. In the theory of FIT developed by Homolka et al. [7], Samec et al. [6], Kakiuchi and Sendai [8], and Girault et al. [2, 9, 10], simple IT of the metal species is a point of reference from which the efficiency and selectivity of FIT can be quantified. This treatment can be used to obtain the overall stoichiometry, $n$, and complexation constant, $\beta$, of equation 1.6. These values can, in turn, be used as a quantitative measurement of the effectiveness of various ligands and biphasic systems [9, 10]. However, because metal ions transfer beyond the PPW their formal transfer potentials cannot be measured directly. This becomes a bottleneck for the study of FIT reactions at the interface and their potential applications.

A microhole apparatus can be employed in order to limit the current response to the nanoampere scale, which also virtually eliminates most $iR$ drop and thereby increases the sensitivity [4, 5]. Additionally, this technique should employ no supporting electrolyte since any additional ions in solution would only mask or interfere in the analyte IT through mechanisms that are not easily predictable. However, in doing so there is a cost: migration effects. While supporting electrolytes (or excess analyte concentration) are used to mitigate the migrational component, without them it can no longer be ignored. In
essence a system under these conditions (without convection) can be described using the Nernst-Planck equation:

\[
J = -u_m F \nabla \phi \sum_i z_{i,\alpha} c_{i,\alpha} - \sum_i D_{i,\alpha} \nabla c_{i,\alpha}
\]  

(6.4.1)

that describes the total flux \(J\) of ions and can be broken down into the two components of migration and diffusion, respectively, as shown. In equation 6.4.3, \(u_m\) is the ionic mobility, \(F\) is Faraday constant, \(\nabla\) or del is the vector or gradient operator, \(\phi\) is the potential, along with \(D_{i,\alpha}\) and \(c_{i,\alpha}\) representing the diffusion coefficient and concentration of species \(i\) in phase \(\alpha\). The Nernst-Planck model was used describe the current-potential response obtained for a solid ultramicroelectrode (UME) for conventional redox chemistry with little to no supporting electrolyte by Oldham [11, 12]. Oldham’s model was then translated for use at a microhole ITIES by Wilke [3] so that, through a sophisticated curve fitting technique applied directly to the CV/LSV experimental data [4, 5], the formal IT potential of ions limiting the PPW could be ascertained.

It is important to note that in systems with no supporting electrolyte, Oldham [11, 12] demonstrated a current response increase by as much as 3 times versus conventional fully supported systems, owing to the migrational contribution of the counterion.

While Wilke’s process [3] is easy to apply it is limited to metal salts whose charge ratio is equivalent, \textit{i.e.} \(z_i = -z_j\); where \(z_i\) is the charge of the metal ion and \(-z_j\) is the charge of its counterion. As an example, for strontium nitrate \((\text{Sr(NO}_3\text{)}_2, \text{Sr}^{2+} \text{ and NO}_3^-)\) this is not the case. Strontium is a major nuclear fission byproduct and has been separated from spent nuclear fuel (SNF) for use in a broad range of applications since the early beginnings of the commercial nuclear industry [13]. Therefore its, transfer thermodynamics are of great interest, which necessitates the development of a more universal approach.

Herein is described the simple IT of strontium, \(\text{Sr}^{2+}\), at a microhole ITIES such that no supporting electrolyte was used – in order to expand the PPW – in accordance with the theory articulated by Oldham [11, 12] and Wilke [3], but adapted such that any charge ratio can be described. Additionally, finite element analysis, incorporating Nernst-
Planck mass transport, has been used to approximate the experimental results with simulated LSVs overlaid onto the experimental curves. The present approach could be extrapolated towards various metal salts and biphasic systems and is not limited to strontium nitrate, which is used here for example.

6.4.2 - Simulations

**Figure 6.4.1:** Schematic representation of the computational domain used in finite element method simulation; the 2D cross section with axial symmetry is indicated with red arrows. The boundary designations utilized in the model are listed on the right. The microhole was conical and this has been faithfully reproduced in the simulation geometry.

Finite element analysis was performed using the arrangement depicted in Figure 6.4.1. In order to conserve computational efforts (processing power and time), this geometry was limited to a two-dimensional cross section, which was further reduced by half by taking advantage of the remaining axial symmetry. This framework consisted of 16 external boundaries enclosing two subdomains, representing the aqueous and 1,2-dichloroethane (DCE) phases, separated by one internal boundary. As detailed in Figure 6.4.1, the boundary designations were chosen to best approximate the experimental disposition. Boundaries 1, 3, 4, 6, and 7 were axial symmetry; boundaries 9 through 14
represented the polyimide film so an insulator description was chosen; 8 and 17 were concentration boundaries (used to represent an infinite solution) in the aqueous phase but were also used for the application of an electrical potential; 2, 15, and 16 in the organic phase were concentration boundaries as well as the ground or zero charge for the electrostatics. Finally, the most important boundary was the ITIES, labelled as 5, this was the internal boundary separating the two phases. Mass transport within each phase was carried out using the Nernst-Planck model, equation 6.4.1. IT at the interfacial boundary was handled using Butler-Volmer kinetics regime through equations 2.3 and 2.4.

The current was calculated as an integral of the total flux across the interface, with $r$ representing the interfacial radius, as given below:

$$I = 2\pi z_{i,a}F\int \left( -z_{i,a}F\mu_m \nabla \phi_{c_{i,a}} - D_{i,a} \nabla c_{i,a} (r,z,t) \right) r dr$$  \hspace{1cm} (6.4.2)

A linear function applied at boundaries 8 and 17 was used to represent the potential field generated by an electrode as follows:

$$\Delta^w\phi = \Delta^w\phi_i + vt$$  \hspace{1cm} (6.4.3)

where $\Delta^w\phi_i$ is the initial potential while $v$ and $t$ are the scan rate and time. The dielectric constants, $\epsilon_r$, for water and DCE at 298.15 K, 78.4 and 10.1 [14], respectively, were used to represent the relative permittivity of each phase to the electric field through the Poisson equation:

$$\epsilon_o \epsilon_r \nabla \phi + \rho = 0$$  \hspace{1cm} (6.4.4)

Where $\epsilon_o$ is the permittivity of a vacuum and $\rho$ is the charge density; the charge density was taken to be: $\rho = -F \sum z_i c_{i,a}$. 
Figure 6.4.2: Simulated linear sweep voltammograms for ion transfer at a microhole ITIES. The sigmoidal curve at 1 V is the result of anion IT from o to w, while the IT curves at 1.25 V designate a transfer of cations of charge number +1, +2, and +3 corresponding to the black, green, and blue curves, respectively. The red line details the curve fitting obtained using Oldham/Wilke’s original equations for the simple case of $z_i = -z_j$ [3, 12].

Figure 6.4.2 illustrates the simulated LSVs obtained implementing 1:1, 2:1, and 3:1 charge ratios of metal ions to their counter ions; the first IT is that of anions at 1.000 V, from o to w while the second sigmoidal wave at ~1.250 V corresponds to cation transfer from w to o. The standard rate constant for both IT’s were set equal to 1 cm⋅s$^{-1}$. As the magnitude of the charge on the cation increased its steady state current intensity increased. IT at a microhole ITIES is analogous to electrochemistry at a recessed disc, or ultramicroelectrode, whereby the current is proportional to charge [15, 16]. In this way, the result shown in Figure 6.4.2 is in good agreement with established theory. As shown, the anion transfer of the 1:1 case utilizing Oldham/Wilke’s equation [3] for a system with $z_i = -z_j$ correlates well with the simulated curves; details of the curve fitting procedure can be found in Appendix A.

By overlaying computational LSVs onto experimental ones, it is possible to ascribe approximate kinetic/thermodynamic values. Additionally, the geometry of the simulation can be tailored to meet the exact physical conditions of the experiment.
**Computations.** All simulations were performed using COMSOL Multiphysics 3.5a Software, a finite element analysis platform, using an Acer Aspire Laptop (Acer America Corporation (Canada), Mississauga, ON) equipped with a 1.66 GHz processor and 2 GB of DDR2 RAM; typical simulation runtimes ranged from 3 to 15 minutes. Appendix B contains the detailed COMSOL model reports. Curve fitting utilizing Oldham/Wilke's equation [3, 12] was performed with a procedure developed in Igor software (Igor version 6.31, Wavemetrics Inc., Portland, OR); this code is also available in Appendix A.

**6.4.3 - Experimental Methods**

Bis(triphenylphosphoranylidine)ammonium chloride (BACl) and lithium tetrakis(pentafluorophenyl)borate ethyl etherate (LiTB purum) were purchased from Acros Organics (Thermo Fisher Scientific, Geel, Belgium). These salts were used to prepare the organic phase supporting electrolyte, BATB, as previously described [4], through a facile metathesis reaction in a methanol:water solution (2:1, v:v); the salt was purified through recrystallization in acetone. Strontium nitrate, Sr(NO$_3$)$_2$, and 1,2-dichloroethane (DCE) were purchased from Sigma-Aldrich Chemie GmbH (Buchs, Switzerland).

The w|1,2-dichloroethane (w|DCE) interface was supported at a microhole drilled in a 25 μm thick polyimide film (Kapton, Dupont; purchased from Goodfellow, U.K.) by photoablation using a 193 nm ArF excimer laser beam (Lambda Physik, Göttingen, Germany, fluence = 0.2 J, frequency = 50 Hz). This process results in a conical hole with two distinct diameters on either side of the film; they were measured using a scanning laser microscope (VK 8700, Keyence, Courbevoie, France) to be 22.39 and 26.14 μm.

A specialized microhole apparatus was constructed out of two Teflon blocks. Each block contained a cylindrical chamber fashioned with an inverted “T” joint such that the two blocks could be screwed together with the polyimide film, and microhole, between dividing the two chambers. This apparatus has been described in detail elsewhere [4, 5] and is shown in Figure 6.4.3. After assembly, one chamber was first filled with the aqueous phase containing 0.5 mM Sr(NO$_3$)$_2$; the second chamber was partially filled with a 0.5 mM BATB DCE solution then topped off with an aqueous reference solution containing 10 mM LiCl and 0.5 mM BACl. Two electrodes, one
attached to the working electrode (WE) lead of the potentiostat and inserted into the strontium nitrate aqueous phase, the second attached to the counter/reference (CE/RE) leads of the potentiostat and placed in the aqueous reference solution, served as quasi-reference electrodes. Owing to the small amount of current utilized at a micro-ITIES only two electrodes are required [4, 5, 17-19] and, combined, this results in the electrochemical cell arrangement, Cell 6.4.1, shown below:

\[
\begin{array}{c|c|c|c|c|c|c|c|c}
\text{Ag} & \text{AgNO}_3 & 0.5 \text{ mM Sr(NO}_3)_2 & \text{0.5 mM BATB} & 10 \text{ mM LiCl} & \text{AgCl} & \text{Ag} \\
\text{(aq)} & \text{(aq)} & \text{(DCE)} & \text{(aq ~ ref)} & & & \\
\end{array}
\]

(Cell 6.4.1)

**Figure 6.4.3:** The experimental setup for IT measurements across a microhole ITIES (not to scale). Two teflon blocks (on the left and right) are held together using long screws with the polyimide film (and microhole) sandwiched between them, separating two hollow chambers fabricated in each.

The side of the polyimide film with the larger diameter was positioned facing the aqueous phase and, along with the progression in the experimental set up just described (i.e. filling the aqueous chamber first), results in the microhole being filled with
the aqueous phase and the micro-ITIES being flush with the organic phase side of the polyimide film. It has been shown that the position of the micro-ITIES, at the organic or aqueous phase or between, is crucial and can have significant influences on the current-potential response \([20, 21]\); with this experimental set up, ion transfer, from \(w\) to \(DCE\), will exhibit behaviour similar to a solid recessed disc ultramicroelectrode. All electrochemical measurements were performed using an Autolab potentiostat (PGSTAT30, Metrohm, Utrecht, Netherlands).

### 6.4.4 - Results and Discussion

Figure 6.4.4 shows the linear sweep voltammogram (LSV) of \(\text{Sr}^{2+}\) and \(\text{TB}^-\) transfer trough the microhole ITIES where the potential was scanned from 0.420 to 1.070 V at a rate of 0.020 V\(\cdot\)s\(^{-1}\). The current begins at approximately 0.000 nA but experiences a linear ramp that begins at ca. 0.502 V and continues to the end of the LSV. Since the IT of \(\text{TB}^-\) from \(o\) to \(w\) at 0.709 V is well established \([4, 5]\) it can, therefore, be concluded that \(\text{TB}^-\) transfer contributes to the linear ramp shown in Figure 6.4.4. It was recently demonstrated that \(\text{Sr}^{2+}\) transfers at 0.768 V \([22]\) using cyclic voltammetry (CV) and, therefore, it is likely that strontium IT also contributes to the \(i\)-V response illustrated in Figure 6.4.4.

![Linear sweep voltammogram](image)

**Figure 6.4.4:** Linear sweep voltammogram obtained using Cell 6.4.1 with an initial and final potential of 0.400 and 1.100 V and a scan rate of 0.020 V\(\cdot\)s\(^{-1}\).

To ascertain the formal IT potential of these two ions, conventionally, two data treatment steps are generally observed. First, the experimental half-wave potential,
\[ \Delta_o \phi_{1/2} \], is determined [16], commonly by plotting \( \Delta_o \phi \) vs. \( \log \left( \frac{(i_{ss} - i)}{i} \right) \), where \( i_{ss} \) is the steady state current; the point at which this curve crosses the x-axis is taken to be \( \Delta_o \phi_{1/2} \).

Second, at the liquid|liquid interface the polarized potential window is calibrated using a non-thermodynamic assumption, typically the TATB or Parkers assumption [23, 24], using the known IT potential of an internal standard added to the system and through the equation 2.9.

In the 1980’s and early 1990’s Oldham [11, 12] explored electrolytic systems with little or no supporting electrolyte at ultramicroelectrodes and developed a mathematical/numerical model utilizing the Nernst-Planck series of equations. Wilke developed this further in the form of IT theory [3, 12] in systems with little or no supporting electrolyte; equations 6.3.1, 6.3.2, and 6.3.3 form the basis of this theory.

The limiting current, \( I_{lim} \), found in equations 6.3.2 and 6.3.3 can be described by the following [12]:

\[
I_{lim} = 4(1 - z_i / z_j)z_iFD_{i,a}c_{i,a}r_d
\]  

(6.4.5)

where \( r_d \) is the radius of the electrode or, in this case, ITIES surface with \( D_{i,a} \) and \( c_{i,a} \) representing the diffusion coefficient and concentration of species \( i \) in phase \( a \). Equation 6.3.3 was used effectively, through curve fitting, to determine the formal IT potentials (as well as evaluating the possibility of ion pair formation) of several cations and anions at the w|DCE interface [4]. However, as was the case in a recent publication [5] evaluating the formal IT potential of \( \text{UO}_2^{2+} \) and \( \text{NO}_3^- \), this equality does not hold for strontium and nitrate whose charges are +2 and −1, respectively. Therefore, by inverting the potential and current axis of the CV, equation 6.3.2 was used to perform the curve fitting through an inverse-master-equation method [5]. In this way, by a simple inversion of the experimental data, a great deal of tedious mathematical treatment can be avoided.

Four coefficients were used to perform the fitting, including \( z_i, z_j, \Delta_o \phi_{1/2} \), and \( I_{lim} \). Indeed, the charges of the two ions were fixed or not allowed to vary and so, in this way, the curve fitting function resolves to only 2 coefficients. The charges of the cation and anion were added as coefficients simply for the sake of convenience. For \( \text{TB}^- \) and \( \text{Sr}^{2+} \), the respective charge ratios were held as 1 and 2 while an initial value for \( I_{lim} \) was
estimated using equation 6.4.13 with $D_{TB^{-}}$ and $D_{Sr^{2+}}$ equal to 0.5 and $1.2 \times 10^{-5}$ cm²·s⁻¹, respectively; note that $D_{Sr^{2+}}$ was obtained from the literature [25]; however, $D_{TB^{-}}$ was estimated.

Figure 6.4.5 shows the curve fitting results applied to the two baseline-corrected sections of the LSV obtained; the separation between the TB⁻ and Sr²⁺ IT waves was estimated to occur at 0.800 V whereby a subtle – but observable – change of slope (from 2.2 to $2.4 \times 10^{-8}$) in the linear ramp can be observed. Using TB⁻ as the internal reference, the formal transfer potential of Sr²⁺ was estimated to be 0.879 V. This formal IT potential indicates that strontium is extremely hydrophilic, and comparable to the dioxouranium cation [5]. Using the Gibbs free energy/potential relationship, $\Delta G = zF\Delta_f^\theta \phi'$, the Gibbs free energy of strontium transfer at the w|DCE interface, $\Delta G_{Sr^{2+}}^{w\rightarrow DCE}$, was calculated to be 169.6 kJ·mol⁻¹.

![Figure 6.4.5:](image)

**Figure 6.4.5:** The experimental linear sweep voltammogram (—) as shown in Figure 6.4.4 after axis inversion and baseline correction for each proposed IT. The red trace (▬) details the curve fitting performed through equation 6.3.2.
The Wilke model [3], and thus equations 6.3.1, 6.3.2, 6.3.3, and 6.4.5, were based on a bi-hemispherical microelectrode geometry [26] with steady state response, which he described as a “theoretical construction without any physical meaning”. The approximation of geometries was justified by recognizing that uniform ion accessibility is key and, in this way, there is no significant difference between a planer or recessed disk electrode and a hemispherical, or in this case a bi-hemispherical model. However, while this may be the case for metal-electrolyte interfaces, the model Wilke employs as an analog [26], it is not all together clear if this is true for liquid|liquid or soft interfaces. Of particular concern is the application of potential. In the metal-electrolyte case the potential is applied to the metal and decays with increasing distance from the electrode surface. In liquid|liquid electrochemistry a Galvanic potential difference develops across the interface as a result of an applied potential across two electrodes immersed at effectively an 'infinite' distances from the ITIES. It has been recognized that the potential distribution at liquid junctions is non-linear [27-31] and can extend into either phase – in a system with an abundance of supporting electrolyte – by as much as a nanometer.

With this in mind, a finite element analysis simulation was prepared using the Nernst-Planck series of equations, which includes an electrostatics component in order to examine the influence of the applied potential. Most computational and theoretical publications [29, 30, 32-43] of liquid junction potentials studied ion partitioning/exchange with respect to the development of the electric field as a consequence of the charge separation between the cationic and anionic components of the salt that, in turn, is a result of their differing diffusion coefficients/ionic mobilities. The present chapter, however, focuses on the use of an applied external electric field and the effect of migration and diffusion on the i-V response with respect to IT across a microhole ITIES. This simulation provides a facile, universal method of analyzing the kinetics/thermodynamics of IT in systems with or without supporting electrolyte.

The simulation was constructed to mimic the experimental polyimide film and included the conical shaped microhole with radii of 11.20 and 13.10 μm at the organic and aqueous sides, respectively.

Figure 6.4.6A shows the experimental LSV with 3 overlaid simulation curves. Curve (a) in Figure 6.4.6A was acquired experimentally, curve (b) was obtained using the
Nernst-Planck simulation, whilst curves (c) and (d) show the system with mass transport described by only Fick’s laws of diffusion (*i.e.* no migrational component); this was performed to contrast the current response for excess supporting electrolyte. The $k^o$ values were set equal to 1 and $1 \times 10^{-6}$ cm$\cdot$s$^{-1}$ for curves c and d, respectively; in either instance $k^o$ values were the same for both Sr$^{2+}$ and TB$^-$. The diffusion coefficients for Sr$^{2+}$ and NO$_3^-$ were set equal to 1.2 and $3.0 \times 10^{-5}$ cm$^2$·s$^{-1}$, and based on published values for strontium chloride [25] and nitric acid [44] calculated using the Onsager-Fuoss equation, respectively.

![Figure 6.4.6](image)

**Figure 6.4.6:** (A) Experimentally obtained linear sweep voltammogram (LSV) (red curve) with overlaid simulated LSVs generated using only Fick’s laws of diffusion to describe mass transfer (*i.e.* no migration, $k^o$ equal to 1 and $1 \times 10^{-6}$ cm$\cdot$s$^{-1}$ for the c and d, respectively), and the Nernst-Planck model (○). (B) The potential profile surrounding the interface captured at several initial points in time as indicated.
The diffusion coefficients for TB$^{-}$ and BA$^{+}$ were estimated to be $0.5 \times 10^{-5}$ cm$^2$s$^{-1}$ as, to the best of my knowledge, no diffusion data is available in the literature for these two species. The diffusion coefficient of each species was considered equal for both aqueous and DCE phases. The ionic mobility, $u_m$, of all species was calculated based on the Einstein-Smolchowski equation [16]; however, using COMSOL’s formalism, $u_m = D_i / (RT)$.

Figure 6.4.6B highlights the potential profile at the ITIES ($x = 0$), as it moves towards the source of the applied potential in the aqueous phase (positive $x$), and as it transitions into the organic phase (negative $x$). The dip in the potential as it approaches the ITIES correlates well with the position of the microchannel, and thus the question becomes: what is the influence of this extended potential gradient on the IT? Indeed, the simulated diffusional behaviour of species at the ITIES could not mimic the experimental conditions employed and a high degree of discrepancy between theoretical prediction and experimental result was observed.

The linear waveform function used to describe the applied potential was then employed directly within the Butler-Volmer kinetic formulation via equations 6.4.4 and 6.4.5 at the interface (curves c and d); note that only the flux of Sr$^{2+}$ and TB$^{-}$ was integrated to determine the current at the interface in this instance.

Finally, curve (a) is the system under NP, or migrational and diffusive mass transport. This was accomplished by introducing a physics model describing electrostatics and applying the potential wave function at boundaries 8 and 17; the current at the interface was the integral sum of all ion fluxes. As shown, the simulated data was in good agreement with experimental observations confirming the validity of the present approach to account for the IT in the absence of supporting electrolyte. The estimation of formal transfer potentials determined for TB$^{-}$ and Sr$^{2+}$ (0.709 and 0.879 V, respectively) during curve fitting for the simulations also correlates well with experimental data.

Comparing the curves in Figure 6.4.6A derived using Fick’s laws of mass transport and Butler-Volmer IT to that calculated using NP mass transport, the steady state current obtained with the latter is 3 times greater in the latter. This is in excellent agreement with Oldham and Wilke’s prediction [3, 12] regarding the change in current response between the case with and without supporting electrolyte. Once all ions are
considered, however, the linear ramp in the current-potential response dominates with the two sigmoidal wave features, indicative of each IT, being obscured. For the Butler-Volmer case, it is also interesting to note the change in IT potential incurred with decreasing $k^o$; as $k^o$ decreases the IT potential is delayed and the slope of the LSV decreases.

It is important to note that the present NP simulation neglects any ion-pair effects as described by the Bjerrum and Fuoss models [45]. Ion-pairing may play a significant role particularly in solvents of low dielectric constants, such as DCE, where the radius of this interaction has been shown to increase to a few nanometers [45] while also being prevalent at charged interfaces [46]. These effects ultimately mean that strontium IT may be assisted or facilitated by TB$^-$ or even nitrate; therefore, the formal IT potentials presented herein should be considered as estimates. In order to integrate these ion-pair models, microscopic solvent changes in the dielectric constant [47] as well as a Gouy-Chapman type interfacial structure [46] might be considered; however, are beyond the scope of the present communication.

Figure 6.4.6B shows the potential drop experienced at the ITIES and was extracted from a surface plot of the potential at 10, 20, 50, 80, and 100 second time intervals with a distance, $x$, away from the ITIES equal to roughly $\pm 250 \, \mu m$. The potential shows an almost sigmoidal drop as it approaches the interface and then crosses it. The potential profile is in good agreement with that shown recently [48] for a system in the absence of adsorbed species at the ITIES between water and DCE; however, the potential drop occurs over a large distance – commonly measured in nm it is shown here measured in $\mu m$. This may be attributed to the lack of supporting electrolyte in the system; however, this is still under investigation.

6.4.5 - Conclusions

A general curve fitting method using the inverse-master equation approach allows access to the free metal ion transfer potentials at a microhole-ITIES. As an example, the formal transfer potential for Sr$^{2+}$, $\Delta_o^{\text{w}} \phi_{\text{Sr}^{2+}}$, has been determined to be $0.879 \, V$ at the w|DCE interface. This is a useful constant for the evaluation of Sr$^{2+}$, or any metal of interest, towards FIT or metal extraction in biphasic systems. It is critical to
note that this universal curve fitting method, unlike the previous approach, is not limited by the charge ratio between the metal ion of interest and its counterion.

Finite element analysis was used to investigate simple IT in a system with no supporting electrolyte through the use of Nernst-Planck mass transport within each phase and Butler-Volmer kinetics at the ITIES. The simulation results showed good overlap with the experimentally obtained LSV through the use of known diffusion coefficients and apparent ionic mobilities.

6.4.6 - References

Chapter 6.5 - Facile determination of formal transfer potentials for hydrophilic alkali metal ions at water|ionic liquid microinterfaces

6.5.1 - Introduction

Room temperature ionic liquids (ILs) have come under considerable attention since it was discovered that higher efficiencies in metal extraction could be achieved in water|IL (w|IL) biphasic systems versus conventional molecular solvents [1] (water|organic, w|o). In these systems, a large organic ligand dissolved in the IL or organic phase complexes with the metal ions of interest and improves their miscibility (hydrophobicity) towards the organic/IL phase. However, elucidating the mechanisms and thermodynamics of ligand-assisted metal extraction can be challenging and often makes use of expensive and even hazardous analytical techniques such as radioisotopic distribution analysis [2, 3].

Interestingly, electrochemistry at the interface between two immiscible electrolytic solutions (ITIES) has been the focus of multiple studies into simple ion transfer at the water|1,2-dichloroethane [4-12] (w|DCE) and water|nitrobenzene [4, 13-16] (w|NB) interfaces with recent developments moving towards biphasic systems for specialized applications; including, liquid|gel [17-19] and w|IL [12, 20-23] interfaces, Aoki explored the theory of ion-transfer kinetics at a viscous immiscible liquid|liquid interface by means of the Langevin equation [24]. Simple IT is detailed below in equation 6.5.1:

\[ i_w^+ \xrightleftharpoons[k_f]{k_s} i_{IL}^+ \]  

(6.5.1)

where ion \( i \) with charge \( z^+ \) transfers from aqueous to organic or IL. In this electrochemical experiment, ions are pushed/pulled from one phase to the other through the application of a potential to either phase. For example, a positive potential, administered to the aqueous phase, will repel cations causing them to transfer into the organic or IL phase; similarly, a negative potential can then draw them back across the ITIES. This electrochemical technique can also be used to study ligand-assisted or facilitated ion transfer (FIT) [10-12, 20, 21] as described in equation 6.5.2:

\[ i_w^+ + nL_{IL} \]  

(6.5.2)
where \( n \) is the stoichiometric ratio of the ligand \((L)\) to metal ion. Cyclic voltammograms (CVs) can be used to characterize \( n \) as well as the overall complexation constant, \( \beta \), of the FIT via the exceptional theoretical work of Mareček et al.\([25, 26]\), Kakiuchi and Senda \([27]\), as well as Girault et al. \([8]\). These two key parameters allow for the facile quantitative evaluation of w|IL systems with various ligands.

However, in order to describe FIT, simple IT must first be characterized via the determination of the formal transfer potential, \( \Delta^{\circ}_{\text{IL}} \phi_{i} \), of the metal ion of interest. The formal transfer potential is indicative of the amount of applied potential required in order to elicit charge transfer and is related to the Gibbs free energy of transfer; \( \Delta G = zF\Delta^{\circ}_{\text{IL}} \phi_{i} \). This is analogous to electrochemistry at a traditional metal-electrolyte interface whereby the formal redox potential, \( E^{\circ} \), can also be related to the Gibbs free energy; \( \Delta G = -zFE^{\circ} \).

In a liquid|liquid electrochemical system, the region within which the potential can be swept using CV, called the polarizable potential window (PPW), is typically limited by the transfer of the supporting electrolytes. This means that hydrophilic metal salts are usually employed in the aqueous phase, while large, hydrophobic organic salts compose the IL phase. The size of the PPW is directly related to the hydrophilicity/hydrophobicity of the supporting electrolytes/IL components, which results in the PPW being limited by their transfer. Therefore, their formal transfer potentials are very difficult to observe through CVs.

Most w|IL electrochemistry is performed at a micro-interface since this reduces the amount of IL required to perform the experiment, which is advantageous since most ILs are expensive \([22]\), while this also decreases the the \( iR \) drop, or solution resistance, through the use of lower (nanoampere) current.

Interestingly, diffusion across a micro-ITIES housed at the tip of a pulled capillary is usually asymmetric when molecular solvents like DCE are used; however, this diffusion regime becomes symmetrical when moved to the w|IL case. For both w|DCE and w|IL, when the ion transfer originates in the aqueous phase a peak-shaped current response is generated \([5]\). This is owing to the small volume of material next to the
interface which is rapidly consumed such that material from higher up in the microchannel must then diffuse to the ITIES; this is referred to as consumption control.

ITs moving from o to w, or IL to w, vary radically from each other owing to the high viscosity of the IL phase. In the w|DCE case, because of the large volume of solution (relative to the interfacial size) surrounding the interface, species can diffuse rapidly to the ITIES such that diffusion occurs faster than consumption; this is often referred to a diffusion controlled resulting in a sigmoidal-shaped wave with a steady state current [5]. CVs with a peak-shaped wave in the forward scan and steady-state plateau in the reverse scan, or vice versa, are asymmetric. The difference in the w|IL scenario is that diffusion is decreased and IT from IL to w shows a peak-shaped voltammetric response. Therefore, while ion transfer at a w|DCE capillary micro-ITIES is asymmetrical, it becomes symmetrical at a w|IL interface due to the slow diffusion in the IL. This symmetrical diffusion regime also results in a return peak at the edge of the PPW, which resemble a cropped IT wave. It is this curve feature, not available at the w|DCE micro-interface, that can be utilized to estimate the formal transfer potential of species limiting the potential window.

With this in mind, and using finite element analysis to simulate simple IT, the profile at the edge of the PPW can be used to predict the formal transfer potential of metal ions at a micro-ITIES housed at the tip of a glass capillary through comparison to a working curve. This approach agrees well with a method developed by Girault et al. [28] for their approximation of metal ion formal transfer potentials limiting the PPW at a large (centimeter scale) w|DCE interface. In that report [28], the authors used a numerical technique in order to generate simulated CVs; however in the present report, through Comsol 3.5a Multiphysics software, the physical geometry of the pipette tip can be approximated and used to better tailor the simulated CVs to match those acquired experimentally.

Herein, for the first time, the formal transfer potential of alkali metal ions at a w|IL interface have been estimated. These values will be used to evaluate alkali metal extraction in w|IL systems with various ligands in order to gauge their efficiency and selectivity towards the reprocessing of spent nuclear fuel.
6.5.2 - Theory

Simple ion transfer (IT), as shown in equation 6.5.1, was simulated for a micropipette geometry, using finite element analysis with Comsol 3.5a Multiphysics software. Figure 6.5.1 illustrates the two dimensional geometry used in the simulation such that the 25 μm diameter micro-ITIES is positioned at the tip.

![Figure 6.5.1: Micropipette simulation geometry.](image)

A microchannel led up towards a larger reservoir within which the walls of the channel were designated as an insulator while the top of the reservoir was a concentration boundary in order to represent an infinite source of bulk solution form which ions could diffuse. The exterior of the pipette was also insulating with the bulk IL solution being represented by concentration boundaries along the outside walls of the simulation. Diffusion within each phase was approached using Fick’s laws of diffusion which results in equation 2.1. A facile system of mass transfer, using only Fick’s laws, was utilized over a more complex system integrating a Nernst-Planck-Poisson (NPP) equation set, as demonstrated recently in the literature [15, 16], for two reasons. First, the predominate motivation towards utilizing an NPP approach is to take into account migration and charge separation along with diffusion; the experimental conditions, that these simulations are aimed to replicate, are at sufficient concentrations (~5 mM) as to satisfy the exclusion of migration effects that are likely minor contributors. Secondly, the NPP system is incredibly complex to implement, and the approximation of current-potential responses for systems with migration effects have been approximated using slow ion transfer
kinetics previously [29]. Therefore, while a more complex NPP mass transfer is possible, the model presented herein is a facile, good approximation.

The geometry consisted of two subdomains separated by the micro-ITIES. IT, as shown in equation 6.5.1, was described for a reversible system with forward, \( k_f \), and reverse, \( k_b \), rate constants defined through Butler-Volmer kinetics:

\[
\begin{align*}
    k_f &= k^o e^{-\alpha f(\Delta w \phi - \Delta \phi^o)} \\
    k_b &= k^o e^{(1-\alpha) f(\Delta w \phi - \Delta \phi^o)}
\end{align*}
\] (6.5.4) (6.5.5)

here, \( k^o \) is the standard rate constant, \( \alpha \) is the transfer coefficient, \( \Delta w \phi \) is the applied Galvani potential difference across the interface, \( \Delta \phi^o \) is the formal transfer potential, and \( f = z_i F/RT; z_i \) is the charge of species \( i \), \( F \) is Faraday’s constant, \( R \) is the gas constant, and \( T \) is temperature in Kelvin.

The current was calculated as an integral of the diffusive flux at the interface, with \( r \) representing the interfacial radius, as given in equation 3.3. The potential was implemented as a triangular wave function [9] applied at the interfacial boundary through equations 6.5.3 and 6.5.4 as shown in equation 2.5. Comsol Models are provided in reference [30].

6.5.3 - Experimental

Chemicals. Chemical reagents were used as purchased without further purification. Lithium nitrate (LiNO\(_3\)), sodium nitrate (NaNO\(_3\)), potassium nitrate (KNO\(_3\)), rubidium nitrate (RbNO\(_3\)), cesium nitrate (CsNO\(_3\)), tetramethylammonium nitrate (TMANO\(_3\)), dichloromethane (DCM), trimethylchlorosilane, nitric acid (HNO\(_3\)), and hydrochloric acid (HCl) were obtained from Sigma-Aldrich Canada (Mississauga, ON). Trihexyltetradecyolphosphonium chloride (P\(_{66614}\)Cl) and potassium tetrakis(pentafluorophenyl)borate were ordered from Strem Chemicals Inc. (Newburyport, MA (USA)) and Boulder Scientific Co. (Longmont, CO ), respectively; the IL used in these liquid|liquid electrochemistry experiments was prepared by a facile metathesis of these two salts dissolved in DCM. A detailed description of the IL preparation is described elsewhere [12, 22].
Micropipettes. The micropipettes were prepared, as has been previously described [10, 12, 22, 29], and can be found in section 2.3.3.

Instrumentation. Cyclic voltammograms were obtained using the Modulab System (Ametek Advanced Measurement Technology, Farnborough, New Hampshire (United Kingdom)) with a potentiostat and femto-ammeter. The working electrode lead of the potentiostat was linked to the BNC connector integrated into the modified pipette holder (HEKA Electronics, Mahone Bay, NS (Canada)), which was in turn attached to an internal silver wire operating within the aqueous phase. The counter and reference leads were coupled together and clipped to a second silver wire which was placed in the IL phase. Similar to some ultramicroelectrode experimental set ups, this micro-ITIES method uses a reduced amount of current (nanoampere range) and, therefore, only requires two electrodes. The following electrochemical cell was used such that X was either Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), or Cs\(^+\):

\[
\text{Ag} | \text{AgNO}_3 | 5 \text{ mM XNO}_3 | \text{P}_{66614} \text{TB} | \text{AgTB} | \text{Ag} \quad (\text{aq}) | (\text{IL}) \quad (\text{Cell 6.5.1})
\]

The tip of the micropipette, fixed in the modified holder and supporting the aqueous phase, was dipped into the vial containing the IL phase, which was positioned on a stage equipped with copper tubing connected to a circulating water bath (VWR, Mississauga, ON) that maintained the temperature of the ITIES at 60°C.

6.5.4 - Results and Discussion

Figure 6.5.2A and 6.5.2B illustrate the CVs obtained using Cell 6.5.1 with X equal to Cs\(^+\) with and without 1.5 mM tetramethylammonium nitrate (TMANO\(_3\)) added to the aqueous phase, respectively. In the absence of TMANO\(_3\), or the blank solution, the CV was initiated at 0.000 V and scanned towards more positive potentials at a rate of 0.020 V s\(^{-1}\) until 0.530 V was reached. At 0.530 V, the current begins to rise and this marks the edge of the PPW; this is limited by the transfer of the supporting electrolytes, Cs\(^+\) from w to IL, along with the anionic component of the IL, TB\(^-\), from IL to w. The scan was then reversed, travelling from 0.530 to −0.215 V where the current response decreased, indicating the lower limit of the PPW; this is characterized by the transfer of
NO$_3^-$ from w to IL and P$_{6614}^+$ from IL to w. The CV was then scanned back to a final potential of 0.000 V.

**Figure 6.5.2:** Cyclic voltammograms obtained using Cell 6.5.1 with X equal to Cs$^+$ (A) and after addition of 1.5 mM TMANO$_3$ to the aqueous phase (B). The instrument parameters were as follows: scan rate of 0.020 V∙s$^{-1}$, initial potential of 0.000 V, and a potential range from −0.215 to 0.530 V. The two data points used for comparison against the working curve are indicated in A; $I_{cos}$ and $I_{ip}$, $\Delta w_{IL} \phi_{ip}$.

After addition of TMANO$_3$, a peak-shaped wave can be observed during the initial forward scan from 0.000 to 0.530 V at approximately 0.341 V; this is indicative of the transfer of TMA$^+$ from w to IL. During the reverse scan, from 0.530 to −0.215 V, another peak-shaped wave can be seen at 0.249 V and this is owing to the return of TMA$^+$ back across the ITIES. The current-potential response for the simple IT of TMA$^+$ is in good agreement with previous reports in the literature [21, 22, 29, 31] and its shape is a consequence of two factors: pipette geometry and the viscosity of the IL. TMA$^+$ IT was used to calibrate the potential scale using the tetraphenylarsonium tetraphenylborate
TATB) or Parker’s assumption [32]; the formal transfer potential of TMA$^+$ was taken to be 0.293 V [22].

During the forward scan, the small volume of material within the microchannel is rapidly consumed, generating an exponential increase in the current, and to replenish this concentration ions must diffuse from higher up in the capillary – this results in an exponential decay of the signal.

The high viscosity in the IL phase (1206 mPa·s at 60°C) [22] results in the slow diffusion of material in that phase. In this way, when the scan is reversed, a peak-shaped current-potential profile is obtained since ions close to the interface are rapidly consumed, which is followed by very slow diffusion of ions from the bulk solution. Solution resistance in both phases is of critical importance and has been previously measured [22] for this IL in the homogeneous case. This measurement showed a resistance of 7.3 MΩ and a current of 0.3 nA, which give a potential shift of ±2.2 mV. This is considered within tolerable error limits. The total resistance in the aqueous phase was not measured; however, the implementation of 5 mM of metal salt in that phase, combined with the fact that no ions were ultimately transferred, would seem to indicate that the overall solution resistance is a minor contributing factor. Of particular interest is the formal IT potential of metal ions, $\Delta^w_{n\ell} \phi_{\ell}^o$, at the w|IL interface. These constants, unique to each metal ion and biphasic solvent system, are used as a point of reference when evaluating, quantitatively, ligand assisted, or facilitated ion transfer (FIT). Equation 6.1.2, derived in part from the Nernst equations describing the metal ion and charged metal-complex species, describes the linear relationship between the formal IT potential of the metal-ligand complex, $\Delta^z_{n\ell} \phi^o_{\ell}$, and the initial ligand concentration in the IL phase, $c_{L, o}^*$ [8]. Equation 6.1.2, while appearing complex, is actually in the straightforward, linear form of $y = mx + b$; with the slope and intercept comprising the metal ion to ligand stoichiometry and overall complexation constant, respectively. By incrementally altering the initial ligand concentration in the IL phase and plotting the natural logarithm of this value versus $-z_{\ell}^F \left( \Delta^z_{n\ell} \phi^o_{\ell} - \Delta^z_{n\ell} \phi^o_{\ell}^c \right)$, developing this linear relationship and evaluating various ligand and solvent systems becomes facile. In theory, $\Delta^w_{n\ell} \phi^o_{\ell}$ can be determined directly from
simple ion transfer experiments. However, metal ions are usually very hydrophilic, typically limiting the PPW, and therefore $\Delta_{\text{IL}}^w \phi^\circ_i$ cannot be measured directly using cyclic voltammetry.

![Cyclic voltammograms generated using finite element analysis with Comsol Multiphysics 3.5a.](image)

**Figure 6.5.3:** Cyclic voltammograms generated using finite element analysis with Comsol Multiphysics 3.5a.

The symmetric diffusion regime described in Figure 6.5.2 for the w|IL micropipette system results in a current-potential profile at the edge of the PPW that resembles an incomplete IT segment. Using this profile, it is possible to estimate the formal IT potential of the ions limiting the PPW. Finite element analysis at an ITIES geometry housed at the tip of a micropipette, as shown in Figure 6.5.1, was used to construct a profile of simple IT. Each iteration of the CV simulation was given a smaller potential range such that they began to resemble the potential profile at the edge of the PPW; overlays of these CV’s are depicted in Figure 6.5.3. For the purposes of the demonstration a formal IT potential of 0.200 V was assumed.

Within the simulation, the standard rate constant, $k^\circ$ was set equal to $5 \times 10^{-6} \text{ m s}^{-1}$ with a transfer coefficient equal to 0.5. These values are analogous to those employed in a previous study [33], which further demonstrated $k^\circ$’s direct influence over the peak-to-peak separation; thus, its value was chosen in order to replicate the 0.090 V peak-to-peak separation observed in that study and indicated elsewhere in the literature [20]. Through these CVs a working curve was developed using the ratio of the current at the edge of
scan and return peak current \( (I_{\text{cos}}/I_{\text{rp}}) \) versus \( (\Delta_{w}^{w}\phi'_{r} - \Delta_{IL}^{w}\phi_{rp}) \); where \( \Delta_{w}^{w}\phi'_{r} \) was the formal transfer potential established in the simulation and \( \Delta_{IL}^{w}\phi_{rp} \) is the return peak current. These two data points formed the basis of the working curve and were also taken from the experimental CVs as indicated in Figure 6.5.2A. In this way, both axes of the working curve, illustrated in Figure 6.5.4, have been normalized. This curve was developed for species transferring from \( w \) to \( IL \) with a charge, \( z \), of 1+. The viscosity of the IL phase was approximated by using a diffusion coefficient, \( D_{IL} \), equal to \( 5.0 \times 10^{-13} \text{ m}^2\text{s}^{-1} \) while that of the aqueous phase was \( 2.0 \times 10^{-9} \text{ m}^2\text{s}^{-1} \). These diffusion coefficients were derived from a recent study involving the IT of \( \text{TMA}^{+} \) in which, using a similar code, a simulated CV was overlaid onto an experimental one such that these thermodynamic parameters were optimized [22]. Similarly, 333.15 K, or 60°C, was used in the simulation in order to approximate typical experimental conditions.

**Figure 6.5.4:** Working curve compiled from the cyclic voltammograms illustrated in Figure 6.5.3 using the ratio of the current at the edge of scan \( (I_{\text{cos}}) \) to the return peak current \( (I_{\text{rp}}) \) versus \( (\Delta_{w}^{w}\phi'_{r} - \Delta_{IL}^{w}\phi_{rp}) \); where \( \Delta_{w}^{w}\phi'_{r} \) is the formal IT potential of a cation as defined by the simulation and \( \Delta_{IL}^{w}\phi_{rp} \) is the return peak current obtained from Figure 6.5.3.
The working curve is in good agreement with that developed by Girault et al. [28] for their evaluation of alkali metal ion transfer limiting the large (centimeter scale) water|1,2-dichloroethane (w|DCE) ITIES. In that report [28] they used a numerical approach in order to develop their working curve, but, here the geometry of the finite element analysis can be tailored to mirror critical physical aspects of any experimental apparatus. The advantages of building a geometric model have been demonstrated for the case of a microhole [34] ITIES where the position of the interface was investigated and recently for the IT of dioxouranium at a microhole with limited supporting electrolyte [29].

Moving forward, Figure 6.5.5 demonstrates the experimental CVs obtained using Cell 6.5.1 with X equal to Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), or Cs\(^+\). Using Li\(^+\) as an example, the CV was scanned until 0.572 V at a rate of 0.020 V\(\cdot\)s\(^{-1}\) and then swept in the reverse direction. The edge of the PPW elicited a ‘current at the edge of scan’ of 1.338 nA, while the ‘return peak current’ was −0.330 nA; this gives an \(I_{\text{cos}}/I_{\text{rp}}\) of 4.06, translating to +0.078 V from the return peak potential. For this case, \(\Delta\phi_{\text{IL}}\) was determined to be 0.487 and, combined with the value from the working curve, the formal transfer potential for Li\(^+\) was calculated to be 0.565 V. The formal transfer potentials of the other alkali metals ions were found to be 0.548, 0.521, 0.531, and 518 V for Na\(^+\), K\(^+\), Rb\(^+\), and Cs\(^+\), respectively. This follows the general order of decreasing hydrophilicity, Li\(^+\)>Na\(^+\)>K\(^+\)>Rb\(^+\)>Cs\(^+\), with increasing atomic radii 1.82, 2.27, 2.75, 3.03, and 3.43 Å [35], and agrees well with the trend shown by Girault et al. [28] at the w|DCE interface. It should be noted that these are estimates and were lower than expected when compared to recent formal transfer potentials obtained at w|DCE interfaces [36]. Admittedly, interference from the simultaneous transfer of the anionic component of the IL, tetrakis(pentafluorophenyl)borate (TB\(^-\)), may impact the results presented here; however, w|DCE numbers indicate that alkali metal ion transfer occurs before TB\(^-\) [36]. Whether this is the case at the w|IL interface is unclear, but at present this methodology is the only process available by which these valuable constants can be determined.
Figure 6.5.5: Cyclic voltammograms obtained using Cell 6.4.1 with X equal to Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$, as indicated. The instrument parameters were as follows: scan rate of 0.020 V s$^{-1}$, initial potential of 0.000 V, and a potential range from −0.215 to 0.530 V.

6.5.5 - Conclusions

Herein is described, for the first time, a facile determination of the formal transfer potentials of hydrophilic alkali metal ions Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ typically limiting the PPW. The transfer values were found to be 0.565, 0.548, 0.521, 0.531, and 518 V, respectively, at a w|P$_{66614}$TB interface. Their approximation was made possible through the use of a working curve established via finite element analysis for a micropipette geometry mimicking the current-potential response of a cyclic voltammetric experiment.
at the edge of the PPW. The working curve was developed as a ratio of the CV current at the edge of scan and the return peak current versus $\Delta_{w}^{m} \phi_{p} - \Delta_{w}^{m} \phi_{p}$. This methodology allows for the geometry of the experimental apparatus to be replicated within the simulation having implications towards understanding geometric effects.

Additionally, the geometry of the micropipette and high viscosity of the IL phase are the two factors that augment the current-potential response at the PPW edge and make the implementation of this technique possible.

It should be noted that since this technique makes use of the profile at the edge of the PPW, the transfer of the anionic component of the IL may interfere with the determination of the alkali metal formal transfer potential if its transfer potential is close to that of metal ions; therefore, the constants in this case should be treated as estimates.

6.5.6 - References

Chapter 7.1 - Electrochemical evaluation of uranyl ion extraction by conventional PUREX/TRUX ligands using liquid-liquid micro-interfaces

7.1.1 - Introduction

The continued debate over climate change has sparked a resurgence of interest in alternative energy resources to replace fossil fuels; included amongst these is nuclear power generation. One of the most effective nuclear power generation techniques has been the Canadian Deuterium Uranium (CANDU) heavy water reactors owing to their capability to utilize natural sources of uranium and spent nuclear fuel from conventional light water reactors [1-4]. This ability stems from the high efficiency of neutron capture within the deuterium heavy water system and the use of materials, such as zirconium, that have a minimal neutron absorption cross-section [5]. Fission products, however, have high neutron absorptions and limit the life time of the fuel bundle despite the continued presence of significant fissile material [4]. Additionally, it has been demonstrated that recycled uranium fuel, with 0.9% $^{235}$U, shows improved energy production versus naturally occurring uranium [4] in a CANDU reactor. Therefore, of particular interest is the recycling/reprocessing of nuclear fuels to remove high neutron absorbers and reclaim valuable energy producing nuclear isotopes – extending the life of nuclear fuel.

Additionally, since the unfortunate events of March 11, 2011, which saw a massive earthquake-generated tsunami cripple the Japanese Fukushima nuclear power plant, techniques towards nuclear waste clean-up or environmental reclamation of nuclear waste contaminated regions are also of practical interest.

The Plutonium URanium EXtraction (PUREX) process has been the dominant method of nuclear fuel reprocessing for half a century [6-8], with an improvement to the process being introduced towards the end of the 1980’s in the form of the TRans-URanium EXtraction (TRUEX) process [6, 9-14]. Both methods are solvent extraction techniques using an aqueous-organic interface and phosphine oxide organic ligands [6-14]. The PUREX process utilizes tributylphosphate (TBP) [6-8, 10, 15] as the primary ligand, whilst TRUEX uses a combination of TBP and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) [6, 9, 13, 16-20]. Since its inception, the TRUEX process has employed TBP to gain improved selectivity and specificity for transuranic elements [17, 18] and prevent the formation of a third emulsion
phase. Conventional uranium reprocessing, using n-dodecane as the solvent, makes use of a series of centrifugal reactors whose engineering complexity is intimidating but necessary in order to achieve the degree of selectivity and recovery. Maintenance costs for this equipment is high, owing to its saturation with radioactive material, and this process also generates a considerable quantity of radioactive raffinate. Thus, a simplified more cost effective technique towards the separation of these valuable materials is desirable. The focus of research has recently switched from the development of new ligands to alternative solvents such ionic liquids (ILs, organic salts whose melting point is less than 100 °C) [10-12, 15, 21-26], which have been discovered to have high distribution ratios in metal extraction [10, 11, 14, 21, 25, 26].

Predominant methods of analyzing the effectiveness of the TRUEX extraction process, conducted with these alternative solvents, has utilized radioactive tracer elements in order to monitor metal distribution ratios between the two phases [19, 20] or expensive analytical techniques such as Inductively Coupled Plasma Atomic Emission Spectroscopy [21]. This analysis is often carried out in the presence of both CMPO and TBP, specifically a solution of 0.2 M CMPO and 1.2 M TBP [9, 19, 20], on the industrial scale. However, the continued roles of CMPO and TBP in these alternative solvents are still of interest and yet to be identified. Therefore, in the current study, they were evaluated individually through an inexpensive, facile electrochemical technique at a micro-interface between two immiscible electrolytic solutions (micro-ITIES). In this initial study, a molecular organic solvent was used with the goal that the thermodynamic data obtained will be used for future comparative research towards IL electrochemical extraction methodologies. It should be noted that common chemical form of uranium found in conventional PUREX or TRUEX processes is uranyl or dioxouranium [6, 7], UO$_2^{2+}$, with uranium in the 6+ oxidation state; this is owing to the dissolution of solid uranium using a 3-6 M nitric acid solution. Therefore the salt, UO$_2$(NO$_3$)$_2$·6H$_2$O, was used in all analysis.

The ITIES, commonly between water and nitrobenzene(NB) [27, 28] (w|NB) or 1,2-dichloroethane (DCE) [27, 29-35] (w|DCE), has been developed as a powerful technique for the evaluation of ion transfer (IT) [34-38] and assisted or facilitated ion transfer (FIT) [28, 30-33, 39-43] using cyclic voltammetry (CV). The simple IT mechanism can be shown through equation 1.4, where metal ion species transfers from
the aqueous phase (w) to the organic phase (o). Complexation of a metal ion, interfacially with ligands in the organic phase lowers the metals Gibbs free energy of transfer, increasing its miscibility towards the organic phase and results in increased partitioning of the ion from w to o; this describes the principle of FIT and is shown in equation 1.6.

The theory of IT across an ITIES has been developed for both IT [34, 35, 44] and FIT [33, 41, 42]. A convenient method of generating and maintaining an ITIES of known dimensions is by micro-ITIES [29, 34, 35, 45, 46]. The interface is often prepared by submerging a pulled borosilicate glass capillary, with an aqueous phase inside, into a vial containing the organic/DCE phase; the interface is held at the tip of the micro-pipette. The micro-ITIES is advantageous since the low current required to perform a CV experiment results in a negligible iR-drop [34] and can employ a simple two-electrode system. The micro-scale of the experiment results in rapid ion transfer generating sensitive kinetic measurements [35] and, in conjunction with the asymmetric diffusion regime – linear diffusion inside the pipette and hemispherical outside, allows for the discrimination of species based on their charge. The methodology for FIT has been developed and experimental data have been accumulated utilizing a large-ITIES [41, 42], which can be used to describe the stoichiometry, the metal to ligand ratio (1:n), and the overall complexation constant, β, of the reaction shown in equation 7.1.2. These can be extrapolated to the micro-ITIES [33], harnessing its sensitivity. The two apparent thermodynamic parameters were quantified with respect to the traditional PUREX and TRUEX ligands, TBP [6, 7, 10, 15] and CMPO [6, 9, 13, 16-20]. However, to the best of my knowledge, this is the first time at a micro-ITIES, that complexes of varying coordination numbers have been resolved simultaneously.

7.1.2 - Experimental

Chemicals. All chemicals were of reagent grade and used as purchased without further purification. Tri-n-butylphosphate (TBP), tetrabutylammonium tetrakis(4-chlorophenyl)borate (TDATPBCl), 1,2-dichloroethane (DCE) (anhydrous), lithium sulphate monohydrate (Li₂SO₄·H₂O), and tetrabutylammonium perchlorate (TBAClO₄) were obtained from Fluka/Sigma-Aldrich Canada Ltd. (Mississauga, ON). Octyl(phenyl)-N,N’-diisobutylcarbamoylmethylphosphine oxide (CMPO) was bought
from Strem Chemicals Inc. (Newburyport, MA). Uranyl nitrate hexahydrate was purchased from Thermo Fisher Scientific Canada (Ottawa, ON); all aqueous solutions were prepared using 18.2 MΩ Milli-Q water.

**Micro-ITIES.** The micro-ITIES experimental setup consisted of a specialized micro-ITIES glass capillary, containing a silver electrode (the working electrode) and the aqueous phase, that was held in a Heka capillary holder (HEKA Electronics, Mahone Bay, NS); and a 4 mL glass vial, which contained the organic phase and a second silver electrode.

The specialized micro-ITIES capillary was fabricated as described in section 2.3.3 and elsewhere [29].

The pipette holder was equipped with a syringe that, under pressure, sustained the aqueous phase and subsequently the liquid-liquid interface at the tip of the glass capillary. The glass capillary was then submerged into the organic (DCE) phase contained in the small glass vial; careful attention was paid to maintaining the aqueous-organic interface at the orifice of the micropipette by means of the attached syringe under monitoring of an optical microscope. A second silver electrode, which served as both the counter and reference electrodes, was then placed in the organic phase. The electrochemical cells for the micro-ITIES are detailed below:

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<td>5 mM UO₂(NO₃)₂·6H₂O (aq)</td>
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<td>5 mM UO₂(NO₃)₂·6H₂O (aq)</td>
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**Instrumentation.** Electrochemical measurements were performed using the Modulab System from Solartron Analytical (Ametek Advanced Measurement Technology,
Farnborough, Hampshire, United Kingdom) equipped with a femto-ammeter and using a feedback control loop.

**Calibration of the Polarizable Potential Window (PPW).** Simple IT of the nitrate anion (NO$_3^-$) was used to calibrate the polarizable potential window (PPW) according to the TATB assumption [47-49], such that the formal IT potential of NO$_3^-$, $\Delta_o^w \Phi_{NO_3}^{\alpha'}$, was taken to be $-0.314$ V [27]. By convention, the transfer of a positively charged species from aqueous to organic generates a positive peak current and the transfer of a negatively charged species generates a negative peak current. The TATB assumption culminating in equation 2.9 [49].

The half-wave potential ($\Delta_o^w \Phi_{1/2}$) of nitrate and the metal ion-ligand complex were obtained by evaluating the limiting current ($i_{ss}$) of the steady state wave and graphing $\Delta_o^w \Phi$ vs log($i_{ss} - i)/i$), as detailed by Bard and Faulkner [50]. $\Delta_o^w \Phi_{M^{2+}}^{\alpha'}$ is the formal IT potential for the metal-ligand complex and $\Delta_o^w \Phi_{M^{2+}}^{\alpha'}$ is the formal IT potential for the free metal species, UO$_2^{2+}$; free UO$_2^{2+}$ IT was taken to be 0.865 V [51].

NO$_3^-$ was used as the internal reference since it is a common counter ion in metal salts [6, 21, 52-54] and, therefore, typically already present. The nitrate concentration should remain relatively consistent throughout as it is housed in the aqueous phase inside the capillary and additions of the ligand were made directly to the DCE phase; this would cause a fluctuation in the concentration of any internal standard applied in that phase that would have to be addressed. Any changes in the concentration of the nitrate species could also be immediately recognized as fundamental to the extraction process and not an error in procedure. The formal IT potential of the nitrate species is highly negative – directly opposite to any assisted-metal transfer potentials – therefore, the nitrate transfer and any FIT were unlikely to interfere with each other or overlap in the CV. Additionally, it is well recognized that NO$_3^-$ participates in the assisted ion transfer of UO$_2^{2+}$ during traditional PUREX and TRUEX industrial applications generating a neutral metal-nitrate species ‘UO$_2$(NO$_3$)$_2$’ [6, 52, 53, 55]. While the participation of nitrate in the complexation reaction is well documented [19], any replacement anion may have unknown or undesirable effects that may not be so easily recognized.
DCE was chosen as the molecular solvent since it has been widely studied in electrochemical solvent extraction systems [30-33, 39-43].

Two considerations must be taken into account concerning electrochemically assisted complexation reactions at the micro-ITIES between w | DCE. First, the partitioning of free metal species into DCE (from w to o) is considered to be negligible except where its transfer limits the PPW and, similarly, the ligand is considered miscible only in the organic phase. The mechanism of metal partitioning is therefore limited to transfer through interfacial complexation (TIC) of the metal with the ligand directly at the interface during the forward reaction and subsequently, during the reverse reaction, transfer through interfacial dissociation (TID). Two other extraction mechanisms have been identified [41, 42] but are not considered: transfer of the metal species into the organic phase followed by organic phase complexation (TOC), and partitioning of the ligand species, o to w, then aqueous complexation followed by transfer (ACT).

Second, diffusion of species in the aqueous and DCE phases is considered equivalent, \( D_{i,w} = D_{i,o} \); where \( D_{i,\alpha} \) is the diffusion coefficient of species \( i \) in phase \( \alpha \). All CVs shown have had their potential scale calibrated according to the \( \text{NO}_3^- \) IT.

7.1.3 - Results and Discussion

7.1.3.1 - Facilitated Ion-Transfer (FIT) of \( \text{UO}_2^2+ \) utilizing TBP

The first ligand to be examined was TBP, using Cell 7.1.1. Typical CVs whilst increasing the ligand concentration are shown in Figure 7.1.1. During this series of CV experiments, the calibrated potential range was set from approximately \(-0.700\) to \(0.800\) V; the range was altered in order to observe a wider potential window and ensure other peaks had not developed at higher (or lower) potentials. The first CV in Figure 7.1.1A is a “blank” showing the system with no ligand present in the organic phase. The blank experiment began by scanning in the forward direction, towards more positive potentials, with the initial potential equal to \(0.000\) V; the initial potential was determined by measuring the open circuit potential before each CV. The limit of the PPW was reached at \(0.650\) V, this limit is defined by the transfer of the supporting electrolytes; specifically, the free metal transfer of \( \text{UO}_2^{2+} \) from w to o and tetrakis(4–chlorophenyl)borate anion (TPBCl) from o to w. The scan direction was then reversed, heading towards more
negative potentials; a peak-shaped wave was observed at $-0.414 \text{ V}$. This peak has been identified as the transfer of nitrate ($\text{NO}_3^-$), by linear diffusion, out of the aqueous phase, housed in the capillary, and into the organic phase (DCE), w to o.

**Figure 7.1.1:** CVs obtained using Cell 7.1.1 and altering the concentrations of the ligand (y), TBP, in the organic phase to 0.0, 36.8, 64.3, 91.9, 110.2, and 128.2 mM for curves A, B, C, D, E, and F, respectively; the scan rate was set at $0.020 \text{ V} \cdot \text{s}^{-1}$, with a calibrated potential range from $-0.750$ to $0.650 \text{ V}$, and an initial potential of $0.0 \text{ V}$.

Subsequently, the lower limit of the PPW was reached at approximately $-0.645 \text{ V}$ and this is defined by the Galvani transfer potential of the hydrophobic, organic supporting electrolyte tetrabutylammonium. The potential was then scanned again in the positive direction until the final potential of $0.000 \text{ V}$ was reached. During this last segment, from $-0.600$ to $0.000 \text{ V}$, a sigmoidal-wave was observed with a half-wave
potential at approximately $-0.314 \text{ V}$. This constitutes the hemispherical diffusion of $\text{NO}_3^-$ towards the interface and transfer across the ITIES, back into the aqueous phase; o to w. The asymmetric diffusion regime described is in agreement with established theory concerning IT at micropipette ITIES [34, 35]. The half-wave potential for nitrate transfer can also be determined using equation 3.4 [50].

In the case of nitrate transfer, the half-wave potential, $\Delta_{w, \text{NO}_3^-}$, was determined to be $-0.371 \text{ V}$. Subsequently, the lower limit of the PPW was reached at approximately $-0.645 \text{ V}$ and this is defined by the Galvani transfer potential of the hydrophobic, organic supporting electrolyte tetradodecylammonium. The potential was then scanned again in the positive direction until the final potential of 0.000 V was reached. During this last segment, from $-0.600$ to 0.000 V, a sigmoidal-wave was observed with a half-wave potential at $-0.314 \text{ V}$. This constitutes the hemispherical diffusion of $\text{NO}_3^-$ towards the interface and transfer, across the ITIES, back into the aqueous phase; o to w. The asymmetric diffusion regime described is in agreement with established theory concerning IT at micropipette ITIES [34, 35]. Considering the correction factor of 50 mV [29], the two half-wave potential values determined above are in good agreement.

Figure 7.1.1B depicts the electrochemical behaviour of the system with 36.8 mM of TBP in the DCE phase. During the initial forward scan, from 0.000 to 0.733 V, a positive peak-shaped wave is observed at 0.588 V; this positive peak current was significant since it indicates the transfer of a positive ionic species. Subsequently, the potential was scanned from 0.733 to $-0.614 \text{ V}$ with a sigmoidal half-wave and negative peak-shaped wave potential obtained at 0.493 and $-0.407 \text{ V}$, respectively. The sigmoidal-wave is indicative of the hemispherical diffusion and transfer of a cation across the interface from o to w, whilst the negative peak current indicates the continued presence of $\text{NO}_3^-$ and its transfer from w to o. The final portion of the CV, scanned from $-0.614$ to 0.000 V, again showing the steady state current and hemispherical IT of the nitrate anion from o to w.

Interestingly, with increasing concentrations of the ligand in the organic phase the peak, originally observed at 0.588 V, shifts to more negative potentials. Figures 7.1.1 C to F illustrate the system as the concentration of the ligand was increased further from 64.3 to 91.9, 110.2, and 128.2 mM with shifts in potential of 0.493, 0.458, 0.437, and
0.417 for curves C, D, E, and F, respectively. This shift in potential is indicative of FIT [33, 41, 42]. Since uranyl was the only free metal cationic species in solution, according to Cell 7.1.1, and only the concentration of TBP was being altered, it was therefore concluded that the positive peak current obtained in Figure 7.1.1B to F is the result of assisted ion transfer of uranyl ions through a TIC mechanism with TBP acting as the ligand. With increasing ligand concentration the half-wave potential of the hemispherical steady state curve decreases, analogous to the positive peak current, from 0.493 to 0.392, 0.364, 0.338, and 0.320 V, respectively, for curves B, C, D, E, and F in Figure 7.1.1.

At higher ligand concentrations (curves C to F in Figure 7.1.1), the positive peak current resolved into two distinct peaks (labelled peak 1 and 2), which show the same movement as the steady state wave towards more negative potentials as the ligand concentration increases. The two peaks could be attributed to two different stoichiometries for the interfacial complexation reactions assisted by the Galvani potential difference. The presence of multiple metal ion-ligand stoichiometric peaks agrees well with the work of Homolka and Wendt [28]. It was therefore deemed prudent to evaluate these features individually. $\Delta^o_{\phi_{1/2}}$ was approximated using the potential at the peak current, $\Delta^o_{\phi_p}$, through equation 3.4 [50]. Therefore, analysis of $\text{UO}_2^{2+}$ FIT by TBP was carried out on the CVs two peak currents.

As the ligand concentration was increased, the assisted ion transfer of metal species became more facile and the $iL_n^{z+}$ peak moved to more negative potentials. It has been shown that a cation with hydrophilic character will have higher (or more positive) IT potentials, whilst a hydrophilic anion will demonstrate the opposite; i.e. lower (or more negative) potentials [38]. While increasing the concentration of the ligand it became easier to transfer the metal ion species and the IT potential for the cation decreased. By examination of this trend, and using equation 6.1.2 developed by Girault et al. [42], the metal ion to ligand stoichiometry ($1:n$) and the overall complexation constant ($\beta$) can be inferred.

Therefore, using equation 6.1.2, a linear relationship of $-\frac{zF}{RT} (\Delta^o_{\phi_{1/2}} - \Delta^o_{\phi_p'})$ vs. $\ln[c^*_{\text{TBP,o}}]$ was developed utilizing the data obtained from the series of CV experiments on Cell 7.1.1. To ensure accurate results, four CVs were taken at each concentration
interval; the full concentration range tested was from 18.3 to 137.9 mM. After careful analysis it was decided to reject the first scan as it provided inconsistent peak current results that were not comparable between ligand concentration steps; however, subsequent scans showed excellent agreement. A linear fit of these data was used to evaluate the metal ion to ligand ratio (1:n) and the complexation constant (β) through the slope and y-intercept of the line, respectively. Figure 7.1.2 illustrates the linear fitting data analysis of TBP-assisted metal IT of the uranyl ion based on the two peak-shaped waves. The data garnered through this analysis are summarized in Table 1 which includes the R², z_{eff} (effective charge of the metal transferred), n, and β values.

![Figure 7.1.1](image)

**Figure 7.1.1.** ln[\( c^{*}_{\text{TBP,o}} \)] vs. \(-zF/(RT)(\Delta^{w}\phi_{L_n}^{o} - \Delta^{w}\phi_{I}^{o})\) for the two curve features found in Figure 7.1.1.

The multiple stoichiometries analyzed using peaks 1 and 2 are shown in Figure 7.1.2 and possess a very good linear relationship to the increasing ligand concentration; \( R^2 \) equal to 0.9728 and 0.9778, respectively. These data indicate a metal ion to ligand stoichiometry of approximately 1:3 and 1:4 whilst the complexation constants are \( 3.2 \times 10^{11} \) and \( 2.0 \times 10^{13} \) for peak 1 and 2, respectively; both species were evaluated with an effective charge of 1+. Peak 2 is the most negatively shifted peak, indicating the ligand assisted metal transfer is more facile than that of peak 1 and this is consistent with the
high ligand association and complexation constant observed. The more ligands coordinated to the metal center, the higher the complexation constant and, therefore, the more easily the metal ion will transfer.

Table 7.1.1. Results of the linear curve fittings shown in Figure 7.1.2 and using equation 7.1.5; details the effective charge used ($z_{\text{eff}}$), stoichiometry ($n$), and complexation constant ($\beta$) for the three curve features: peak 1, and peak 2.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Curve Feature</th>
<th>$R^2$</th>
<th>$z_{\text{eff}}$</th>
<th>$n$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td>peak 1</td>
<td>0.9728</td>
<td>1</td>
<td>3</td>
<td>$3.2 \times 10^{11}$</td>
</tr>
<tr>
<td></td>
<td>peak 2</td>
<td>0.9778</td>
<td>1</td>
<td>4</td>
<td>$2.0 \times 10^{12}$</td>
</tr>
</tbody>
</table>

The study by Homolka and Wendt [28] appeared in 1985 and their analysis was performed at a large-ITIES without the benefit of modern FIT theory [41, 42]. In their report [28] they assumed a static formal IT potential for each metal to ligand stoichiometry and that increasing the ligand concentration leads to an increase in the peak current response. Presently it has been shown that this is not the case and, using uranium as an example, when the ligand is in excess the peak current is static and the potential shifts towards more positive potentials with increasing ligand concentration [41, 42, 45]. The analyses by Dassie et al. [56] and Kakiuchi et al. [45] were hampered by the fact that the two peaks they observed for the FIT of cesium with dibenzo-18-crown-6 were poorly resolved; however, computational curve fitting and novel simulation analysis overlaid on the experimental results allowed them to elucidate the stoichiometric ratios, complexation constants and, thus, the mechanism of the reactions. What appears herein for the first time is the thermodynamic quantification of multiple, resolved FIT peaks at the micro-ITIES and using modern FIT theory [41, 42].

Moving forward, the data for the two peaks were also evaluated using an effective charge of 2+ (data not shown), as is present in freely solvated uranyl ions, and leads to a ligand stoichiometry of 8. It may be possible for 8 TBP molecules to surround a single dioxouranuim cation; however, it was proposed that a single nitrate species participating in the complexation would reduce the net charge of the metal-ligand complex to 1+ and
provide a sustainable metal ion:TBP ratio of 1:4. Qualitative examination of the NO₃⁻ IT peak reveals a slight drop in peak current intensity between the blank curve and the curves obtained after TBP was added. This drop in peak current is most likely indicative of a drop in the concentration of NO₃⁻ available for transfer and could be the result of two phenomena.

First, because the FIT portion of the CV was scanned initially, the proposed uranyl-nitrato-TBP complex is initially transferred to the organic phase and then, on the reverse scan, transfers back to the aqueous phase. It follows that the system is most likely quasi-reversible and some complexed ions will be lost to the organic phase thus reducing the nitrate concentration available for simple IT.

Secondly, the structure of the liquid-liquid interface has been proposed to consist of a compact inner layer with bracketing diffuse layers [57-60] and has been evaluated using a model similar to the Gouy-Chapman theory for the metal-liquid interface. A measure of controversy remains concerning the, as yet to be defined, final structure of the ITIES; however all theories agree on the importance of adsorbed species at the interface as well as ion-ion interactions [57-60]. These adsorbed species would provide a mechanism whereby a completely hydrated uranyl-ion may have its hydration sphere penetrated by a nitrate anion, thereby one water molecule is replaced, and the amount of nitrate available for IT is reduced. Additionally, nitrate participation in the extraction process is in agreement with the neutral metal-nitrato species observed in the conventional PUREX/TRUEX processes [52, 53] and is a fundamental requirement of these extraction procedures.

The maximum coordination number to the uranium (U) metal center (including the two oxygen species), has been described to be 14 [61]. Since uranium is such a large atom, the predominate force limiting this number is the steric hinderance between ligands. The formation of UO₂NO₃TBPₙ complexes with n = 3 and 4 provide a total coordination number of 7 and 8 with nitrate acting as a bidentate ligand; the proposed structure, with n = 4 TBP ligands, is shown in Figure 7.1.3A. The formation of UO₂ complexes with TBP of the form UO₂(NO₃)₂(TBP)₂ have long been identified [52, 53, 62] and UO₂ complexes with a high number of large organo-phosphorous complexing agents have also been demonstrated recently [63, 64]. Powell et al. [64] in their study of the radiolytic
breakdown of TBP to dibutyl phosphoric acid (HDBP) in the storage tanks of UO₂ fuel recovered using the PUREX process, reported the formation of UO₂(NO₃)ₙ(HDBP)ₙ with a NO₃⁻/UO₂²⁺ ratio (m) of 0.9 and a HDBP/UO₂²⁺ ratio (n) of 3.7, at high nitrate concentrations; this is evidence towards the viability of the UO₂-TBP proposed structures, as shown in Figure 7.1.3A and 7.1.3B.

The proposed structures shown on Figure 7.1.3A and 7.1.3B illustrate hexagonal bipyramidal and pentagonal bipyramidal geometries for $n = 4$ and $n = 3$, respectively.

![Figure 7.1.2](image_url)

**Figure 7.1.2**: Proposed structures of **A**: UO₂NO₃TBP⁴⁺ and **B**: UO₂NO₃TBP³⁺; for simplicity, solvent molecules have been neglected.

7.1.3.2 - *Evaluation of Uranyl Facilitated Ion Transfer using CMPO*

Having quantified the FIT of the uranyl ion with TBP, attentions were turned to CMPO, the primary ligand of the TRUEX process. Figure 7.1.4 illustrates experimental progression of increasing CMPO concentration and its effect on the $ML_n^{2+}$ peak using Cell 7.1.2. The initial, calibrated potential was set equal to $-0.050$ V and the upper and lower calibrated potential range was approximately $0.750$ and $-0.570$ V. The blank CV, with no ligand added to the organic phase, is shown in Figure 7.1.4A and shows that no FIT is present during the forward scan, from $0.0$ V to $0.600$ V, within the PPW.
Figure 7.1.3. CMPO CV experiments utilizing Cell 7.1.2 with increasing CMPO concentration, 0.0, 9.5, 15.3, 22.7, and 31.1 for curves A, B, C, D, and E respectively; the initial potential was equal to −0.050 V, the upper and lower limits of the calibrated potential range were approximately 0.650 and −0.600 V respectively, with \( v = 0.020 \text{ V} \cdot \text{s}^{-1} \).

During the backward scan, the linear diffusion of nitrate in the aqueous phase and transfer into the organic phase was observed at −0.414 V as a peak-shaped wave. After the lower switching potential was reached, the CV was swept again in the forward direction, from −0.570 to −0.050 V, the steady state current with a half-wave potential at −0.314 V was observed and this was indicative of hemispherical diffusion of the nitrate species in the organic phase and transfer back across the interface from o to w. After addition of CMPO, the FIT can be observed during the forward scan; however, three
distinct peak currents can readily be distinguished. Just as in the case of TBP, the CMPO peak potentials were evaluated using equation 7.1.5. No singularly distinct steady state wave could be described and, therefore, could not be evaluated.

The metal:ligand stoichiometry and complexation constant evaluated for the three peaks have been plotted in Figure 7.1.5A and 7.1.5B, indicating values of \( n \) equal to 2, 3, and 5 with \( \beta \) values of \( 8.0 \times 10^{11} \), \( 8.8 \times 10^{14} \), and \( 6.5 \times 10^{32} \) for peaks 1, 2, and 3, respectively; these results have been summarized in Table 7.1.2. As in the case of TBP, the effective charge of the metal ion transferred was considered to be 1+ with a nitrate molecule participating in the FIT for all cases except peak 3, which used the full 2+ charge. Considering a full charge of 2+ on the uranyl ion leads to a metal ion:ligand stoichiometry of 1:4 and 1:6 for peaks 1 and 2, respectively.

Figure 7.1.4: \( \ln[c_{CMPO, \text{initial}}] \) vs. \( -\frac{zF/(RT)(\Delta_{o}^{\omega} \phi_{o}^{\omega} - \Delta_{o}^{\omega} \phi_{M^{2+}}^{\omega})}{N} \) for the three curve features found in Figure 7.1.4: A peak 3 (\( \Delta \)); B peak 1 (\( \bigcirc \)) and peak 2 (\( \square \)).
Table 7.1.2: Results of the linear curve fittings shown in Figure 7.1.5 and using equation 7.1.5; details the effective charge used ($z_{eff}$), stoichiometry (n), and complexation constant ($\beta$) for the three curve features: peak 1, peak 2, and peak 3.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Curve Feature</th>
<th>$R^2$</th>
<th>$z_{eff}$</th>
<th>n</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMPO</td>
<td>peak 1</td>
<td>0.9593</td>
<td>1</td>
<td>2</td>
<td>$8.0 \times 10^{11}$</td>
</tr>
<tr>
<td></td>
<td>peak 2</td>
<td>0.9912</td>
<td>1</td>
<td>3</td>
<td>$8.8 \times 10^{14}$</td>
</tr>
<tr>
<td></td>
<td>peak 3</td>
<td>0.9586</td>
<td>2</td>
<td>5</td>
<td>$6.2 \times 10^{32}$</td>
</tr>
</tbody>
</table>

Interestingly, the size of the nitrate peak after addition of the ligand undergoes a dramatic change from 11.1 to 6.1 nA, which indicates a large change in the apparent nitrate concentration. This drastic change may indicate that CMPO FIT is transitioning from a quasi-reversible reaction to an irreversible one and also lends further evidence to the proposed interaction of nitrate in the complexation reaction of CMPO.

The $\beta$ values and ligand stoichiometry are consistent with the peak positions. The potential at peak 1 is more positive than peak 2 and, hence, demonstrates a lower solubility consistent with fewer ligands coordinated to the metal center; the stoichiometry is also consistent with the calculated $\beta$ values, that is $\beta$ is proportional to the ligand stoichiometry following the trend: $\beta_{\text{peak 1, } n=2} < \beta_{\text{peak 2, } n=3} < \beta_{\text{peak 3, } n=5}$.

Figure 7.1.5: Proposed structure for one of the observed UO$_2$-CMPO complex; [UO$_2$NO$_3$CMPO$_3$]$^+$. 
The proposed structure of \(\text{[UO}_2\text{NO}_3\text{CMPO}_3]^+\), shown in Figure 7.1.6, is consistent with the hexagonal bipyramidal geometry reported by Rogers et al. [13] for bidentate CMPO in the \(\text{UO}_2(\text{NO}_3)_2\text{CMPO}_2\) complex. The coordination number for \(\text{[UO}_2\text{NO}_3\text{CMPO}_n]^+\) is 8 and 10 for \(n\) equal to 2 and 3, respectively; CMPO is proposed to be bidentate. For \(n\) equal to 5 and 10 with all ligands considered monodentate, the total coordination numbers for these two complexes are 6 and 11. It has been shown that the most likely extraction route of lanthanides and trivalent actinides using CMPO is thought to occur (using Am\(^{3+}\) as an example) via [9, 19]:

\[
\text{Am}^{3+}_\text{(aq)} + 3\text{NO}^-_\text{(aq)} + 3\text{CMPO}_\text{(org)} \rightleftharpoons \text{O}_3\text{CMPO}_3\text{(org)}
\]  

(7.1.1)

It is reasonable to conclude, therefore, that steric hindrance in the formation of \(\text{[UO}_2\text{NO}_3\text{CMPO}_3]^+\) is not prohibitive and even \(\text{[UO}_2\text{CMPO}_5]^{2+}\) and \(\text{[UO}_2\text{NO}_3\text{CMPO}_{10}]^+\) are possible, although most likely small, contributors.

### 7.1.4 - Conclusions

To the best of my knowledge, the simultaneous evaluation of distinct complexation steps using modern FIT theory [42, 65] in an electrochemical micro-ITIES experiment was quantified, herein, for the first time.

When comparing these two ligands the stoichiometry can be useful, however, the strength of this technique [42] is the quantitative evaluation of the complexation constant, \(\beta\), which, together with the concentration range, garners a more holistic chemical description of FIT. CMPO demonstrated three complexation constants equal to \(5.7 \times 10^{11}\), \(9.0 \times 10^{14}\), and \(1.77 \times 10^{34}\) for \(n\) equal to 2, 3, and 5, respectively, whilst TBP showed \(\beta = 6.8 \times 10^{11}\) and \(2.0 \times 10^{13}\) for \(n\) equal to 3 and 4 for the peak potentials and \(\beta = 2.00 \times 10^{12}\) for \(n = 4\) calculated using the sigmoidal return wave. That the counter ion nitrate participates within the complex will be confirmed by future, tandem spectroscopic-electrochemical analysis.

These results indicate that CMPO and TBP have similar complexation strengths since both show similar complexation constants for \(n = 2\). While the mutual strength of CMPO and TBP have long been established [17, 18, 20, 66-68] this technique has the
potential to evaluate these and other ligands for lanthanide and actinide separations across a range of alternative solvents including room ILs [13, 14, 23, 24].

7.1.5 - References


Chapter 7.2 - Interfacial complexation reactions of Sr$^{2+}$ with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide for understanding its extraction in reprocessing spent nuclear fuels

7.2.1 - Introduction

The use of radiological isotopes, including $^{131}$I, $^{99}$Mo, and $^{90}$Y, for medical imaging and the treatment of cancers has undergone a rapid change in the last two decades with the advent of radioimmunological treatment (RIT) and the incorporation of radioisotopes within monoclonal antibodies (mAb) [1-6]. RIT uses the high specificity of mAbs in conjunction with powerful $\beta$-emitters to target solid tumours, but reduces the radiological toxicity to other organs and tissue [3, 6, 7]. The most effective isotope for use in RIT is $^{90}$Y; since the half-life time of the $^{90}$Y is short (64 h), it produces only $\beta$ with no $\gamma$-emissions, and the energy of these emissions are high (2.2 MeV) resulting in increased penetration into the tumour mass [3]. The $^{90}$Y isotope can be acquired through neutron-irradiation of yttrium metal oxide [8] or through the isotopic decay of $^{90}$Sr [9-11]. Owing to its short half-life and the expense of transporting radioactive material, an in-house $^{90}$Y generator is deemed preferable with several designs having been proposed to use $^{90}$Sr as a perpetual feed stock [9-11]. $^{90}$Sr can, in turn, be acquired during nuclear fuel reprocessing since it is one of many uranium fission byproducts from nuclear power facilities [8, 12].

Several nuclear fuel reprocessing [12, 13] technologies are currently being implemented around the world on an industrial and laboratory scale, including the TRUEX, or transuranic extraction, process [8, 14-22]. This method uses octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide (CMPO), as a chelating agent, in a biphasic solvent extraction procedure between water and an organic solvent, typically n-dodecane [8, 14-22]; this process can be summarized through the following:

$$\text{Sr}^{2+}_{(aq)} + 2\text{NO}_3^{-}_{(aq)} + 2\text{CMPO}_{(org)} \rightleftharpoons \text{Sr(NO}_3)_{2}\text{CMPO}_{2_{(org)}} \quad (7.2.1)$$

However, the stoichiometry is not clear.

Prompted by the pioneering work of Dai et al. [23], recent research towards improving the TRUEX process [13, 15, 16, 22] and other metal extraction techniques [24-26] has focused on replacing the organic solvent with a room temperature ionic liquid.
ILs are organic salts with a melting point below 100°C. In their paper, Dai et al. [23] showed a 5000× greater distribution ratio for a strontium-dicyclohexyl-18-crown-6 complex using an imidazolium-based IL versus a conventional molecular solvent. Beyond this, ILs also have several properties that make them amiable replacements for organic solvents, including low volatility, good electrical conductivity, and the ability to tailor the IL to meet specific physicochemical requirements [27]. The techniques used to quantify the distribution ratios between phases have focused on ICP-AES measurements of the aqueous phase after extraction [14, 23, 28], extended X-ray fine structure (EXAFS) measurements [15], or through the use of radioactive tracer isotopes [16, 18].

Interestingly, an electrochemical technique employed at the liquid|liquid interface between two immiscible electrolytic solutions (ITIES), typically between water and 1,2-dichloroethane (DCE), is able to acquire sensitive thermodynamic data that can be used to further characterize the metal-ligand extraction process [29-38]. Electrochemistry at a liquid|liquid junction has been the subject of numerous excellent reviews [39-42] and often involves simple ion transfer (IT) through a push/pull mechanism, whereby the potential is increased linearly within the aqueous phase (w) causing any positive metal ions (i), with charge z, to be ejected into the organic phase (o); this process is summarized in equation 1.4.

When the potential scan is reversed, or proceeds towards negative potentials, the ions are “pulled” back across the ITIES or transferred from o to w. The current can be measured during this process and the current-potential curve obtained is analogous to that obtained in conventional redox electrochemistry. The potential at which IT takes place is called the standard transfer potential and is denoted as $\Delta_0\phi^0$; this, in turn, is related to the potential and the activity of species i in each phase through the Nernst equation, equation 6.1.1.

If the metal species is very hydrophilic then this will result in a high formal IT potential and thus a greater amount of applied potential required. However, the transfer potential can be reduced through the use of organic ligands and the transfer through interfacial complexation (TIC), which can be generalized by equation 1.6. Equation 1.6 is the electrochemical equivalent of equation 7.2.1 when $L = \text{CMPO}$ and $i = \text{Sr}^{2+}$. This type of electrochemical reaction is referred to as facilitated ion transfer (FIT), and the
thermodynamics have been thoroughly described by Homolka et al. [43], Kakiuchi et al. [34], and Girault et al. [35, 36]. In this context, the stoichiometry, \( n \), and complexation constant, \( \beta \), for equation 1.6 can be discerned through the use of cyclic voltammetry (CV). Additionally, it has been discovered that sensitive data, without the use of \( iR \) compensation, can be obtained using micro-ITIES typically held at the tip of a pulled micropipette [24, 25, 31, 32, 38, 44, 45], while also reducing the amount of sample required.

Mirroring the developments in solvent extraction research, recent work surrounding liquid|liquid electrochemistry has focused on the aqueous|IL (w|IL) interface [24-26, 38, 44, 46-48], such that IT and FIT have both been observed.

Thus, using the theory of FIT [34-36, 43], described herein is the thermodynamics of strontium transfer through the use of CMPO at the w|DCE and w|IL micro-ITIES. In order to verify the ligand stoichiometries, Biphasic Electrospray Ionization Mass Spectrometry (BESI-MS) and conventional Electrospray Ionization Mass Spectrometry (ESI-MS) have also been employed.

7.2.2 - Experimental

7.2.2.1 - Chemicals
Strontium nitrate (Sr(NO\(_3\))\(_2\)), dichloromethane, tetradecylammonium tetrakis(4-chlorophenyl)borate (TDATPBCl), and 1,2-dichloroethane were purchased from Sigma-Aldrich Canada Ltd. (Oakville, ON). Octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO) and trihexyltetradecylphosphonium chloride were obtained from Strem Chemicals Inc. (Newsburyport, MA). Potassium tetrakis(pentafluorophenyl)borate was bought from Boulder Scientific (Boulder Scientific Co., Longmont, CO). Trihexyltetradecylphosphonium tetrakis(pentafluorophenyl)borate was prepared through a facile metathesis reaction of the their constituent chloride and potassium salts, respectively at a 1:1 ratio in a solution of dichloromethane as described elsewhere [44].

7.2.2.2 - Micropipettes
The interface between two immiscible electrolytic solutions (ITIES) was maintained at the tip orifice of a specially fabricated borosilicate glass capillary (Figure 7.2.1). The capillary fabrication procedure is described in section 2.3.3 and elsewhere [38, 44, 45].
Figure 7.2.1: Modified HEKA capillary holder with pulled capillary containing the aqueous phase and a silver electrode attached to the WE lead of the potentiostat through a BNC connector. The capillary is immersed into the DCE or IL phase held in a 1.8 mL glass vial, which also contains a silver electrode connected to the RE/CE leads of the potentiostat.

The prepared capillary was held in a capillary holder (HEKA Electronics, Mahone Bay, NS), specially modified by the Electronics Shop at the University of Western Ontario, and equipped with a syringe, which was used to maintain the aqueous phase at the tip of the capillary; a Moticam 2000 CCD camera (Motic, Richmond, BC) attached to a Navitar 12× magnification lens assembly (Navitar, Rochester, N.Y.) was used to monitor the interface. The holder also possessed an integrated silver wire attached to a BNC connector connected to the working electrode lead of the potentiostat. A second silver wire, placed in the DCE or IL phase, was connected to the counter and reference leads of the potentiostat. These silver wires functioned as quasi-reference electrodes.
The assembled micro-ITIES apparatus is shown in Figure 7.2.1. The following electrochemical cells were used:

<table>
<thead>
<tr>
<th></th>
<th>AgNO₃</th>
<th>6 mM Sr(NO₃)₂ (aq)</th>
<th>y mM CMPO (DCE)</th>
<th>5 mM TDATPBCl (DCE)</th>
<th>AgTB</th>
<th>Ag</th>
</tr>
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<tr>
<td>(Cell 7.2.1)</td>
<td></td>
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<table>
<thead>
<tr>
<th></th>
<th>AgNO₃</th>
<th>2 mM Sr(NO₃)₂ (aq)</th>
<th>y mM CMPO (P₆₆₆₁₄TB)</th>
<th>AgTB</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cell 7.2.2)</td>
<td></td>
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<table>
<thead>
<tr>
<th></th>
<th>AgNO₃</th>
<th>2 mM TMANO₃ (aq)</th>
<th>neat (P₆₆₆₁₄TB)</th>
<th>AgTB</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cell 7.2.3)</td>
<td></td>
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</table>

7.2.2.3 - Electrochemistry
All electrochemical experiments were performed using the Modulab potentiostat system (Ametek Advanced Measurement Technology, Farnborough, Hampshire, United Kingdom) equipped with a femto-ammeter. The vial containing the DCE or IL phase was placed in a vial holder with a jacket for flow of temperature-controlled water to/from a heating circulator (VWR, Mississauga, ON), which maintained the system at 25 and 60 ± 1°C for DCE and IL experiments, respectively, unless otherwise stated.

7.2.2.4 - Biphasic Electrospary Ionization Mass Spectrometry (BESI-MS)
The mass spectrometric interface for the measurement of the complexes has been described in previous reports [49-53]. In brief, a LTQ (velos) linear ion trap mass spectrometer (Thermo Fisher Scientific, San Jose, CA), operating in the positive ionization mode, was used with a fabricated polyimide (PI) dual-sprayer microchip (DiagnoSwiss SA, Monthey, Switzerland) fixed on a plate mounted opposite to the spray cone intake; this assembly was situated in place of the commercial ion source housing as shown in Figure 7.2.2. The aqueous and 1,2-dichloroethane (DCE) phase was infused separately through two ports in the microchip, which was held inside a microchip-holder, fabricated in-house. Two syringes (100 μL, Hamilton Co., Reno, NV) held by syringe pumps (KdScientific, Holliston, MA) regulated the flow rate of each line at 2 μL-min⁻¹;
thus the final flow rate at the electrospray was 4 μL·min⁻¹. These two immiscible phases, in separate micro-channels (125 μm × 50 μm × ~1.5 cm each), were mixed immediately after ejection, inside the Taylor cone (the ionized aerosol jet or plume), during electrospray. The tip of the dual sprayer microchip is displayed in the image at the bottom of Figure 7.2.2, which was obtained using a VK-8710 color 3D laser scanning microscope (Keyence Corp., Japan). For operation, after MS power supply onset (U = 4 - 4.5 kV), the microchip was moved close to the entrance of MS (the use of high voltage should be handled under extreme caution). The current, set between 20 and 200 nA, by adjusting the distance between the dual-spray emitter and the entrance to the MS, was monitored by a custom-made nano-ammeter. The temperature of the transfer capillary was set at 200°C. The ion optics parameters were kept constant for each experiment.

Figure 7.2.2: Picture of the BESI-MS set-up with the microchip assembly (top left) and the LCT intake (top right). (Bottom) Front view of the microchip ejection ports under a microscope.

7.2.2.5 - Electro-Spray Ionization-Time of Flight Mass Spectrometry (ESI-MS).
Conventional ESI-MS data, was collected using a Micromass LCT Mass Spectrometer (Waters, Milford, MA) in the positive ion mode. The capillary, sample cone, and extraction cone voltages were 5000, 50, and 15 V, respectively, while the acquisition and interscan delay time were set to 4.0 and 0.1 s. A 250 μL syringe (Hamilton Co.), placed inside a syringe pump operating at 10 μL·min⁻¹, was used to perform these injections.
7.2.3 - Results and Discussion

7.2.3.1 - Facilitated Ion Transfer (FIT) of Sr$^{2+}$ at the w|DCE micro-ITIES

Figure 7.2.3: Cyclic voltammograms of (A) Cell 7.2.1 at a scan rate of 0.020 V·s$^{-1}$ in which the two sections were scanned with initial, upper, and lower potentials of 0.271, 0.718, and −0.139 V for the first section and −0.086, −0.086, and −0.402 V for the second section, respectively; and (B) Cell 7.2.2 (solid trace) with an initial potential of −0.106 V, a scan rate of 0.020 V·s$^{-1}$, and a potential range of 0.442 to −0.283 V, and Cell 7.2.3 (dashed curve) having an initial, upper, and lower potential of 0.131, 0.427, and −0.270 V at a scan rate of 0.020 V·s$^{-1}$.

Figure 7.2.3A shows the CV obtained at the w|DCE interface using Cell 7.2.1, with no CMPO present and at a scan rate of 0.020 V·s$^{-1}$. The CV was acquired in two sections. In the first section, the cell was initially scanned in the positive direction from 0.271 V. At 0.718 V the limit of the polarizable potential window is reached and is marked by the sudden increase in current brought about by the transfer of the supporting...
electrolytes; in this instance both Sr$^{2+}$, transfer from w to o, and tetrakis(parachlorophenyl)borate (TPBCl$^-$), transfer from o to w are possible. The potential was then scanned in the reverse direction, towards more negative potentials, from 0.718 to −0.139 V. Finally the potential was scanned in the forward direction again from −0.139 to 0.271 V. The latter two scan segments show no distinct features indicating that no detectable adsorption or ion transfer (IT).

Cell 7.2.1 was then scanned from −0.086 V towards more negative potentials, until −0.402 V, in the second section. A wave can be observed with a peak potential at −0.342 V and this is indicative of nitrate transfer, from w to o. The potential was then scanned towards more positive potentials, from −0.402 to −0.086 V, and a sigmoidal or “s” shaped wave can be observed with a steady state current from −0.086 V; this is indicative of nitrate transfer back across the ITIES, from o to w. The IT and current response are in good agreement with established IT voltammetry at a micro-ITIES hosted by a pipette [31, 32, 38]. The CV was broken down into the two sections in order to limit the number of ions transferring, thus fostering a greater interface stability and improved reproducibility. This is not so integral in the case of Cell 7.2.1, i.e. in the absence of CMPO, but becomes so after its introduction to the system.

Figure 7.2.4A illustrates the CV obtained with the addition of 33 mM CMPO to the DCE phase. Analogous to the blank experiment, the CV was split into two regions. The first scan was initiated at a calibrated potential of −0.100 V in the forward direction towards more positive potentials until the switching potential at 0.500 V was reached. During this first segment, two peaks can be observed with current maxima at 0.266 and 0.410 V; these are indicative of the ion transfers through interfacial complexation of Sr$^{2+}$ from the aqueous to organic phase assisted by CMPO. As the potential was scanned from 0.500 to −0.100 V, two sigmoidal shaped waves can be observed with half-wave potentials at approximately 0.166 and 0.369 V; this is indicative of the transfer of metal ions through interfacial decomplexation (TID) reactions at the ITIES. Similar to the blank curve in Figure 7.2.3A, the IT of nitrate was then observed while scanning the potential from −0.086 to −0.402 V and back. All CVs acquired at the w|DCE interface were calibrated using NO$_3^−$ formal transfer potential, $\Delta_0^\alpha\Phi_{NO_3}^\circ$ as −0.314 V [33]. based on the TATB [29, 39] assumption.
Figure 7.2.4: Using instrument parameters similar to those described for Figure 7.2.3A and using Cell 7.2.1 with [CMPO] equal to 33, 65, 82, 106, and 142 mM for curves A, B, C, D, and E, respectively.

As the concentration of CMPO was increased in the DCE phase from the 33 mM, shown in Figure 7.2.4A, to 65, 82, 106, and 142 mM in Figures 7.2.4B, C, D, and E, respectively, the peak potentials of the multiple peaks shift towards less positive potentials such that peak 1 becomes 0.388, 0.378, 0.374, and 0.374 V, respectively. The shift in peak 2 is more dramatic eliciting changes of 0.266 to 0.248, 0.237, 0.231, and 0.206 V for curves A, B, C, D, and E in Figure 7.2.4, respectively. Shifting peak potentials with increasing ligand concentration is in good agreement with established
theory concerning FIT [34-36]. The potential shift of the two peaks shown in Figure 7.2.4 were examined individually using the theory of FIT described by Girault et al. [35] such that the stoichiometry, \( n \), and overall complexation constant, \( \beta \), are related to the initial ligand concentration, \( c^*_{i,o} \), in the organic phase through equation 6.1.2.

The formal IT potential of strontium, \( \Delta_o^{w} \phi_{\text{Sr}^{2+}}^{o} \), was taken to be 0.900 V [54]; this was determined using a microhole experiment described recently [54, 55]. \( \Delta_n^{w} \phi_{\text{L}^{n+}}^{o} \) is the formal IT potential of the metal ion-ligand complex, at a given ligand concentration, and was considered equivalent to the calibrated half-wave potential of the metal ion-ligand complex, \( \Delta_o^{w} \phi_{1/2,\text{L}^{n+}}^{o} \). The half-wave potential was obtained from the CVs shown in Figure 7.2.4 using their peak potentials, \( \Delta_o^{w} \phi_{\rho}^{o} \), and equation 3.4 [56]. The final term in equation 6.1.2, \( \xi \), is equal to the square root of the ratio of diffusion coefficients between each phase, \( \xi = \sqrt{D_o / D_w} \) [35, 36]. In the case of the w|DCE interface and for the purposes of simplification, the diffusion coefficients for each phase were considered equivalent and thus, \( \xi = 1 \), and the final term in equation 6.1.2 reduces to zero. In this way the change in potential versus the change in ligand concentration can be plotted as a linear relationship with the slope and y-intercept providing the stoichiometry and complexation constant of the interfacial complexation reaction. Figure 7.2.5 shows the linear graphs of \(-z_iF / (RT)(\Delta_o^{w} \phi_{\text{L}^{n+}}^{o} - \Delta_o^{w} \phi_{\rho}^{o}) \) versus \( \ln(c^*_{i,o}) \) while Table 7.2.1 summarizes the data obtained after linear regression analysis.

**Figure 7.2.5:** Plot of \(-z_iF / (RT)(\Delta_o^{w} \phi_{\text{L}^{n+}}^{o} - \Delta_o^{w} \phi_{\rho}^{o}) \) versus \( \ln(c^*_{i,o}) \) with data obtained from the curves shown in Figure 7.2.4.
Table 7.2.1. Thermodynamic data obtained from the linear fitting generated in Figure 7.2.4 for peaks 1 and 2, including the metal to ligand ratio (1:n), the overall complexation constant, $\beta$. The success of the linear fitting was described using the $R^2$ value as shown.

<table>
<thead>
<tr>
<th>Curve Feature</th>
<th>$n$</th>
<th>$\beta$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>2</td>
<td>$4.5 \times 10^{19}$</td>
<td>0.9615</td>
</tr>
<tr>
<td>Peak 2</td>
<td>3</td>
<td>$5.5 \times 10^{25}$</td>
<td>0.9647</td>
</tr>
</tbody>
</table>

The $R^2$ values shown in Table 1, 0.9615 and 0.9674 for peaks 1 and 2, respectively, illustrate the good linear fitting obtained. The stoichiometry for peaks 1 and 2 were determined to be 2 and 3 whilst the complexation constants were $4.5 \times 10^{19}$ and $5.5 \times 10^{25}$, respectively. The two electrochemically induced complexation reactions can be described for peaks 1 and 2 using equations 7.2.2 and 7.2.3, respectively:

$$\text{Sr}^{2+}_{(aq)} + 2\text{CMPO}_{(org)} + 2\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{PO}_2\cdot 2\text{H}_2\text{O}^{2+}_{(org)}$$  \hfill (7.2.2)

$$\text{Sr}^{2+}_{(aq)} + 3\text{CMPO}_{(org)} \rightleftharpoons \text{PO}^{2+}_{3,(org)}$$  \hfill (7.2.3)

The presence of two or more metal to ligand stoichiometries agrees well with the extraction data obtained by Makrlık et al. [20, 21] during their recent work concerning Sr$^{2+}$ from an aqueous solution to nitrobenzene; in these reports they described strontium complexes such as SrCMPO$_2^{2+}$, SrCMPO$_3^{2+}$, and even SrCMPO$_4^{2+}$ in the nitrobenzene phase. In their publication, Makrlık et al. [20] used the radioisotope of strontium, $^{85}\text{Sr}$, determining the distribution ratios of the radioactive species between the aqueous and nitrobenzene phases via $\gamma$ emission and then plotting the result as a function of ligand concentration in the organic phase. This report [20] is evidence towards the stoichiometries observed; however, in the present article no radioactive species were used and this certainly points to a benefit of this as a diagnostic technique although radioactive isotopes can certainly be used should there be a need.

The appearance of two or more metal to ligand stoichiometries has been observed previously using cyclic voltammetry at a liquid|liquid interace [25, 30, 34, 37]. The first time was by Homolka et al. [30] for transfers of Fe(II), Fe(III), Ni(II), and Zn(II)
complexes with bipyridine and phenanthroline from water to nitrobenzene; in that paper, however, the complexes were introduced as a methanolic/aqueous mixture to the aqueous phase followed by ion transfer through the use of an applied electric field. The next series of reports surrounded the cesium FIT using crown ethers as the ligand and were studied by Kakiuchi et al. [25, 34] and Dassie et al. [37] at w||IL and w||DCE interfaces, respectively. Finally, the emergence of multiple peaks within a CV, indicative of multiple FIT stoichiometries, was demonstrated recently [45] for dioxouranium and CMPO at w||DCE interfaces. Thus, the appearance and analysis of multiple peaks are in good agreement with previously published voltammetric results [25, 30, 34, 37, 45].

7.2.3.2 - Mass Spectrometry

In order to further verify the presence of these two Sr-CMPO complexes, the w||DCE solvent system was studied using BESI-MS through in-situ mixing of Sr$^{2+}$ in water and CMPO in DCE, along with conventional ESI-MS by a “shaking flask” mixing and direct injection.

Shown in Figure 7.2.6A is the mass spectrum obtained using BESI-MS, with 15 μM CMPO in DCE and 100 μM Sr(NO$_3$)$_2$ in the aqueous phase, such that four main peaks were obtained; doubly charged complexes observed at m/z = 451.3 and 654.9 Th were identified as [SrCMPO$_2$]$^{2+}$ and [SrCMPO$_3$]$^{2+}$, respectively. The isotope distribution patterns of these two peaks are an excellent match for the characteristic isotopes of strontium and other elements in these two complexes towards the theoretically calculated 451.25 and 654.90 Th. Two other peaks were observed and attributed to [CMPO + H]$^+$ and [Na$^+$CMPO$_2$]$^+$. The BESI-MS spectrum confirms the formation of the Sr$^{2+}$-CMPO complexes observed by the above electrochemical methods at the w||DCE interface.

Tandem MS, or MS/MS, was performed on these two complexes to further explore the coordination strength. MS/MS involves the linear combination of quadrupole mass analyzers whereby the mass spectrum is first scanned, the ion stream undergoes collision with an inert gas, and finally the fragments are analyzed with the second MS. According to tandem MS spectra, [SrCMPO$_3$]$^{2+}$ easily lost one CMPO during collision-induced dissociation with very low collision energy while the other two CMPO complexes, including [SrCMPO$_2$]$^{2+}$, displayed much stronger binding force and continued
binding even with the introduction of a 2× higher collision energy than in the previous case of [SrCMPO$_3$]$^{2+}$.

Figure 7.2.6: (A) BESI-MS of interfacial reactions using 15 μM CMPO in DCE and 100 μM Sr(NO$_3$)$_2$ in aqueous (B) ESI-MS obtained from direct injection after “shake flask” experiment, i.e. by mixing 100 μL each of a 2.1 mM Sr(NO$_3$)$_2$ aqueous phase and 100 mM CMPO DCE phase to form an emulsion. Close-ups of the [SrCMPO$_2$]$^{2+}$ and [SrCMPO$_3$]$^{2+}$ peaks are shown inset in each spectrum with calculated isotopic profiles shown in (B).

The “shake flask” experiment consisted of combining 100 μL of a 2.1 mM Sr(NO$_3$)$_2$ aqueous solution with a 100 mM CMPO DCE solution into a small vial and shaking. The emulsion was then drawn up into a 250 μL syringe and injected into the ESI-MS. The complete mass spectrum obtained is shown in Figure 7.2.6B. Four major mass peaks can be observed at m/z of 408.1, 430.0, 450.9, and 654.6 Th; these peaks have been identified as [CMPO + H]$^+$, [NaI$^+$CMPO + H]$^+$, [Sr$^{II}$CMPO$_2$]$^{2+}$, and [Sr$^{II}$CMPO$_3$]$^{2+}$, respectively. The peak at 408.1 m/z is in very good agreement with the CMPO peak observed using BESI-MS, while the peak at 430.0 m/z is proposed to be a sodium-CMPO complex. Sodium is often a contaminant in metal salts with the manufacturer indicating a
0.05% Na content and this is in good agreement with the result obtained for the BESI-MS experiment that saw a similar Na-CMPO complex, \([\text{Na}^1\text{CMPO}_2]^+\). The observed peaks at 450.9 and 654.6 Th were isolated, shown as insets in Figure 7.2.6B, along with their respective calculated isotopic distribution profiles (shown above each inset spectrum) for the proposed strontium-CMPO complexes: \([\text{Sr}^{II}\text{CMPO}_2]^{2+}\), and \([\text{Sr}^{II}\text{CMPO}_3]^{2+}\). There is a small, 0.3 Th, difference between the BESI-MS and ESI-MS spectrums and this is most likely the result of a variation in calibration.

The experimental and calculated mass peak profiles are in excellent agreement and are characteristic of the stable strontium isotopes \(^{86}\text{Sr}\), \(^{87}\text{Sr}\), and \(^{88}\text{Sr}\), which have an abundance of 9.86, 7.00, and 82.58\% [57], respectively. The isotopic ratios result in two short peaks preceding a large main peak; these were faithfully reproduced in the calculated and experimental profiles. The trailing peaks are common MS features associated with hydrocarbon species.

Therefore, the data obtained from the two injection methods, BESI-MS and ESI-MS, are in good agreement with each other and have confirmed the stoichiometry of the \(\text{Sr}^{2+}\)-CMPO complexes observed electrochemically at the w\hspace{1pt}|\hspace{1pt}DCE interface.

7.2.3.3 - Facilitated Ion Transfer of \(\text{Sr}^{2+}\) using CMPO at the micro w\hspace{1pt}|\hspace{1pt}IL Interface

Next the FIT of strontium was investigated at the w\hspace{1pt}|\hspace{1pt}IL interface using a newly discovered IL, P\(_{66614}\)TB. Figure 7.2.3B shows the CV obtained using Cell 7.2.2, with \(y = 0\), or no CMPO, added to the IL phase, and constituted a “blank” CV; this is overlaid with a CV taken using Cell 7.2.3 such that 2 mM of TMANO\(_3\) have been added to the aqueous phase.

The blank curve in Figure 7.2.3B was initiated at 0.131 V where the current was almost zero, and scanned in the forward direction toward more positive potentials at a scan rate of 0.020 V\cdot s\(^{-1}\). The potential was scanned to a switching potential of 0.427 V, at which point the scan direction was reversed and scanned to the lower potential limit of \(-0.270\) V. The final scan segment was from the lower limit, \(-0.270\) V, back to the initial potential of 0.131 V. This blank curve shows an increase in the current response during the forward scan at 0.427 V and a decrease in the current response at \(-0.270\) V during the reverse scan; this is indicative of supporting electrolyte ion transfer, specifically \(\text{Sr}^{2+}\) from w to o and TB\(^-\) from o to w for the former current response and NO\(_3^-\) from w to o and
P_{66614} from o to w for the latter. Aside from these two features, the blank curve is devoid of any peaks and this is an excellent indication of the purity of the prepared ionic liquid. The polarizable potential window (PPW) spanned more than 0.8 V. It should be noted that the PPW is limited predominantly by TB\textsuperscript{−} at the positive end and NO\textsubscript{3}\textsuperscript{−} at the negative end [55] and since the estimated IL bulk concentration of the potential-limiting TB\textsuperscript{−} is 1.0 M, this is a good indication considering the PPWs size.

The CV of Cell 7.2.3 in Figure 7.2.3B employed similar parameters as those chosen for the blank; the initial potential was −0.106 V with the upper and lower potential range set at 0.442 and −0.283 V. During the initial forward scan an anodic wave with a peak at 0.321 V can be observed and this is indicative of TMA\textsuperscript{+} transfer from w to o, while a cathodic peak is shown with at current maximum 0.179 V during the reverse scan; this is TMA\textsuperscript{+} transferring from the ionic liquid phase back to the aqueous phase. This description concerning the transfer of TMA\textsuperscript{+} across the ITIES formed at the tip of a micropipette agrees well with previous results [44] and with the results of Kakiuchi et al. [24, 46]. The peak-to-peak separation between the forward and reverse peak-shaped waves was 0.142 V. This large peak separation was observed previously at the w\mid IL micro-ITIES [26, 44, 46] and in homogeneous IL electrochemistry [58, 59]; it is proposed to be either uncompensated resistance or slow IT/electron transfer kinetics. TMA\textsuperscript{+} IT was used to calibrate the potential scale at the w\mid P_{66614} TB ITIES using the TATB assumption [29, 39]; with $\Delta_{\text{IL}}^{\text{w}} \phi_{\text{TMA}^+}^{o} = 0.293$ V [44]. The half-wave potential was determined using equation 3.4 and the peak potential of the forward scan, i.e. TMA\textsuperscript{+} transfer from w to o.

Figure 7.2.7 illustrates the CVs obtained using Cell 7.2.2 with y equal to 35, 50, 62, 85, and 111 mM for curves A, B, C, D, and E, respectively. In Figure 7.2.7A, the CV was initiated at −0.083 V and scanned in the forward direction towards positive potentials at a rate of 0.020 V\textperiodcentered s\textsuperscript{−1}. A peak-shaped wave showed a maximum current at 0.099 V and this is indicative of the transfer through interfacial complexation (TIC) of Sr\textsuperscript{2+} from w to o with CMPO. The scan continued until 0.356 V, at which point the scan direction was reversed and headed towards negative potentials until −0.190 V. During this scan segment, a peak-shaped wave was observed with a peak potential at −0.080 V and this has been attributed to the transfer of Sr\textsuperscript{2+} back across the ITIES through interfacial
decomplexation of the Sr$^{2+}$-CMPO complex. Interestingly, only one pair of peaks was observed in contrast to two at the w|DCE interface.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure7_2.png}
\caption{CVs obtained using Cell 7.2.2 with similar instrument parameters as described for Figure 7.2.3B but with $y$, or [CMPO], = 35, 50, 62, 85, and 111 mM for curves A, B, C, D, and E, respectively.}
\end{figure}

To verify that only one stoichiometry is present at the w|IL interface, differential pulse voltammetry (DPV) was applied to Cell 7.2.3 with [CMPO] = 111 mM using the following parameters: step potential, pulse amplitude, pulse period, pulse width, initial and final potentials equal to 0.010 V, 0.050 V, 0.5 s, 0.1 s, −0.090 and 0.400 V, respectively; a reverse scan was also obtained with initial and final potentials of 0.400 and −0.090 V.
Figure 7.2.8: DPV using Cell 7.2.2, [CMPO] = 111 mM; with an initial and final potential of −0.090 and 0.400 V; step, pulse amplitude, pulse period, and pulse width of 0.010 V, 0.050 V, 0.5 s, and 0.1 s, respectively. For the reverse scan the initial and final potentials have simply been switched and negative pulse amplitude applied.

The DPV obtained is shown in Figure 7.2.8 with only one peak potential at 0.157 V during the forward scan, indicating that only one ion transfer has taken place. It should be noted, however, that this peak is broad and may be the result of two stoichiometries having effectively merged; that is to say, the difference in the nominal, overall complexation constant between the complexes with \( n = 2 \) and \( n = 3 \) may be small. Additionally, a CV was taken using Cell 7.2.3 and [CMPO] = 111 mM, but at a scan rate of 0.001 V·s\(^{-1}\) (data not shown). In this CV a single ion transfer was observed with one peak on the forward scan, indicative of TIC, and another on the reverse scan, typical of TID. However, the peak to peak separation becomes very large (>0.300 V), and this may be indicative of the system transition from one controlled by diffusion of the ligand in the IL phase to one in which it is controlled by the consumption of species at the interface, i.e. a system that generates a steady state current response. Both of these experiments point to a scenario in which the kinetics of the interfacial reactions is slow although the Gibbs energy is favourable. Moving forward, as the concentration of the ligand increases, in Figure 7.2.7 the peak potential of the forward wave shifts to less positive potentials; \( \Delta_{\text{RTIL}}^{\phi_p} \) equal to 0.088, 0.085, 0.065, and 0.050 V for curves B, C, D, and E, respectively. Similar to strontium FIT at the w|DCE interface, the series of CVs obtained
at the w\|P$_{66614}$TB interface were analyzed using equation 7.2.5. Two critical points concerning the analysis of the present case must be made initially.

First, the $\xi$ term in equation 6.1.2 cannot be neglected, therefore the diffusion coefficient for the IL was estimated based on a recent publication [44], concerning diffusion in ILs using the ferrocene/ferrocenium redox couple as a probe. In this previous work, ferrocene was oxidized to ferrocenium and the diffusion coefficient was obtained through two electrochemical techniques: cyclic voltammetry, by altering the scan rate, and chronoamperometry using two curve fitting methods described by Shoup and Szabo [60] and Aoki and Osteryoung [61]; ferrocene is a relatively large organic molecule which we considered analogous to CMPO and the Sr-CMPO complex. In this way the diffusion coefficient for the IL phase was estimated to be $3.5 \times 10^{-8}$ cm$^2$·s$^{-1}$ [44]. The diffusion coefficient for strontium in the aqueous phase was obtained from the literature [62]; $1.2 \times 10^{-5}$ cm$^2$·s$^{-1}$. Secondly, the formal free metal ion transfer potential of Sr$^{2+}$ at the w\|P$_{66614}$TB ITIES could not be measured, therefore, the formal transfer potential at the w\|DCE interface [54] was used to approximate its value. It was noticed that the formal transfer potential of TMA$^+$ at the w\|P$_{66614}$TB interface was shifted positively by 0.133 V relative to its transfer at the w\|DCE interface, therefore, considering this a general trend, it was incorporated such that: $\Delta_{\text{DCE}}^w \phi_{\text{Sr}^{2+}} + 0.133$ V $\approx \Delta_{\text{IL}}^w \phi_{\text{Sr}^{2+}} \approx 1.033$ V.

The latter assumption was based on three factors. First, the recent work by Samec et al. [26] and Kakiuchi et al. [46] showed a correlation between the trends in formal transfer potentials of ions at the w\|DCE and w\|IL interfaces; each ion showed distinct transfer potentials but the trends in hydrophilicity between w\|DCE and w\|IL paralleled each other. Secondly, our recent work [45, 54] surrounding UO$_2^{2+}$ FIT and IT, in conjunction with Sr$^{2+}$ IT at the w\|DCE, point to the extreme hydrophilicity of these ions and thus a large formal transfer potential is expected. Finally, the size and position of the calibrated PPW suggests that this value is a good approximation.

Therefore, continuing with the analysis, the plot of $-z_i F / (RT) \left( \Delta_{\text{DCE}}^w \phi_i \left[ \alpha_i \right] - \Delta_{\text{IL}}^w \phi_i \right)$ vs. In($c_{\text{CMPO,IL}}^*$) is shown in Figure 7.2.9 with a linear fit giving a slope equal to 3 and a y-intercept of 75; the plot shows good correlation to the FIT theory with an $R^2 = 0.9777$. Looking at equation 7.2.5, the slope of the line is independent of the formal IT coefficient.
and $\xi$, therefore, it is also independent of the assumptions made surrounding the diffusion coefficients and formal transfer potential of the free strontium metal species. Using these estimations, the accumulated complexation constant was calculated to be $1.5 \times 10^{34}$.

**Figure 7.2.9:** Plot of $-z_i F / (RT) \left( \Delta_{IL}^{w} \phi_{z_i}^{w} - \Delta_{IL}^{w} \phi_{i}^{w} \right)$ versus $\ln(c_{CMPO,IL}^*)$ with data obtained from the curves shown in Figure 7.2.7.

Figure 7.2.10A and 7.2.10B show proposed structures of SrCMPO$_2$$^{2+}$-2H$_2$O and SrCMPO$_3$$^{2+}$, respectively, with an octahedral geometry. In a recent publication by Cole *et al.* [63], they described the crystal structures of several strontium complexes with a maximum coordination number to the strontium center of 7. The octahedral geometry shown in Figure 7.2.10B has a coordination number of 6; this geometry minimizes steric hindrance, however, a trigonal bipyramidal geometry may also be possible with two CMPOs in a bidentate configuration and one monodentate. In this case, the monodentate CMPO would most likely coordinate through the oxygen of the phosphine oxide [17, 64, 65]. Junk and Steed [66] recrystallized a strontium nitrate salt from an aqueous solution of 18-crown-6 and obtained Sr(NO$_3$)$_2$(18cr6) salt with strontium held within the ring of the crown ether, coordinated to the six ring-oxygens, and the two nitrates located on opposite sides of the ring plane with O,O'-bidendate coordination; therefore the total coordination number of their crystal structure was 10.

The structure in Figure 7.2.10A was proposed on the basis with the work of Junk and Steed [66] in mind, as the CMPO molecules lie in a plane around the strontium metal
with two solvent water molecules on opposite sides; thus, an octahedral geometry is formed. While no water molecules were observed during either the BESI-MS or ESI-MS experiment, it is possible they are only weakly coordinated and easily removed during the harsh ionization conditions. The total number of ligands participating in the interfacial complexation reaction is in agreement with the results shown by Makrlík et al. [20, 21] and these previous structural reports [63, 66] are evidence towards two or three CMPO molecules participating in the interfacial complexation.

Figure 7.2.10: Proposed structures for (A) \([\text{SrCMPO}_2\cdot2\text{H}_2\text{O}]^{2+}\) and (B) \([\text{SrCMPO}_3]^{2+}\); solvent molecules in the case of \([\text{SrCMPO}_3]^{2+}\) have been neglected for simplicity.

The complexation constant at the w|IL interface is 9 orders of magnitude greater that that observed at the w|DCE interface. This large equilibrium constant further explains why \([\text{SrCMPO}_3]^{2+}\) can be formed at the interface where of the reaction kinetics are very slow; thermodynamics, in this case, are the driving force. This is in agreement with the large increase in distribution ratios observed using ILs versus molecular solvents in conventional solvent extractions [15, 16, 23].
7.2.4 - Conclusions

The FIT of Sr\(^{2+}\) assisted by the CMPO ligand at the w|DCE and w|IL interface was investigated for the first time. At the w|DCE interface two metal:ligand stoichiometries of 2 and 3 for the interfacial complexation reactions were observed with accumulated equilibrium constants, \(\beta\), of \(4.5 \times 10^{19}\) and \(5.5 \times 10^{25}\), respectively. These stoichiometries have been confirmed through the use of BESI-MS and ESI-MS using a “shake flask” experiment; mass peaks observed at 451.3 and 654.9 have an isotopic fingerprint that suggests they belong to [SrCMPO\(_2\)]\(^{2+}\) and [SrCMPO\(_3\)]\(^{2+}\) complexes, respectively. Comparing these two MS experiments, BESI-MS is valuable for short-lived chemical species; however, the “shake flask” technique, while not experimentally sophisticated, was able to obtain similar data is most likely owing to the strength of the metal ion-ligand complexes.

Only one stoichiometry was observed at the w|IL interface, with \(n = 3\) and \(\beta = 1.5 \times 10^{34}\), interestingly the complexation constant is 273 million times greater than that observed using molecular solvent; it should be noted that, because of the assumptions made concerning the diffusion coefficients in the aqueous and IL phases, along with \(\Delta_{\text{IL}} \phi_{\text{Sr}^{2+}}\), that this is an estimation. The high \(\beta\) value, however, may provide an additional explanation as to why the reported distribution constants for IL extractions are higher than those of conventional organic solvents.

The above studies will provide guidelines for reprocessing spent nuclear fuels to obtain Sr to be used in radioimmunology. As well it should be noted that, while a non-radiogenic, stable form of strontium (\(^{88}\)Sr) was used, this was only for convenience of handling and is shown here as a model system; these data are assumed to be transferrable to any isotopic form of strontium.

7.2.5 - References

Chapter 7.3 - Correlation of stoichiometries for Rb\(^+\) extraction determined by mass spectrometry and electrochemistry at liquid|liquid interfaces

7.3.1 - Introduction

In 2002, Hoffert et al. [1] reviewed the contemporary perspectives on climate change along with measures necessary to mitigate future adverse effects of anthropogenic CO\(_2\) production from fossil fuels; in particular, alternative energy sources including solar, wind, hydroelectric, fusion, and nuclear power generation. Barring the sudden implementation of an as yet unrealized technological advancement [1, 2], solar and nuclear power offer the only viable solution to the world’s growing energy demands. While present concerns surrounding the exhaustion of fossil fuels have given rise to terms like ‘peak oil’ [3], it is interesting to note that an analogous term could be applied to the present treatment of nuclear fuel: ‘peak uranium’. However, a parallel situation in the nuclear industry can be avoided through the use of breeder reactors and the implementation of a closed loop nuclear fuel cycle, such that nuclear waste is recycled; such action could extend the life of the nuclear industry by hundreds of years [1, 4].

This strategy would also divert tonnes of radioactive material from entirely unnecessary, proposed geological [5] and surface waste repositories that are the subject of numerous controversies. Indeed, spent nuclear fuel (SNF) contains approximately 95% useable uranium [6] with the other 5% coming from fission byproducts that are typically neutron absorbers, poisoning the fission reaction and reducing the efficiency of the fuel rod; should these impurities be removed, the efficiency would be restored. Likewise, these contaminants should be viewed as a potential resource; many of these isotopes have uses in medicinal [7-9] or other applications. This begs the question: how can the selectivity of current separation techniques be improved?

Interestingly, alkali metals comprise 6% of nuclear waste, including rubidium oxide [6]; however, little specific information seems to exist for the extraction of elements such as rubidium from SNF. Isotopes, such as \(^{82}\)Rb, have been used in positron emission tomography for myocardial perfusion imaging and the diagnosis of coronary artery disease [10-12]. Strontium, another major component of SNF, has also found medicinal applications [7, 13, 14] and, therefore, distinguishing between Rb and Sr, along with their behavior in SNF reclamation streams, would be of special interest.
One contemporary separation method, called TRans Uranic EXtraction (TRUEX), uses the ligand octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) in a biphasic system composed of water and a paraffinic organic solvent, typically an n-dodecane/tributylphosphate mixture [4, 15]. Presently, efforts to improve this process have been directed towards alternative solvents to replace n-dodecane; these include room temperature ionic liquids (ILs) [4, 16-19]. With the development of air-stable versions and separate research groups establishing the improved extraction efficiency obtained through their use [16-19], ILs have become a major focus in metal separation research.

In a recent publication [14], it has been showed that electrochemistry at a liquid|liquid micro-interface between two immiscible electrolytic solutions (micro-ITIES) [20-22] can evaluate the interfacial complexation reactions easily and inexpensively. This specialized form of electrochemistry typically involves simple ion transfer (IT) and facilitated ion transfer (FIT) reactions, shown in equations 1.4 and 1.6, respectively. Such that ITs from the aqueous phase, w, to the organic phase, o (or IL), through a push/pull mechanism controlled by an applied potential from an electrode immersed in each phase; here, the potential difference across the ITIES becomes the driving force, \( \Delta \phi_w - \phi_o \) [23-25]. FIT is the electrochemical equivalent of ligand assisted metal extraction. In the case of equation 7.3.2, the ligand, \( L \), dissolved in the organic or IL phase improves the miscibility of \( i \), typically a metal, which lowers the Gibbs energy of transfer and, in turn, the amount of applied potential necessary in order to elicit IT; please see Figure 1.2.

Electrochemistry at an ITIES is commonly performed using water and 1,2-dichloroethane [22, 26-29] (DCE) or nitrobenzene [21]; however, recent work in this field has expanded to include the w|IL interface [14, 30-35]. Herein is described the FIT of rubidium using CMPO as a ligand dissolved in DCE and IL phases for the first time. Ion pair phenomena has been explored through its effect on FIT at the w|IL interface by using two rubidium salts dissolved in the aqueous phase and comparing with only one salt. Additionally, the stoichiometry of interfacial complexation reactions was confirmed by electrospray ionization mass spectrometry (ESI-MS) using an emulsion generated by two phase shaking.
7.3.2 - Experimental Section

**Chemicals.** All purchased chemicals were of reagent grade and utilized without further purification unless otherwise specified. 1,2-dichloroethane (DCE), dichloromethane, trimethylchlorosilane, nitric acid, hydrochloric acid, rubidium sulfate (Rb$_2$SO$_4$), and rubidium nitrate (RbNO$_3$) were obtained from Sigma-Aldrich Canada Ltd. (Mississauga, ON). The IL component, trihexyltetracetylphosphonium chloride and CMPO were purchased from Strem Chemicals Inc. (Newburyport, MA), while potassium tetrakis(pentafluorophenyl)borate was ordered from Boulder Scientific Company (Longmont, CO). Ultrapure Milli-Q water (18.2 MΩ) was used to generate all aqueous solutions. The preparation and characterization of our low cost and very hydrophobic IL, trihexyltetracetylphosphonium tetrakis(pentafluorophenyl)borate, were reported elsewhere [35]. The fabrication of micropipettes [14, 28, 34, 35] is described in section 2.3.2.

**Electrochemistry.** All electrochemical measurements were performed using the Modulab System from Solartron Analytical (Ametek Advanced Measurement Technology, Farnborough, Hampshire, United Kingdom). The Modulab is equipped with a femtoammeter and this was employed during all electrochemical experiments. A micro-pipette is incorporated into a modified HEKA pipette holder (HEKA Electronics, Mahone Bay, NS) and back-filled with the aqueous phase using a syringe. The pipette was then submerged into the IL or DCE phase in a glass vial held in a jacket mounted on a microstage, fabricated by the Electronic Shop in Chemistry at Western, and connected to a water circulator (VWR, Mississauga, ON) for heating. The IL and DCE experiments were conducted at 60°C and room temperature, respectively. The following electrochemical cells were used:

\[
\text{Ag} | \text{AgNO}_3 | 5 \text{ mM RbNO}_3 \quad | y \text{ mM CMPO} \quad | 5 \text{ mM P}_{66614} \text{TB} | \text{AgTB} | \text{Ag} \quad \text{(Cell 7.3.1)}
\]

\[
\text{Ag} | \text{AgNO}_3 | 5 \text{ mM RbNO}_3 \quad | y \text{ mM CMPO} \quad | \text{AgTB} | \text{Ag} \quad \text{(Cell 7.3.2)}
\]
In order to ensure that the interface remained at the tip of the micropipette, the micro-ITIES was monitored continuously through the use of a USB CCD camera (Motic, Richmond, BC) attached to a variable 12× magnifying lens assembly (Navitar, Rochester, NY) [14]. Owing to the low current employed in these electrochemical experiments, a two-electrode system was used. The working electrode (WE) lead of the potentiostat was attached, using a BNC connector to the pipette holder, which, in turn, contained an integrated silver wire immersed in the aqueous phase. The counter (CE) and reference electrode (RE) leads were connected to a silver wire placed in the DCE or IL phase.

*Electrospray Ionization Time-of-Flight Mass Spectrometry (ESI-TOF MS).* A Micromass LCT Mass Spectrometer (Waters, Milford, MA, USA), operating in the positive ion mode, with capillary, sample cone, and extraction cone voltages of 5000, 25, and 0 V, respectively, were used for all ESI-TOF MS measurements. The sample time, scan time, and interscan delay were set to 5 min, 4 s, and 0.1 s, respectively. An emulsion was generated by shaking water and DCE phases containing the dissolved metal and ligand, respectively. The emulsion of interest was loaded into a 250 μm syringe (Hamilton Co., Reno, NV, USA) and placed in a syringe pump (Hamilton Co.) operating at 25 μL·min⁻¹. Isotopic distribution modelling was carried out using ‘Molecular Weight Calculator’, a Freeware program developed by Matthew Monroe at Pacific Northwest National Laboratory and available on the web [36].

### 7.3.3 - Results and Discussion

#### 7.3.3.1 - Facilitated Ion Transfer Rb⁺ at the w|DCE micro-ITIES using CMPO

Figure 7.3.1 A shows a typical cyclic voltammogram (CV) acquired using Cell 7.3.1 with no CMPO present in the DCE phase (y = 0). The CV was initiated at a Galvani potential difference of 0.127 V and scanned in the forward direction towards more positive potentials until 0.525 V was reached. Here an increase in current can be observed that is indicative of the transfer of the supporting electrolytes (Rb⁺ from w to o and TB⁻ from o to w); this sharp increase in current describes the limit of the polarizable
potential window (PPW). From here the potential was swept in the reverse direction to −0.492 V. During the reverse scan, a peak-shaped wave was observed with a peak potential of −0.342 V; this is attributed to the IT of nitrate anions from w to o.

Figure 7.3.1: CVs acquired using Cell 7.3.1 with y equal to 0, 14, 39, 60, and 78 mM of CMPO for A, B, C, D, and E, respectively. Two regions, which were swept independently, with the following parameters: a scan rate of 0.020 V·s⁻¹, an initial potential of 0.070 V, and upper and lower limits of 0.675 and −0.450 V.
The half-wave potential of NO₃⁻ IT was used as an internal reference for the purposes of calibrating the potential scale through the use of the TATB or Parker’s assumption [37-39]; the formal IT potential, $\Delta^\circ_{\text{w},\text{NO}_3^-}$, at the w|DCE ITIES was taken to be −0.314 V [40]. The half-wave potential of NO₃⁻ IT was determined using its peak potential and equation 3.4 [41].

The potential was then swept in the positive direction from −0.492 to 0.127 V, where a sigmoidal-shaped wave with a steady state current was observed that is indicative of simple NO₃⁻ IT back across the ITIES from o to w. This asymmetrical current response is typical of IT at a micro-ITIES housed at the tip of a micropipette and agrees well with established theory [26, 27]. This asymmetry is a direct result of the pipette physical geometry. If the CV range is increased at the positive end, an exponential increase in the current response is observed and may result in a disruption of the interface. The potential scale was calibrated through the TATB assumption [37-39] via the equation 2.9. All CV results have undergone this treatment using nitrate as an internal standard with $\Delta^\circ_{\text{w},\text{NO}_3^-} = −0.380$ V [42].

Figure 7.3.1 illustrates CVs obtained as the concentration of CMPO on the DCE phase is increased; B, C, D, and E show the system with 14, 39, 60, and 78 mM of CMPO respectively. Each CV was scanned in two parts using a scan rate of 0.020 V·s⁻¹.

At first the system was scanned in the negative direction from approximately 0.070 to −0.450 V, returning to 0.070 V; this segment, again, details NO₃⁻ IT.

The second section was from an initial potential of approximately 0.070 to 0.670 V and back; during this sweep, a peak current can be observed during the forward scan with peak potentials of 0.567, 0.511, 0.470, and 0.469 V for the respective curves, B, C, D, and E. This peak-shaped wave is indicative of the FIT of Rb⁺ from w to o via a mechanism referred to as transfer by interfacial complexation (TIC) with the CMPO ligand [43]. The reverse sweep shows a sigmoidal-shaped current response and this is indicative of transfer through interfacial decomplexation (TID) [43].

Interestingly, as the concentration of the ligand in the DCE phase increases, the FIT peak shifts to more negative potentials. This trend, along with both current response features, are in good agreement with the theory of FIT at a micro-ITIES held at the tip of a
micropipette as established by the pioneering work of Homolka et al. [21], Kakiuchi and Senda [20], and Girault et al [22, 43, 44], and demonstrated recently [14, 28].

**Figure 7.3.2.** A: Plot of \(-z_f F(\Delta_F) (\Delta_{o/w} \phi_o^{0'} - \Delta_{w/o} \phi_{w/o}^{0'})\) versus \(\ln \left( c_{CMPO,o}^* \right) \). B: Proposed structure for RbCMPO$_2^+$.  

Figure 7.3.2A shows a linear relationship developed over a series of CMPO concentrations by graphing \(-z_f F(\Delta_F) (\Delta_{o/w} \phi_o^{0'} - \Delta_{w/o} \phi_{w/o}^{0'})\) versus \(\ln \left( c_{CMPO,o}^* \right) \). As developed by Girault et al. [22], the linear relationship can be used to determine the stoichiometry, \(n\), and overall complexation constant, \(\beta\) (equation 6.1.2).

The formal IT potential of rubidium at the w|DCE interface, \(\Delta_{o/w} \phi_{o,\text{Rb}}^{0'}\), was taken to be 0.576 V, which was estimated through simple IT at a micro-ITIES [45, 46]. The diffusion coefficients in either phase, aqueous (\(D_w\)) and organic (\(D_o\)), were taken to be equal such that the final term in equation 6.1.2, \(\xi = \sqrt{D_o/D_w}\), was equal to 1. In this way, equation 6.1.2 is greatly simplified.
The half-wave potentials for FIT were determined using equation 3.4 and calibrated with equation 2.9, through the TATB assumption [37-39].

The linear relationship is such that the slope is the ratio of ligand to metal ion, \( n:1 \), and the intercept is the natural logarithm of the overall complexation constant. Linear regression analysis was applied to the data giving a slope of 2 and a y-intercept of 10.4 ± 0.6 with an \( R^2 \) of 0.9363. Therefore, owing to the reasonable linear fit, it can be concluded that a stoichiometry of 2 CMPOs for each metal as illustrated by Figure 7.3.2B with an overall complexation constant of 3.3 \( \times \) \( 10^4 \) was obtained.

Many alkali metal complexes [47-52] have been reported and alkali coordination chemistry has been frequently reviewed [53]. Dissolved in water, a rubidium ion typically has an inner hydration sphere consisting of 8 coordinate water molecules [54] and this relatively high coordination number (c.n.) is also reflected in its ligand/complexation chemistry with typical c.n. ranging from 6 to 8 [47-52]. Recently, Chekhlov [51] elucidated the crystal structure of (2,2,2-cryptand)rubidium chloride and bromide such that the 6 oxygens and 2 nitrogens on cryptand were coordinated to the metal center. Interestingly, Meng [55] reported the crystal structure of poly[(\( \mu \)-2-hydroxy-3,5-dinitrobenzoato)rubidium] in which the rubidium center is coordinated to 10 oxygens from eight 3,5-dinitrosalicylate complexes with \( \pi-\pi \) stacking between these groups contributing to the stability of the compound. This is further evidence of the viability of the ligand stoichiometry determined voltammetrically for Rb with CMPO, indicating that steric hinderance is not a issue in this case.

In fact, the coordination of 2 to 3 CMPOs to a metal center seems typical [14, 17, 56, 57] and a proposed RbCMPO\(_2\)\(^+\) structure is shown in Figure 7.3.2B.

7.3.3.2 - Interfacial Complexation Stoichiometry Determined by Mass Spectrometry
To confirm the ligand to metal ion stoichiometry (\( n:1 \)) observed at the w/DCE interface, direct injection of an aqueous/DCE emulsion generated through a shake-flask experiment, into an ESI-MS was performed [14]. 100 \( \mu \)L of a 20 mM RbNO\(_3\) aqueous solution and 100 \( \mu \)L of 100 mM CMPO in DCE were placed in a small flask and mixed by shaking. The formed emulsion was subsequently injected into the ESI-MS analyzer. Figure 7.3.3 depicts a typical mass spectrum highlighting the experimental region corresponding to [RbCMPO]\(^+\) and [Rb(CMPO)\(_2\)]\(^+\). The insets illustrate the calculated
(red, or top inset) and experimental (blue, or bottom inset) isotopic distribution profiles at 493.2 and 900.4 Th, respectively. There are two naturally occurring isotopes of Rb: $^{85}\text{Rb}$ and $^{87}\text{Rb}$ with abundances of approximately 72.17 and 27.83%, respectively [58]. Interestingly, these isotopes are reflected in the calculated profile for $[\text{RbCMPO}]^+$ with two large peaks separated by 2 Th; the other peaks, at intervals of 1 Th, are typical of hydrocarbon material with a charge of 1+.

![Mass Spectrum](image)

**Figure 7.3.3.** Mass Spectrum of the emulsion formed with 100 μL of 20 mM RbNO$_3$ aqueous solution and 100 mM CMPO in DCE. Inset: the isotopic distribution of RbCMPO$^+$ and RbCMPO$_2^+$ calculated (red, or top insets) and experimental (blue, or bottom insets).

The RbCMPO$_2^+$ complex observed spectroscopically corroborates the electrochemical data. The investigation of alkali metal complexes using ESI-MS was also demonstrated by Leize *et al.* [47] and Lawrance *et al.* [50]. In both articles the authors reported avoiding a biphasic system by using either a methanol:water mixture [47] in order to dissolve the ligands and metals in one solution, or through the use of short chain alcohols as ligands [50], which could be dissolved easily in water. Leize *et al.* [47] used 18-crown-6 ether (18Cr6) and cryptand[2,2,2] as ligands and observed 1:1 metal to ligand complexes for Li, Na, and K, but for Rb and Cs, with 18Cr6, they also observed
sandwich compounds of 1:2 ratios. This earlier discovery using 18Cr6 also serves to demonstrate that higher c.n. in Rb complexes are possible; giving a total c.n. of 12.

It is interesting to note that, while the potential difference across this emulsified interface was not measured, the shaking process resembled a simple open circuit potential experiment and assisted rubidium ion transfer along with the CMPO ligand from w to o.

7.3.3.3 - Facilitated Ion Transfer of Rb\(^+\) at the micro w|IL interface using CMPO

Figure 7.3.4 shows typical CVs acquired at a w|IL micro-ITIES using Cell 7.3.2 for curves A, B, C, and D with CMPO concentrations \(y\) equal to 0, 30, 44, and 69 mM whilst curves E, F, G, and H used Cell 7.3.3 and \(y\) of 0, 60, 70, and 90 mM, respectively.

Trace A in Figure 7.3.4 illustrates the current response versus the applied Galvani potential difference with no CMPO added to the IL phase, *i.e.* a blank solution. The potential was swept linearly starting at 0.184 V and moving towards more positive potentials with a scan rate of 0.010 V\(\cdot\)s\(^{-1}\). The edge of the PPW was reached at approximately 0.782 V, limited by the transfer of the supporting electrolytes; Rb\(^+\) from w to IL and the anionic component of the IL, TB\(^-\), from IL to w. The CV was subsequently swept in the reverse direction towards more negative potentials form 0.782 to −0.365 V; a peak-shaped wave was observed at −0.333 V and this is attributed to the simple IT of NO\(_3^-\) from w to the IL. The edge of the PPW, at the negative end, is limited by the transfer of the cationic component of the IL, P\(_{66614}^+\). The potential was then scanned in the forward direction with a final potential of approximately 0.184 V. A second peak-shaped wave was observed during this final segment with a peak potential at −0.078 V; this is attributed to the IT of nitrate back across the ITIES. Unlike at the w|DCE interface, the w|IL experiences consumption control in both directions, such that IT from outside to inside the pipette is effected by the high viscosity of the IL phase (*i.e.* low diffusion coefficient). These observations of IT at an w|IL interface are in good agreement with the pioneering works of Kakiuchi *et al.* [30, 31, 59] and Samec *et al.* [32, 33], as well as in recent publications [14, 35].

With the addition of CMPO to the IL phase another peak, can be observed in the forward and reverse scans; similarly to the w|DCE case, this was attributed to the FIT of Rb\(^+\) through TIC during the forward sweep and TID when the potential is scanned back. This peak shifts from 0.595, 0.587, and 0.580 V for curves B, C, and D using Cell 7.3.2
which contains only RbNO$_3$ in the aqueous phase and $y$ equal to 30, 44, and 69 mM CMPO in the IL phase, respectively. The half-wave potentials for FIT and IT were taken to be the mid-point between their respective forward and reverse transfer waves, which were then treated using equation 3.4 in order to determine the formal IT potential of the metal ion-ligand complex.

**Figure 7.3.4.** CVs A, B, C, and D were taken using Cell 7.3.2 with $y$ equal to 0, 30, 44, and 69 mM and a scan rate of 0.010 Vs$^{-1}$. Curves E, F, G, and H were acquired using Cell 7.3.3 with $y$ values of 0, 60, 70, and 90 mM; all CVs used a scan rate of 0.020 Vs$^{-1}$.

A similar relationship to w|DCE can be developed at the w|IL ITIES for FIT, however the final term in equation 7.3.5, $\ln(\xi)$, as well as the free metal ion transfer potential of Rb$^+$, $\Delta_{w}^{w} \phi_{Rb}^{\omega}$, must be evaluated to obtain the complexation equilibrium constant.

$\Delta_{w}^{w} \phi_{Rb}^{\omega}$ was taken to be 0.706 V and was obtained through a working curve for the microinterface by means of Comsol Multiphysics software through finite element
analysis, similar to the numerical approach in the case of a large interface by Girault et al. [45], and described in chapter 6.5. This working curve method utilizes the ratio between the current at the edge of scan, \( I_{\text{eos}} \), and the return peak current, \( I_{\text{rp}} \), \( (I_{\text{eos}} / I_{\text{rp}}) \); developing a relationship with this normalized current and the return peak potential, \( E_{\text{rp}} \). This technique for finding the formal transfer potential of species limiting the PPW was first demonstrated by Girault et al. [45] at a large (centimeter scale) w|DCE ITIES where a well defined return peak is observed.

\( \zeta \) was estimated using the diffusion coefficient of ferrocene in P<sub>66614</sub>TB, \( D_{w}^{\text{Fc}} = 3.5 \times 10^{-8} \text{ cm}^2 \text{s}^{-1} \), to represent the ligand/complex while the diffusion coefficient of tetramethylammonium (TMA\(^+\)), \( D_{w}^{\text{TMA}^+} = 2.0 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \), was used for the free metal in the aqueous phase [35]. Ferrocene is a relatively large organometallic compound; thus it is a good approximation towards the metal ion-ligand complex and its movement through the IL medium. The van der Waals radius for rubidium is listed as 3.03 Å [60] which is comparable to the size of TMA\(^+\) [61, 62], and while this does not take into account specific intermolecular forces, it is believed to establish a good analogue for metal ion diffusion through an aqueous solution. Additionally, while Rb\(^+\) transfer cannot be observed within the PPW, TMA\(^+\) can, thus its diffusion coefficient can be readily determined through facile CV experiments.

It is important to note that these approximations will only have an effect on the determination of the overall complexation constant and do not influence the evaluation of the metal-ligand stoichiometry.

Based on these assumptions, the linear relationship between

\[-z_i F(\text{RT}) \left( \Delta_{w}^{\text{IL}} \overline{\Phi}^{\alpha^+} - \Delta_{w}^{\text{IL}} \overline{\Phi}^{\alpha^0} \right) \text{ and } \ln \left( c_{\text{CMPO,IL}}^{*} \right) \]

for Cell 7.3.2 was developed and is shown in Figure 7.3.5; the overall stoichiometry for Cell 7.3.2 was determined to be 2 with \( \ln \beta \) equal to 18.4 ± 1.3 or a complexation constant of \( 2.4 \times 10^6 \) with an \( R^2 \) value of 0.9165, indicating reasonably good linear correlation.

Interestingly, the stoichiometry from Cell 7.3.2 closely mirrors that obtained at the w|DCE interface for Cell 7.3.1; however, the complexation constant is 73 times higher. Using conventional means of extraction, the distribution ratio of the metal species has been shown to be higher in water-IL separations versus traditional molecular organic
solvents [16, 18, 19]; therefore, the present result is in good agreement with these previous reports as it further illustrates the improved extraction capabilities of ILs versus organic solvents, as was also demonstrated through electrochemistry recently [14].

In the case of Cell 7.3.2, the peak-to-peak separations for the forward and reverse FIT and simple IT are high, with average values of 150 and 280 V. It was proposed that this may be owing to a lack of electrolyte in the aqueous phase since RbNO₃ was both analyte and supporting electrolyte; since Rb⁺ and NO₃⁻ ions are transferred, a depletion zone may be generated near the ITIES so that no charge carriers are present, resulting in a resistance increase and an increase in peak to peak separation. In order to test this, Cell 7.3.3 was employed; only rubidium salts were used as to avoid unwanted complexation with alternative metal salts which may lead to ambiguous results.

Similarly, for Cell 7.3.3, containing both 2 mM RbNO₃ and 2 mM Rb₂SO₄ in the aqueous phase, the FIT peak shifts from 0.230 to 0.178 and 0.140 V as shown in Figure 7.3.4 E, F, G, and H with CMPO concentrations of 0, 60, 70, and 90 mM, respectively, using a scan rate of 0.020 V s⁻¹. In the same way as Cell 7.3.2, the stoichiometry and complexation constant for Cell 7.3.3 were determined to be 4 and 3.3 × 10¹² (lnβ = 31.982 ± 0.3), respectively with the linear curve fitting shown in Figure 7.3.5A; and R² equal to 0.8992, showing a satisfactory linear trend. Figure 7.3.5B shows the proposed structure of RbCMPO₄⁺ with two CMPOs coordinating in a bidentate fashion and the remaining two CMPO molecules through a single phosphine oxide giving an overall octahedral geometry.

Interestingly, using the Rb₂SO₄ salt in conjunction with RbNO₃ reduced the peak to peak separation to 0.065 and 0.250 V for FIT and IT, respectively. However, the stoichiometry changed from 2 to 4, which may be owing to increased ion-pair formation or coordination between Rb⁺ and SO₄²⁻. Similar to the metal electrode, the liquid|liquid interface has been described using a Gouy-Chapman model [63] as a compact interface with two back to back diffuse layers where non-faradaic processes, such as absorption of chemical species, can occur. Thus, Rb⁺ and NO₃⁻ ions may aggregate at the ITIES and interact or associate more closely, allowing for intermolecular interactions and ion pair formation. These interactions may be strong enough to influence IT or FIT, thus leading to a change in stoichiometry. Recently, Girault et al. [46] demonstrated that metals salts
paired with different anions could possess a change in the free metal IT potential at a w/DCE microhole ITIES. An similar phenomena may also be at work here, increasing the number of CMPO molecules necessary to induce FIT.

**Figure 7.3.5:** A: Plot of \( \frac{zF}{RT} \left( \Delta_{w o}^\phi_{M^{n+}_L} - \Delta_{o}^\phi_{M^{n+}_L} \right) \) versus ln[CMPO]\text{initial} with metal-ligand transfer potentials obtained from CVs shown in Figure 7.3.4. B: Proposed structure of RbCMPO\text{4}^+.

RbCMPO\text{4}^+ was not observed during the ESI-MS experiments. Similar concentrations were employed, including 2 mM RbNO\text{3} and 2 mM Rb\text{2}SO\text{4} with a DCE phase containing 100 mM CMPO (data not shown); the other stoichiometries of 1 and 2 were still present. In a recent publication \[14\], for the analysis of strontium complexation with CMPO, this simple ‘shake’ flask experiment was comparable to the more sophisticated Biphasic Electrospray Ionization Mass Spectroscopic (BEIS-MS) technique,
and confirmed the stoichiometry observed voltammetrically; SrCMPO\(^{2+}\) and SrCMPO\(^{3+}\). A BESI-MS/MS dispersion study [14], showed that the third CMPO was easily lost, producing a marked increase in the SrCMPO\(^{2+}\) ion peak [14].

A similar phenomenon may be occurring with Rb and CMPO such that the two additional CMPOs determined in RbCMPO\(^4+\) are only weakly associated and cannot be observed through ESI-MS. The ESI-MS data is in good agreement with the stoichiometry obtained electrochemically. The direct injection of an aqueous/IL emulsion was deemed unadvisable; first, the viscosity of the IL is prohibitive against its direct injection, and, secondly, the ionic components would most likely mask any signal from the RbCMPO complex owing to their high signal.

**7.3.4 - Conclusions**

The FIT of rubidium ion at liquid/liquid micro-interfaces was reported. At the w|DCE interface a ligand to metal stoichiometry of 2:1 and complexation constant of \(3.3 \times 10^4\) were determined. At the w|IL micro-ITIES two rubidium salts, RbNO\(_3\) and Rb\(_2\)SO\(_4\), were employed. First only RbNO\(_3\) was dissolved in the aqueous phase and the ligand to metal ion ratio was found to be 2:1 with a 73 times higher overall complexation constant of \(2.4 \times 10^6\) versus that obtained at w|DCE. An aqueous solution of RbNO\(_3\) with Rb\(_2\)SO\(_4\) was used to help improve the level of supporting electrolyte, which decreased the peak-to-peak separation of the FIT forward and reverse waves and resulted in a ligand to metal ratio of 4 with the complexation constant equal to \(3.3 \times 10^{12}\). It was proposed that this increase in the stoichiometric equivalents of CMPO is the result of an increase in ion-ion or ion-pair formation between rubidium and sulfate.

The recently developed ESI-MS analysis of emulsions formed by shaking the water and DCE phases is a powerful tool to corroborate the complex stoichiometry obtained by electroanalytical chemistry at micro w|DCE interfaces.

**7.3.5 - References**


7.4 - Electrochemical assessment of water|ionic liquid biphasic systems for nuclear waste reclamation

7.4.1 - Introduction

Room temperature ionic liquids (ILs), large organic salts with melting points below 100°C, have attracted a great deal of attention over the past decade with the development of air and water stable versions. The increased interest is due in no small part to their unique properties including a high electrochemical stability that gives rise to large potential windows [1-3], but with a distinct interfacial structure [4-8]. This, in conjunction with ILs low volatility, non-flammability, and high thermal stability make them desirable solvents for a variety of applications including sensors [9], lithium batteries [10, 11], and in biphasic metal extraction [12-18]. ILs have shown marked improvement over conventional molecular solvents in many of these areas [13].

Interestingly, ILs incorporating quaternary phosphonium cations, such as trihexyltetradeylphosphonium (P\text{66614}+) and tetraoctylphosphonium (P\text{8888}+), have been found to possess higher electrochemical stability over ammonium- or imidazolium-based ILs [3], while also demonstrating greater hydrophobicity [19, 20]. Additionally, the tetrakis(pentafluorophenyl)borate anion (TBF−) has been shown to have good electrochemical stability [21], excellent hydrophobicity [19, 20, 22], and, critically, low ion-pair interactions [21-23]. Combining these cations and anions generates ILs with excellent physico- and electrochemical properties to make them ideally suited, not only in the role of conventional supporting electrolytes, but also as alternative solvents in biphasic metal ion extractions [13] for spent nuclear fuel (SNF) reprocessing.

Recently, ILs combining quaternary alkyl phosphonium cations with TBF− have been prepared to explore their implications in biphasic separations towards SNF reclamation [19, 20]. Typically, metal ion extractions are characterized by first mechanically mixing the two phases and then determining the amount of metal ions distributed between the two phases [13, 24]. Where these methods differ is in the analysis of metal ion distribution between the phases. Some techniques employ radioisotopes and absorption spectroscopy [25] or inductively coupled plasma (ICP) spectroscopy [18], which can be expensive and require a specialized laboratory or handling procedures.
Electrochemistry at a micro-interface between two immiscible electrolytic solutions (micro-ITIES) offers a cost-effective technique for studying metal ion transfer (IT) and ligand assisted, or facilitated ion transfer (FIT) [12, 14, 26-28], which are analogous to ion partitioning and interfacial complexation, respectively. These respective processes are shown in equations 1.4 and 1.6 for the general case of an ion, $i$, of charge $z_i$ with from water, w, to an organic, o, phase. Whereas for FIT, a ligand, L, is added to the organic (or IL) phase and coordinates to the metal ion center interfacially with a stoichiometry of $n$. The mechanism described in equation 1.6 is commonly referred to as transfer through interfacial complexation (TIC) with the return process termed transfer through interfacial decomplexation (TID); however, two other mechanisms are possible and are illustrated in Figure 1.3 [29]. In one scenario the metal transfers to the organic phase with subsequent complexation (TOC), while another pathway is through ligand transfer to the aqueous phase followed by complexation and transfer to the organic phase, often abbreviated as ACT [29].

ITIES or biphasic electrochemistry has been the subject of many reviews [30-33]. The so-called soft interface is a vital electrochemical technique, which has been used for biomimetic studies of oxygen reduction catalyzed by metalloporphyrins [34] and metal-free porphyrins [35], IT and ion absorption studies at microhole arrays utilizing a liquid/organogel interface with possible sensor applications [36-38], kinetic investigations of pharmaceutical micro-extraction/transfer [39, 40], along with nano-pore investigations [41]. These examples simply serve to demonstrate the far reaching implications and impact of this methodology.

Herein, octyl(phenyl)-N,N’-diisobutylcarbamoylphosphine oxide (CMPO), a ligand employed industrially in the TRans-Uranium EXtraction (TRUEX) processes [25], has been used, along with the ionic liquid, P$_{6614}$TB, as a model system to demonstrate the use of ILs in metal extraction at electrified biphasic interfaces. Owing to the hydrophobic character of CMPO only the TIC/TID mechanism has been considered.

FIT can be characterized by electrochemistry such that the overall complexation constant and metal to ligand (1:$n$) ratio can be determined [28]. This technique was pioneered by Samec, Mareček et al. [42], Kakiuchi and Senda [43], and Girault et al. [28]
for the water|organic (w|o) interface but recently the field has expanded to include the water|IL (w|IL) interface [12, 14, 16, 44].

Cesium was chosen as $^{137}\text{Cs}$ is a common fission byproduct that contributes greatly to the radioactivity and thermal heat of SNF (in conjunction with $^{90}\text{Sr}$) [45], while having well established w|1,2-dichloroethane (w|DCE) and w|P$_{66614}$TB free metal ion transfer characteristics [22, 46, 47]. These two factors should elicit interest from the nuclear community.

7.4.2 - Experimental

Chemicals. All chemicals were purchased as reagent grade or higher and used as received without further purification. Cesium nitrate (CsNO$_3$), cesium chloride (CsCl), tetrabutylammonium chloride (TBACl), 1,2-dichloroethane (DCE), and dichloromethane were obtained from Sigma-Aldrich Canada Ltd. (Mississauga, ON). Trihexyltetradecylphosphonium chloride (P$_{66614}$Cl) was bought from Strem (Strem Chemical Inc., Newburyport, MA) while potassium tetrakis(pentafluorophenyl)borate (KTB) was ordered from Boulder Scientific Company (Mead, CO). P$_{66614}$TB was prepared through the metathesis of P$_{66614}$Cl with KTB in dichloromethane; this procedure, along with purification steps, has been described in detail elsewhere [19, 20].

Micropipette Fabrication. A few recent publications describe the micropipette fabrication [19, 20, 46], as well as section 2.3.3.

Electrochemistry. All electrochemical measurements were performed using the Modulab system from Solatron Analytical (Ametek Advanced Measurement Technology, Farnborough, New Hampshire) incorporating a femto ammeter. The working electrode (WE) was fitted with a BNC adaptor and attached to a modified HEKA micropipette holder (HEKA Electronics, Mahone Bay, NS) containing an integrated silver wire held within the aqueous phase that was maintained inside the microcapillary. The counter (CE) and reference electrode (RE) leads were coupled together and clipped to another silver wire which was placed in the organic or P$_{66614}$TB phase. Two biphasic cells were employed and are given schematically below:
All w|DCE measurements were conducted at room temperature, however all IL experiments were performed at 60°C in order to reduce the IL viscosity [19]. Additionally, in order to ensure that the micro-interface was maintained at the tip of the pipette, the micro-ITIES was monitored continuously using a CCD camera (Motic Inc., Richmond, BC) attached to a 12× zoom lens assembly (Navitar, Rochester, NY) and linked to a desktop computer via a USB cable. The ITIES position could be adjusted using a syringe incorporated into the design of the micropipette holder. The holder has previously been described [12, 48].

Electrospray Ionization Mass Spectroscopy (ESI-MS). All mass spectra were obtained using a Micromass LCT (Waters, Milford, MA) in the positive ion mode with the following instrument parameters: capillary, sample cone, and extraction cone voltage of 5000, 42, and 0 V along with a sampling time, scan time, and interscan delay of 5 minutes, 4 seconds, and 0.1 seconds. The spectrum ranged from 80 to 2000 m/z. Solutions were loaded into a 250 μL syringe (Hamilton Co., Reno, NV) and placed in a syringe pump set at 25 μL·min⁻¹.

7.4.3 - Results and Discussion

7.4.3.1 Facilitated ion transfer of Cs⁺ with CMPO at w|DCE micro-ITIES

Figure 7.4.1 shows an overlay of cyclic voltammograms (CVs) acquired at a w|DCE interface utilizing Cell 7.4.1 with 5 mM of CsNO₃ in the aqueous phase while varying the concentration of CMPO in the organic phase.
**Figure 7.4.1:** Cyclic voltamogramms acquired using Cell 7.4.1 with a CMPO concentration \((y)\) equal to 0, 22, 43, 62, 80, and 96 mM, for curves a, b, c, d, e, and f, respectively at a scan rate of 0.025 V·s\(^{-1}\).

Trace (a) in Figure 7.4.1 illustrates the Cell 7.4.1 with no ligand added \((y = 0)\) or a ‘blank’ solution. The CV was initiated at 0.000 V and swept in the forward direction – towards more positive potentials – at a rate of 0.025 V·s\(^{-1}\). The rise in the current response at 0.448 V marks the edge of the polarizable potential window (PPW) and corresponds to the free or simple ion transfer (IT) of cesium cations from the water to organic phase \((w\ to\ o)\) [46]. The system was scanned in the reverse direction to 0.000 V. This generates a featureless curve and is demonstrative of no IT or ligand assisted/FIT. After addition of CMPO, however, the current-potential response undergoes a significant change. It is important to note that the PPW scanned in trace (a) is smaller than that employed for the ligand added cases; this was intentional. As demonstrated recently, free
alkali metal IT can be observed; however, this results in the massive transfer of ions that can undermine interfacial stability [46].

During the forward sweep of trace (b) in Figure 7.4.1 with $y = 22$ mM, from 0.000 to 0.641 V, a peak-shaped wave can be observed at 0.485 V. During the reverse scan, from 0.641 to 0.000 V, an “s”-shaped or sigmoidal wave can be observed with a half-wave potential of 0.330 V. This CV profile is in good agreement with the FIT of cesium by CMPO at a micro-ITIES [49].

The peak-shaped wave on the forward scan and the sigmoidal wave on the reverse are a direct result of the pipette geometry. During TIC, the small volume of material within the microchannel means Cs$^+$ is quickly consumed generating a rapid increase in the current-potential response followed by exponential decay. This is sometimes called linear diffusion owing to the limited direction ions can travel within the microchannel. However, it is also referred to as being under ‘consumption’ control because of the peak-shaped waves dependence on the square root of the scan rate ($v$) according to the Randles-Sevčik equation, equation 2.7 [50, 51]. The sigmoidal wave of TIC is the result of hemispherical diffusion because the flux of ions to the interface can occur from a relatively large hemispherical volume surrounding the ITIES, which elicits a rise in current followed by a plateau. In this way, the FIT observed is in good agreement with established theory surrounding ion transfer at an ITIES housed at the tip of a pulled microcapillary [52] and with that presented recently [12, 14, 27].

Interestingly, as the concentration of CMPO in the organic phase is increased this peak shifts to more positive potentials. With $y$ equal to 43, 62, 80, and 96 mM for curves c, d, e, and f, the peak associated with FIT shifts to 0.479, 0.467, 0.461, and 0.450 V, respectively. As the concentration of ligand in the organic phase increases, this causes a reduction in the amount of applied potential required to elicit ion transfer. Thus, the CVs overlaid in Figure 7.4.1 agree well with the theory of FIT [28]. This can be further elucidated through the following equation 6.1.2 [28].

The formal IT potential of the metal ion-ligand complex, $\Delta_{o}^{\omega} \phi_{z\omega}^{c}$, was obtained directly from the CV. $\Delta_{o}^{\omega} \phi_{z\omega}^{c}$ is the formal IT potential of the free metal ion, which is a constant unique to each metal ion and biphasic system; this was taken to be 0.480 V [22]. The variables $n$, $c_{i \omega}^{\ast}$, and $\beta$, are the metal to ligand stoichiometry (1:$n$), initial ligand concentration, and overall complexation
constant, respectively. In this way, by varying the initial concentration of the ligand and plotting $\ln(c^*_{L,o})$, a linear relationship can be developed such that the slope is the metal to ligand stoichiometry whilst the y-intercept can be used to elucidate the overall complexation constant. The potential scale has been calibrated using the tetraphenylarsonium tetraphenylborate (TATB) [53], or Parker’s [54] assumption which use well established IT potentials of simple ions, such as tetramethylammonium (TMA$^+$; 0.160 V [55]) or nitrate (NO$_3^-$; −0.380 V [46]), as internal standards through equation 2.9. The half-wave potentials were determined from the peak potential, $\Delta_o^+\phi_p$, and through equation 3.4 as described in Bard and Faulkner [50, 51].

Applying this methodology to the CV data illustrated in Figure 7.4.1 we can arrive at the linear graph displayed in Figure 7.4.2. The linear regression results are listed as an inset in Figure 7.4.2 whereby, the slope is 1, the y-intercept is 4.46, and the $R^2$ is 0.971. If the diffusion coefficients in the organic and aqueous phases are assumed to be approximately equivalent then equation 7.4.4 can be simplified and $\ln \beta_n$ directly extrapolated; in this case $\beta_n$ is 86.5. The relatively high $R^2$ value shows a satisfactory linear trend.

![Figure 7.4.2](image)

**Figure 7.4.2:** Graph of $-zF/(RT)\left(\Delta_o^+\phi_p^{w'} - \Delta_o^+\phi_f^{w'}\right)$ versus $\ln(c^*_{L})$ with, inset, linear regression data for the slope ($n = 1$) and $R^2 = 0.971$. 
CMPO coordinates predominantly to the metal ions through the oxygens on the carbamoyl or phosphine oxide groups, while the latter is the most preferred [15, 56]. Alkali ligand coordination chemistry is presented extensively in the literature, with the state of research being reviewed annually [57]. Cesium coordination numbers (c.n.) can be high when considering the ubiquitous dibenzo-crown-ether series of ligands, generating c.n. equal to 6 or, in the case of sandwich compounds, 12 or higher [58, 59]. Comparatively, the electrochemistry detailed herein points to only one CMPO and, therefore a maximum c.n. of 2. Chapters 7.1, 7.2, and 7.3 describe the studies of dioxouranium, strontium, and rubidium FIT and these metals were shown to have w/DCE ligand stoichiometries [12, 14, 27] of 2 or 3; therefore, the result for Cs⁺ was highly feasible. In fact the low Cs:CMPO ratio is more a result of the decreased hydrophilicity of cesium, relative to other alkali and alkali earth metals, rather than its poor coordination [46, 48]. Owing to the relatively high hydrophilicity of rubidium and strontium, they would require a higher number of ligands to elicit IT while cesium does not. Indeed, until recently cesium was one of the few alkali metal ions whose IT could be observed at the w/DCE interface [55, 60].

7.4.3.2 Stoichiometry confirmation using Electrospray Ionization Mass Spectroscopy

Figure 7.4.3 illustrates the mass spectrum obtained through direct injection of an emulsified water-DCE biphasic mixture containing 20 mM CsNO₃ and 100 mM CMPO, respectively, into the Electrospray Ionization Mass Spectrometer (ESI-MS). In this experiment, 100 μL of the cesium nitrate aqueous solution, along with 100 μL of the DCE ligand solution, were placed in a small flask and shaken. Figure 7.4.3 shows the four mass peaks of interest occurring at 132.9, 408.3, 540.2, and 947.5 m/z corresponding to Cs⁺, [CMPO + H]⁺, [CsCMPO]⁺, and [CsCMPO₂]⁺, respectively. ¹³².⁹Cs is the 100% abundant isotope of cesium [61] and thus its peak at 132.9 m/z shows no perceivable distribution pattern. This also greatly simplifies the isotopic distribution analysis for the remaining peaks, which possess the typical descending mass pattern common to most hydrocarbons. This can be seen in the [CMPO + H]⁺ mass peak, but more notably for the [CsCMPO]⁺ and [CsCMPO₂]⁺, which are shown as magnified insets with their respective calculated distribution profiles displayed below. The experimental and calculated profiles are in excellent agreement.
Figure 7.4.3: Mass spectrum recorded through direct injection of an emulsified biphasic solution containing 100 mM of CMPO in the DCE phase and 20 mM of CsNO₃ in the aqueous phase. Inset, above are magnified sections of the mass spectrum whilst below are calculated isotopic distributions for [CsCMPO]⁺ (540.2 m/z) and [CsCMPO₂⁺] (947.5 m/z).

These data generating a 1:1 metal ion to ligand stoichiometry, are in good agreement with that observed electrochemically, along with previous reports for rubidium [14] and strontium [12].

7.4.3.3 Investigation of Cs-FIT at the w|P₆₆₆₁₄TB interface

Figure 7.4.4A illustrates the CV obtained at a w|IL micro-interface using Cell 7.4.2 with no ligand added to the IL phase (y = 0). The scan was initiated at approximately −0.180 V and was swept at a rate of 0.020 V∙s⁻¹ with a potential range from −0.250 to 0.575 V. During the forward scan, a peak-shaped wave can be observed with a peak potential at −0.018 V; this is indicative of TBA⁺ transfer from w to IL. The edge of the PPW was reached at 0.522 V, upon which the scan direction was switched and proceeded towards negative potentials until −0.256 V. Within the reverse scan another peak-shaped wave can be observed and is owing to the transfer of TBA⁺ back from the IL to w.

The w|IL interface is distinct from the w|DCE interface as the increased viscosity within the IL phase translates into a lower diffusion coefficient. Diffusion within the IL
phase is slow enough that the mechanism of IT changes from hemispherical, or diffusion controlled, to linear, or consumption controlled; this is the primary reason that the reverse wave is peak-shaped and not sigmoidal as in the case of the w|DCE interface.

**Figure 7.4.4:** Cyclic voltammograms (CV) obtained using Cell 7.4.2 with CMPO concentrations (y) of 0, 27, 48, 62, and 82 mM for traces A, B, C, D, and E, respectively. Instrument parameters included a scan rate of 0.020 V·s$^{-1}$, an initial potential of ~0.000 V, and a potential range from approximately ~0.250 to 0.575 V. All CVs have been calibrated using the TATB assumption and the simple IT of TBA$^+$; $\Delta_{w}^{w} \phi_{TBA^+}^{0'} = -0.173$ V.

The IT of TBA$^+$ was used as the internal reference, with $\Delta_{w}^{w} \phi_{TBA^+}^{0'} = -0.173$ V, according to the TATB assumption [53, 54] along with equations 2.9 and 3.4. The formal IT potential of TBA$^+$ at the w|P$_{66614}$TB interface was determined relative to the IT of tetramethylammonium [19]. The TBA cation was chosen as it transfers towards the negative end of the PPW and, therefore allows for better observation of the possible Cs$^+$-
FIT peaks. Nitrate ion transfer has been used previously [14] for the study of rubidium FIT. However, employing only CsNO₃ in the aqueous phase resulted in a physical instability in the ITIES when scanning to more negative potentials. Additionally, CsCl afforded a wider PPW as Cl⁻ transfer is more negative.

Utilizing the same strategy employed at the w|DCE interface, the initial ligand concentration was then altered from 27 mM to 48, 62, and 82 mM for traces B, C, D, and E in Figure 7.4.4 and, after the addition of the CMPO, a new peak appears with half-wave potentials at 0.243, 0.203, 0.166, and 0.131 V, respectively. Analogous to the w|DCE case, increasing the ligand concentration lowers the amount of applied potential required to elicit charge transfer. Using equation 7.4.4, with $\Delta_{IL}^{w}\phi_{o}^{\circ}$ equal to 0.518 V [47], the effect of $-zF/(RT)(\Delta_{IL}^{w}\phi_{o}^{\circ} - \Delta_{IL}^{w}\phi_{i}^{\circ})$ versus ln($c_{CMPO}^{*}$) was developed and illustrated in Figure 7.4.5. Linear regression analysis revealed a satisfactory fitting with an $R^2$ of 0.9196, a slope of 3, and a y-intercept of 21.65.

![Graph](image)

**Figure 7.4.5:** Plot of $-zF/(RT)(\Delta_{IL}^{w}\phi_{o}^{\circ} - \Delta_{IL}^{w}\phi_{i}^{\circ})$ versus ln($c_{CMPO,IL}^{*}$) with, inset, linear regression data for the slope (i.e., metal to ligand, 1:n ratio, n = 3), y-intercept relationship [ln$\beta$ + ln$\xi$] = 21.65, and $R^2 = 0.9196$. 
This is interesting as it indicates 3 CMPO molecules participated in the interfacial complexation reaction, which translates to a higher overall complexation constant. Unfortunately, the high viscosity of the IL phase means the diffusion coefficient ratio found in the final term of equation 6.1.2 cannot be ignored. Previous studies of ferrocene diffusion in conventional electrochemistry [19] provide an estimate for the $\xi$ term with a $D_{IL}$ equal to $5.0 \times 10^{-9}$ cm$^2$/s$^{-1}$, while $D_{w}$ was estimated to be $2.0 \times 10^{-5}$ cm$^2$/s$^{-1}$. Ferrocene, an organo-metallic compound, provides a facile analog for the metal ion-ligand complex and its diffusion coefficient was used as an approximation for the metal ion-ligand complex in the IL phase. In this way, the overall complexation constant, for CsCMPO$_3^+$, was calculated to be $1.6 \times 10^{11}$. The relatively high stoichiometry, $n = 3$, points to a possible octahedral ligand coordination geometry to reduce steric hinderance between ligands. This is a common metal ion:ligand ratio, along with $n$ equal to 2, for alkali, alkali earth, and even heavier lanthanide metals undergoing complexation with CMPO [12, 56].

Traditionally, metal ion extraction is evaluated through distribution ratios [17, 18, 25], for example through the following:

$$\delta_\alpha = \frac{[Cs_{RTIL}^+]}{[Cs_{aq}^+]},$$

(7.4.1)

Where a theoretical $\delta_\alpha$ can be determined using the kinetic/thermodynamic parameters described herein and by equation 7.4.8:

$$K_{n,\alpha} = \frac{c_{i\alpha}c_{\alpha}}{c_{i,n-1,\alpha}c_{L,\alpha}} \text{ or } \beta_\alpha = \frac{c_{i\alpha}c_{\alpha}}{c_{i,j,\alpha}(c_{L,\alpha})^n} = \prod_{j=0}^{n} K_{j,\alpha}$$

(7.4.2)

In this way, $(c_{L,\alpha})^\beta \approx \delta_\alpha$ and a general comparison can be made such that the distribution ratio for the $w|DCE$ is only 2 at the highest ligand concentration, but $8.2 \times 10^7$ for the $w|IL$ case.

Interestingly, this result seems to demonstrate that Cs-FIT at the $w|P_{6614}$TB interface using CMPO as a ligand, has some benefits relative to $w|DCE$ complexation. First, a lower applied potential to elicit metal ion complexation is a serious advantage as this means less energy needs to be applied to the system in order to achieve separation.
Additionally, the high w|IL complexation constant reveals a substantial theoretical distribution coefficient, that also suggests improved efficiency.

However, 3 equivalents of ligand are required at the w|P\textsubscript{66614}TB interface versus only 1 at w|DCE. This is in contrast to recent studies surrounding rubidium [14] and strontium [12] described in chapters 7.2 and 7.3, respectively, which demonstrated a marked improvement for the w|IL versus the w|DCE system. Critically, this points to a possible advantage in selectivity towards Rb\textsuperscript{+} and Sr\textsuperscript{2+} versus Cs\textsuperscript{+} that could be capitalized upon for SNF reclamation.

7.4.5 - Conclusions

A model system for biphasic metal ion extraction was developed, comprised of the ionic liquid P\textsubscript{66614}TB. This IL was chosen owing to the excellent electrochemically stable cation/anion pair that have been shown to possess weak ion-pair interactions and extreme hydrophobicity. FIT of Cs\textsuperscript{+} with CMPO, a common ligand employed in industrial SNF recycling, was studied at a IL interface electrochemically and compared to the well established w|DCE interface. The former elicited a metal ion to ligand (1:n) stoichiometry of 1:3 with an overall complexation constant, $\beta$, estimated to be $1.6 \times 10^{11}$, while the latter demonstrated an $n$ equal to 1 with $\beta$ equal to 86.5. Previous results showed higher complexation constants for strontium and rubidium at the w|P\textsubscript{66614}TB interface. This may suggest a higher selectivity for these ions over cesium using this biphasic system.

The CsCMPO stoichiometry at the w|DCE interface was confirmed through the use of ESI-MS and a ‘shake-flask’ experiment.

7.4.6 - References

Chapter 8
8.1 - Conclusions

The overarching goal of this thesis was to investigate the suitability of room temperature ionic liquids (IL) for biphasic metal ion extraction for spent nuclear fuel (SNF) reclamation. The development of possible water|IL (w|IL) sensors for commercial applications was also a powerful motivator. Early ILs were found to have high metal extraction efficiencies [1, 2]; however, loss of the anionic or cationic components through ion exchange presents a serious challenge. Increasing the hydrophobicity of the IL was the most facile approach to preventing the leaching, or ion exchange of IL components to the water phase. In this way, the IL hydrophobicity became a critical physicochemical property; however, the structure of the w|IL and metal-IL interfaces were also of considerable interest.

Evaluation of IL hydrophobicity was approached in two ways as described in Chapter 2. Initially, the behavior of organic solvent/IL and water/IL mixtures using a commercial IL, tributylmethylphosphonium methyl sulphate (P_{4441}CH_{3}SO_{4}), and two redox probes were investigated. In two separate experiments, either water or the organic solvent 1,2-dichloroethane (DCE) as added to the IL containing the electroactive species or redox probe. At each addition of water or DCE the mixtures were evaluated electrochemically through the use of an ultramicroelectrode (UME). The redox couples were found to be quasi-reversible with small variations between the diffusion coefficients of the oxidized and reduced forms, measured using a concentration-independent chronoamperometric (CA) technique [3, 4].

The DCE/IL and water/IL mixtures were discovered to have very different results. In the DCE/IL case, a saturation point was reached such that the mixture took on the diffusion characteristics of a molecular solvent. While the water/IL mixture never became saturated. Therefore, the IL saturation point was concluded to be highly dependent on the ILs properties of hydrophobicity/hydrophilicity. The hydrophobicity of the IL was measured, using ion transfer (IT) electrochemistry at a 25 μm diameter interface between two immiscible electrolytic solutions (ITIES) using water|DCE (w|DCE). The liquid|liquid IT result confirmed that the IL, tributylmethylphosphonium methyl sulfate (P_{4441}CH_{3}SO_{4}), was moderately hydrophobic. Water and organic solvents
are often contaminants in ILs and these data provided critical insight into the electrochemical behaviour of IL mixtures. It was concluded that if the diffusion regime of this moderately hydrophobic IL was not greatly affected by water, then by extension a more hydrophobic IL would be less impacted.

The next step was to find a IL with sufficient hydrophobicity and this search is detailed in Chapter 3. Biphasic electrochemistry was utilized at both w|IL and w|DCE interfaces, and 8 commercially available candidates were analyzed [5]. While none of these ILs were hydrophobic enough, a few valuable cations and anions were identified that may generate a sufficiently hydrophobic IL by pairing them with a suitable counterion. Through the course of these investigations, critical improvements were made to the micropipette holder by incorporation of a syringe to back-fill the pipette, which could also be used to fine tune the position of the ITIES. By means of this improved micro-interface, the volume of material required was greatly reduced. Since ILs can be expensive, this made direct w|IL assessments more feasible. Simulation studies, using finite element analysis, were employed to investigate the effect of pipette geometry on the current-potential or cyclic voltammetric (CV) response. These simulations showed that a simplified fabrication procedure was the best approach and gave current responses close to theoretically predicted values.

Using the information gained in these early investigations, novel ILs were prepared in-house at greatly reduced cost (more than 10× less expensive). Their preparation, physicochemical, and electrochemical characterization are described in Chapter 4 [6, 7]. Simplified preparation and purification methods were introduced that generated electrochemically pure ILs at near quantitative yields [6, 7]. It is conceivable that this new discovery will help lower the cost of ILs and make them more attractive to large scale industrial processes.

The assessment of another 8 ILs prepared for polymer film applications is described in Chapter 5. These additives were made to improve the films, hydrophobicity for better 'non-stick' properties, as well as low quantity, charged monomer additives. Their hydrophobicity was described previously only by qualitative means through wet-ability tests on the finished polymer film; this is disadvantageous as it requires a lot of material (gram scale) to prepare an entire film. Herein, the hydrophobicity was measured
quantitatively at the w|DCE micro-ITIES using a modicum of IL starting material. Owing to their relatively high hydrophobicity, the IT of the IL cationic components appeared outside the PPW. Electrochemistry at the micro-interface developed in this thesis was able to probe these IT potentials that traditionally existed beyond the PPW. While the trend in hydrophobicity of these fluorinated and non-fluorinated ILs agreed very well with the architecture of the compounds (length of alkyl chains and degree of fluorination), it was concluded that fluorinated alkyl chains only provided a small increase in the hydrophobicity over non-fluorinated ILs of similar alkyl chain length. This conclusion does not agree with published results and may point to a disadvantage of these direct electrochemical measurements, since liquid|liquid electrochemistry cannot account for synergistic effects provided by the fully assembled polymer film. Therefore, liquid|liquid electrochemistry was considered a complementary technique that can aid in decision-making early in a synthetic program.

Moving forward, the free metal formal IT potential is an essential thermodynamic constant used to assess ligand-assisted or facilitated ion transfer (FIT). The study of metal IT that limits the polarizable potential window (PPW) was a critical aspect of this work and employed both the w|DCE [8-10], and w|IL interfaces [11] (Chapter 6). An ITIES using a microhole and micropipette electrolytic cells [9] allowed for the estimation of these valuable constants a with no supporting electrolyte and a conventional supporting electrolyte concentrations, respectively. It has been found that large organic salts employed as supporting electrolyte in the organic phase can aid metal IT through mechanism similar to FIT using ligands [12]. Therefore, the constants determined in these studies, at conventional supporting electrolyte concentrations for w|DCE systems, are effective formal IT potentials. In this way, for a known amount of organic phase supporting electrolyte, this approach provided a baseline formal IT potential for a series of metals.

Finally, FIT was investigated at the w|DCE and w|IL interfaces. Several metals, including UO$_2^{2+}$, Sr$^{2+}$, Rb$^+$, and Cs$^+$, were evaluated individually, so that the selectivity and efficiency could be compared [13-15]. The ligand stoichiometry, $n$, and overall complexation constants, $\beta$, were determined electrochemically and verified, for the w|DCE case, by mass spectrometry for the first time. Multiple FIT peaks were observed
in several metal ion-ligand systems; these were resolved and evaluated individually for the first time, herein. Table 8.1 lists the FIT results for w|IL and w|DCE micro-interfaces for the metal salts evaluated in Chapter 7.

**Table 8.1**: Summary of FIT results, ligand stoichiometry, $n$, and overall complexation constant, $\beta$, for the metal salts described in Chapter 7 using the ligand CMPO at both w|IL and w|DCE micro-interfaces; the IL in all cases was trihexyltetradecylphosphonium tetrakis(pentafluorophenyl)borate.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Metal Salt</th>
<th>$n$</th>
<th>$\beta$</th>
</tr>
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<tr>
<td>w</td>
<td>IL</td>
<td>RbNO$_3$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>RbNO$_3$ + Rb$_2$SO$_4$</td>
<td>4</td>
<td>$3.3 \times 10^{12}$</td>
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<tr>
<td></td>
<td>CsNO$_3$</td>
<td>3</td>
<td>$1.6 \times 10^{11}$</td>
</tr>
<tr>
<td></td>
<td>Sr(NO$_3$)$_2$</td>
<td>3</td>
<td>$1.5 \times 10^{34}$</td>
</tr>
<tr>
<td>w</td>
<td>DCE</td>
<td>RbNO$_3$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>CsNO$_3$</td>
<td>1</td>
<td>86.5</td>
</tr>
<tr>
<td></td>
<td>Sr(NO$_3$)$_2$</td>
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<td>$4.5 \times 10^{19}$</td>
</tr>
<tr>
<td></td>
<td>UO$_2$(NO$_3$)$_2$</td>
<td>3</td>
<td>$5.5 \times 10^{25}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>$8.8 \times 10^{14}$</td>
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<tr>
<td></td>
<td></td>
<td>5</td>
<td>$6.5 \times 10^{32}$</td>
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</tbody>
</table>

The values of $n$ and $\beta$ given in Table 8.1 provide an overall picture of CMPO complexation and large increases in the overall complexation constant are recorded for each metal ion when transitioning from w|DCE to the w|IL system. Therefore, it can be concluded that the w|IL interface shows greater efficiency for metal ion extraction than w|DCE. A greater selectivity of CMPO for strontium over uranium or cesium can also be inferred. Because $^{90}$Sr and $^{137}$Cs are major fission byproducts, the w|IL result is of considerable importance since this novel system could possibly provide an increased degree of selectivity for separating these two metal ions; this could be the solution for providing medicinal grade $^{90}$Sr for use within on-site $^{90}$Y generators for anti-cancer treatment [16].
The above micro-scale experiments also served as a proof-of-concept that electrochemistry, rather than the typical physical means of separation, may be used as a possible alternative separation method for SNF remediation. Physical separation requires a great deal of engineering; owing to the inherent radioactivity of the SNF being separated, maintenance of this equipment is prohibitively expensive. If an electrochemical method were to be used, the mechanical engineering could be reduced and thus the cost would go down. This would make reprocessing SNF more attractive and we could avoid long-term geological disposal, which has all kinds of potentially nasty repercussions.

8.2 - References

Appendix

Appendix A – Igor Procedure Files

A1 – Chronoamperometry

Igor fitting using the method developed by Shoup and Szabo; equations 4.1.5 and 4.1.6.

Code:

```plaintext
constant rd=1.25e-3
constant F=96485.33
constant n=1
constant c=7e-6

Function i_response2(w,t) : FitFunc
    Wave w
    Variable t

    //CurveFitDialog/ These comments were created by the Curve Fitting dialog. Altering them will
    //CurveFitDialog/ make the function less convenient to work within the Curve Fitting dialog.
    //CurveFitDialog/ Equation:
    //CurveFitDialog/ f(t) = -4*n*F*D*c*rd*(0.7854+0.8863*(4*D*t/(rd^2))^-0.5+0.2146*exp(-0.7823*(4*D*t/(rd^2))^-0.5))
    //CurveFitDialog/ End of Equation
    //CurveFitDialog/ Independent Variables 1
    //CurveFitDialog/ t
    //CurveFitDialog/ Coefficients 2
    //CurveFitDialog/ w[0] = D
    //CurveFitDialog/ w[1] = nc

    return 4*F*w[0]*w[1]*rd*(0.7854+0.8863*(4*w[0]*t/(rd^2))^-0.5+0.2146*exp(-0.7823*(4*w[0]*t/(rd^2))^-0.5))

End
```

A2 – Linear Sweep Voltammetry Curve Fitting

The following was developed using equation 6.3.3 and 6.3.2, respectively, in an Igor procedure window or, alternatively through the custom curve fitting suite available in version 6 or higher:

Code:

constant F=96485.33
constant T = 298.15
constant R = 8.314

Function Wilke(w,E) : FitFunc
    Wave w
    Variable E

        //CurveFitDialog/ These comments were created by the Curve Fitting dialog.
        Altering them will
        //CurveFitDialog/ make the function less convenient to work with in the Curve
        Fitting dialog.
        //CurveFitDialog/ Equation:
        //CurveFitDialog/ f(E) = lim*(1+exp(z*F/(R*T)*(E
        1+exp((z*F/(R*T)*(E
        //CurveFitDialog/ End of Equation
        //CurveFitDialog/ Independent Variables 1
        //CurveFitDialog/ E
        //CurveFitDialog/ Coefficients 3
        //CurveFitDialog/ w[0] = lim
        //CurveFitDialog/ w[1] = E1/2
        //CurveFitDialog/ w[2] = z

        return w[0]*(1+exp(w[2]*F/(R*T)*(E-w[1])))^2-1))
End

Function inv_master(E,I) : FitFunc //inverse master equation approach
    Wave E
    Variable I

        //CurveFitDialog/ These comments were created by the Curve Fitting dialog.
        Altering them will
        //CurveFitDialog/ make the function less convenient to work with in the Curve
        Fitting dialog.
//CurveFitDialog/ Equation: 
//CurveFitDialog/ f(I) = E1/2+RT/(zAF)*ln((1-zA/zB)(I/(lim-I))*(I/(Ilim-I))^(-
-zA/zB)))
//CurveFitDialog/ End of Equation
//CurveFitDialog/ Independent Variables 1
//CurveFitDialog/ I
//CurveFitDialog/ Coefficients 4
//CurveFitDialog/ E[0] = lim
//CurveFitDialog/ E[1] = E1/2
//CurveFitDialog/ E[2] = za
//CurveFitDialog/ E[3] = zb

return E[1]+E[4]/E[2]*ln((1-E[2]/E[3])*(I/(E[0]-I))*(E[0]/(E[0]-I))^(-E[2]/E[3]))

End
Appendix B – COMSOL Model Reports

Microhole ITIES - Nernst-Planck Model

COMSOL Model Report
1. Table of Contents
Title - COMSOL Model Report
Table of Contents
Model Properties
Constants
Geometry
Geom1
Integration Coupling Variables
Solver Settings
Variables
2. Model Properties

<table>
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<tr>
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File name: D:\documents\xxX-Thesis-\xxx\chapters\zzz-Appendix-Zzz\Nernst_Planck.mph

Application modes and modules used in this model:
Geom1 (Axial symmetry (2D))
Nernst-Planck (Chemical Engineering Module)
Nernst-Planck (Chemical Engineering Module)
Electrostatics

3. Constants

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<td>8.314 [J/(mol*K)]</td>
<td>8.314 [J/(mol*K)]</td>
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<tr>
<td>T</td>
<td>298.15 [K]</td>
<td>298.15[K]</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>96485.33 [C/mol]</td>
<td>96485.33[s A/mol]</td>
<td></td>
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<td>fara</td>
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<td>0.02[V/s]</td>
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<td>n1</td>
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<td>-1</td>
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<td>fara2</td>
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4. Geometry
Number of geometries: 1

4.1. Geom1

4.1.1. Point mode

4.1.2. Boundary mode
### 4.1.3. Subdomain mode

#### 5. Geom1

Space dimensions: Axial symmetry (2D)

Independent variables: r, phi, z

#### 5.1. Scalar Expressions

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<td>$E_i + nu \cdot t$</td>
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<td>kf1</td>
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![Diagram of Geom1](image1.png)
5.3. Application Mode: Nernst-Planck (chnp2)
Application mode type: Nernst-Planck (Chemical Engineering Module)
Application mode name: chnp2

5.3.1. Scalar Variables

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5.3.2. Application Mode Properties

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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default element type</td>
<td>Lagrange - Quadratic</td>
</tr>
<tr>
<td>Analysis type</td>
<td>Transient</td>
</tr>
<tr>
<td>Equation form</td>
<td>Non-conservative</td>
</tr>
<tr>
<td>Frame</td>
<td>Frame (ref)</td>
</tr>
<tr>
<td>Weak constraints</td>
<td>Off</td>
</tr>
<tr>
<td>Constraint type</td>
<td>Ideal</td>
</tr>
</tbody>
</table>

5.3.3. Variables

Dependent variables: V3, BAorg, Srorg, TBorg
Shape functions: shlag(2,'V3'), shlag(2,'Srorg'), shlag(2,'TBorg')
Interior boundaries not active

5.3.4. Boundary Settings

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Inward flux (N)</th>
<th>Concentration (c0)</th>
<th>Potential (V0)</th>
<th>cpType</th>
<th>sType</th>
</tr>
</thead>
<tbody>
<tr>
<td>10, 12, 14</td>
<td>mol/(m^2 s)</td>
<td>mol/m^3</td>
<td>V</td>
<td>Electric insulation</td>
<td>[N0;N0]</td>
</tr>
<tr>
<td>15-16</td>
<td>mol/(m^2 s)</td>
<td>[cSr1_org;cTBorg]</td>
<td>V</td>
<td>Potential</td>
<td>[C;C]</td>
</tr>
</tbody>
</table>

5.3.5. Subdomain Settings

<table>
<thead>
<tr>
<th>Subdomain</th>
<th>Diffusion coefficient (D)</th>
<th>Mobility (um)</th>
<th>Charge number (z)</th>
<th>Subdomain initial value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>m^2/s</td>
<td>s*mol/kg</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

5.4. Application Mode: Nernst-Planck (chnp)
Application mode type: Nernst-Planck (Chemical Engineering Module)
Application mode name: chnp

5.4.1. Scalar Variables

<table>
<thead>
<tr>
<th>Name</th>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>F_chnp</td>
<td>96485.3415</td>
<td>s*A/mol</td>
<td>Faraday's constant</td>
</tr>
</tbody>
</table>

5.4.2. Application Mode Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default element type</td>
<td>Lagrange - Quadratic</td>
</tr>
<tr>
<td>Analysis type</td>
<td>Stationary</td>
</tr>
<tr>
<td>Equation form</td>
<td>Non-conservative</td>
</tr>
<tr>
<td>Frame</td>
<td>Frame (ref)</td>
</tr>
<tr>
<td>Weak constraints</td>
<td>Off</td>
</tr>
<tr>
<td>Constraint type</td>
<td>Ideal</td>
</tr>
</tbody>
</table>

5.4.3. Variables

Dependent variables: V2, NO3aq, Sraq, TBaq
Shape functions: shlag(2,'V2'), shlag(2,'Sraq'), shlag(2,'TBaq')
Interior boundaries not active

5.4.4. Boundary Settings

<table>
<thead>
<tr>
<th>Boundary</th>
<th>5</th>
<th>4, 6-7</th>
<th>9, 11, 13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inward flux (N) mol/(m²s)</td>
<td>{kf1<em>Srorg-kb1</em>Sraq;kf2<em>TBorg-kb2</em>TBaq}</td>
<td>{0;0}</td>
<td>{0;0}</td>
</tr>
<tr>
<td>Concentration (c0) mol/m³</td>
<td>{0;0}</td>
<td>{0;0}</td>
<td>{0;0}</td>
</tr>
<tr>
<td>Potential (V0) V</td>
<td>Ei</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cpType</td>
<td>Potential</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sType</td>
<td>N:N</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Boundary</th>
<th>8, 17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inward flux (N) mol/(m²s)</td>
<td>{0;0}</td>
</tr>
<tr>
<td>Concentration (c0) mol/m³</td>
<td>{cSri_aq;cTBiaq}</td>
</tr>
<tr>
<td>Potential (V0) V</td>
<td>Ei</td>
</tr>
<tr>
<td>cpType</td>
<td>Potential</td>
</tr>
<tr>
<td>sType</td>
<td>{C;C}</td>
</tr>
</tbody>
</table>

5.4.5. Subdomain Settings

<table>
<thead>
<tr>
<th>Subdomain</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient (D) m²/s</td>
<td>{D_NO3;D_Sr;D_TB}</td>
</tr>
<tr>
<td>Mobility (um) s·mol/kg</td>
<td>{u_m3;u_m1;u_m2}</td>
</tr>
<tr>
<td>Charge number (z)</td>
<td>1</td>
</tr>
<tr>
<td>Charge number (z)</td>
<td>{-1;2;-1}</td>
</tr>
</tbody>
</table>

| Subdomain initial value | 2 |
| Potential (V2) V | Ei |
| Concentration, Sraq (Sraq) mol/m³ | cSri_aq |
| Concentration, TBaq (TBaq) mol/m³ | cTBiaq |

5.5. Application Mode: Electrostatics (es)

Application mode type: Electrostatics
Application mode name: es

5.5.1. Scalar Variables

<table>
<thead>
<tr>
<th>Name</th>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>epsilon0</td>
<td>epsilon0_es</td>
<td>8.854187817e-12</td>
<td>F/m</td>
<td>Permittivity of vacuum</td>
</tr>
</tbody>
</table>

5.5.2. Application Mode Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Default element type</td>
<td>Lagrange - Quadratic</td>
</tr>
<tr>
<td>Input property</td>
<td>Forced voltage</td>
</tr>
<tr>
<td>Frame</td>
<td>Frame (ref)</td>
</tr>
<tr>
<td>Weak constraints</td>
<td>Off</td>
</tr>
<tr>
<td>Constraint type</td>
<td>Ideal</td>
</tr>
</tbody>
</table>

5.5.3. Variables

Dependent variables: V
Shape functions: shlag(2,'V')
Interior boundaries not active

5.5.4. Boundary Settings

<table>
<thead>
<tr>
<th>Boundary</th>
<th>2, 15-16</th>
<th>8, 17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Ground</td>
<td>Electric potential</td>
</tr>
<tr>
<td>Electric potential (V0) V</td>
<td>Ei</td>
<td>E_swp</td>
</tr>
</tbody>
</table>
### Boundary Conditions

**Type**: Zero charge/Symmetry

**Electric potential (V0)**: V 0

### Subdomain Settings

<table>
<thead>
<tr>
<th>Subdomain</th>
<th>Relative permittivity (epsilon)</th>
<th>Space charge density (rho)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 {10.1,0;10.1}</td>
<td>-F*(2<em>Srorg+BAorg-TBorg) -F</em>(2*Sraq-NO3aq-TBaq)</td>
</tr>
</tbody>
</table>

### Subdomain initial values

<table>
<thead>
<tr>
<th>Subdomain</th>
<th>Electric potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V Ei Ei</td>
</tr>
</tbody>
</table>

### Integration Coupling Variables

#### 6.1. Geo1

##### 6.1.1. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>Ibar1</td>
</tr>
<tr>
<td>Expression</td>
<td>2<em>pi</em>r<em>F</em>(n1*flux_Srorg_chnp2+flux_NO3aq_chnp+flux_TBaq_chnp-flux_BAorg_chnp2)</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
<tr>
<td>Global</td>
<td>Yes</td>
</tr>
</tbody>
</table>

##### 6.1.2. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>IbarBA</td>
</tr>
<tr>
<td>Expression</td>
<td>2<em>pi</em>r<em>F</em>(flux_BAorg_chnp)</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
<tr>
<td>Global</td>
<td>Yes</td>
</tr>
</tbody>
</table>

##### 6.1.3. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>IbarSr</td>
</tr>
<tr>
<td>Expression</td>
<td>2<em>pi</em>r<em>F</em>(n1*flux_Srorg_chnp2)</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
<tr>
<td>Global</td>
<td>Yes</td>
</tr>
</tbody>
</table>

##### 6.1.4. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>IbarNO3</td>
</tr>
<tr>
<td>Expression</td>
<td>2<em>pi</em>r<em>F</em>(flux_NO3aq_chnp)</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
<tr>
<td>Global</td>
<td>Yes</td>
</tr>
</tbody>
</table>

##### 6.1.5. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>IbarTB</td>
</tr>
<tr>
<td>Expression</td>
<td>2<em>pi</em>r<em>F</em>(flux_TBaq_chnp)</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
<tr>
<td>Global</td>
<td>Yes</td>
</tr>
</tbody>
</table>

##### 6.1.6. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>Ibar2</td>
</tr>
<tr>
<td>Expression</td>
<td>-2<em>pi</em>r<em>F</em>(-n1*flux_Sraq_chnp-flux_TBorg_chnp2)</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
<tr>
<td>Global</td>
<td>Yes</td>
</tr>
</tbody>
</table>

##### 6.1.7. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>Ibar3</td>
</tr>
<tr>
<td>Expression</td>
<td>2<em>pi</em>r<em>F</em>(n1*flux_Sraq_chnp+flux_NO3aq_chnp+flux_TBorg_chnp2+flux_BAorg_chnp2)</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
<tr>
<td>Global</td>
<td>Yes</td>
</tr>
</tbody>
</table>

##### 6.1.8. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>Ibar4</td>
</tr>
<tr>
<td>Expression</td>
<td>2<em>pi</em>r<em>F</em>(n1*flux_Srorg_chnp2+flux_TBaq_chnp)</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
</tbody>
</table>
### Global

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

#### 6.1.9. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>IbarSraq</td>
</tr>
<tr>
<td>Expression</td>
<td>$2\pi r F (n1 * \text{flux}<em>\text{Sraq}</em>\text{chnp})$</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
<tr>
<td>Global</td>
<td>Yes</td>
</tr>
</tbody>
</table>

#### 6.1.10. Source Boundary: 5

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable name</td>
<td>IbarTBorg</td>
</tr>
<tr>
<td>Expression</td>
<td>$2\pi r F (\text{flux}<em>\text{TBorg}</em>\text{chnp2})$</td>
</tr>
<tr>
<td>Order</td>
<td>4</td>
</tr>
<tr>
<td>Global</td>
<td>Yes</td>
</tr>
</tbody>
</table>

### 7. Solver Settings

Solve using a script: off

<table>
<thead>
<tr>
<th>Analysis type</th>
<th>Transient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auto select solver</td>
<td>On</td>
</tr>
<tr>
<td>Solver</td>
<td>Time dependent</td>
</tr>
<tr>
<td>Solution form</td>
<td>Automatic</td>
</tr>
<tr>
<td>Symmetric</td>
<td>auto</td>
</tr>
<tr>
<td>Adaptive mesh refinement</td>
<td>Off</td>
</tr>
<tr>
<td>Optimization/Sensitivity</td>
<td>Off</td>
</tr>
<tr>
<td>Plot while solving</td>
<td>Off</td>
</tr>
</tbody>
</table>

#### 7.1. Direct (UMFPACK)
Solver type: Linear system solver

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pivot threshold</td>
<td>0.1</td>
</tr>
<tr>
<td>Memory allocation factor</td>
<td>0.7</td>
</tr>
</tbody>
</table>

#### 7.2. Time Stepping

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Times</td>
<td>range(0,0.5,50)</td>
</tr>
<tr>
<td>Relative tolerance</td>
<td>1e-5</td>
</tr>
<tr>
<td>Absolute tolerance</td>
<td>1e-5</td>
</tr>
<tr>
<td>Times to store in output</td>
<td>Specified times</td>
</tr>
<tr>
<td>Time steps taken by solver</td>
<td>Free</td>
</tr>
<tr>
<td>Maximum BDF order</td>
<td>5</td>
</tr>
<tr>
<td>Singular mass matrix</td>
<td>Maybe</td>
</tr>
<tr>
<td>Consistent initialization of DAE systems</td>
<td>Backward Euler</td>
</tr>
<tr>
<td>Error estimation strategy</td>
<td>Include algebraic</td>
</tr>
<tr>
<td>Allow complex numbers</td>
<td>Off</td>
</tr>
</tbody>
</table>

#### 7.3. Advanced

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constraint handling method</td>
<td>Elimination</td>
</tr>
<tr>
<td>Null-space function</td>
<td>Automatic</td>
</tr>
<tr>
<td>Automatic assembly block size</td>
<td>On</td>
</tr>
<tr>
<td>Assembly block size</td>
<td>1000</td>
</tr>
<tr>
<td>Use Hermitian transpose of constraint matrix and in symmetry detection</td>
<td>Off</td>
</tr>
<tr>
<td>Use complex functions with real input</td>
<td>Off</td>
</tr>
<tr>
<td>Stop if error due to undefined operation</td>
<td>On</td>
</tr>
<tr>
<td>Store solution on file</td>
<td>Off</td>
</tr>
<tr>
<td>Type of scaling</td>
<td>Automatic</td>
</tr>
<tr>
<td>Manual scaling</td>
<td></td>
</tr>
<tr>
<td>Row equilibration</td>
<td>On</td>
</tr>
<tr>
<td>Manual control of reassembly</td>
<td>Off</td>
</tr>
<tr>
<td>Load constant</td>
<td>On</td>
</tr>
<tr>
<td>Constraint constant</td>
<td>On</td>
</tr>
<tr>
<td>Mass constant</td>
<td>On</td>
</tr>
</tbody>
</table>
### 8. Variables

#### 8.1. Boundary

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>Unit</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>nJ_chnp2</td>
<td>Current density</td>
<td>A/m²</td>
<td>nJ_chnp2 * J_r_chnp2+ nz_chnp2 * J_z_chnp2</td>
</tr>
<tr>
<td>ndflux_BAorg_chnp2</td>
<td>Normal diffusive flux, B_Aorg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * dflux_BAorg_r_chnp2+ nz_chnp2 * dflux_BAorg_z_chnp2</td>
</tr>
<tr>
<td>ncflux_BAorg_chnp2</td>
<td>Normal convective flux, B_Aorg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * cflux_BAorg_r_chnp2+ nz_chnp2 * cflux_BAorg_z_chnp2</td>
</tr>
<tr>
<td>nmflux_BAorg_chnp2</td>
<td>Normal electrophoretic flux, B_Aorg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * mflux_BAorg_r_chnp2+ nz_chnp2 * mflux_BAorg_z_chnp2</td>
</tr>
<tr>
<td>ntflux_BAorg_chnp2</td>
<td>Normal total flux, B_Aorg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * tflux_BAorg_r_chnp2+ nz_chnp2 * tflux_BAorg_z_chnp2</td>
</tr>
<tr>
<td>ndflux_Srorg_chnp2</td>
<td>Normal diffusive flux, S_rorg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * dflux_Srorg_r_chnp2+ nz_chnp2 * dflux_Srorg_z_chnp2</td>
</tr>
<tr>
<td>ncflux_Srorg_chnp2</td>
<td>Normal convective flux, S_rorg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * cflux_Srorg_r_chnp2+ nz_chnp2 * cflux_Srorg_z_chnp2</td>
</tr>
<tr>
<td>nmflux_Srorg_chnp2</td>
<td>Normal electrophoretic flux, S_rorg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * mflux_Srorg_r_chnp2+ nz_chnp2 * mflux_Srorg_z_chnp2</td>
</tr>
<tr>
<td>ntflux_Srorg_chnp2</td>
<td>Normal total flux, S_rorg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * tflux_Srorg_r_chnp2+ nz_chnp2 * tflux_Srorg_z_chnp2</td>
</tr>
<tr>
<td>ndflux_TBorg_chnp2</td>
<td>Normal diffusive flux, T_Borg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * dflux_TBorg_r_chnp2+ nz_chnp2 * dflux_TBorg_z_chnp2</td>
</tr>
<tr>
<td>ncflux_TBorg_chnp2</td>
<td>Normal convective flux, T_Borg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * cflux_TBorg_r_chnp2+ nz_chnp2 * cflux_TBorg_z_chnp2</td>
</tr>
<tr>
<td>nmflux_TBorg_chnp2</td>
<td>Normal electrophoretic flux, T_Borg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * mflux_TBorg_r_chnp2+ nz_chnp2 * mflux_TBorg_z_chnp2</td>
</tr>
<tr>
<td>ntflux_TBorg_chnp2</td>
<td>Normal total flux, T_Borg</td>
<td>mol/(m²s)</td>
<td>nr_chnp2 * tflux_TBorg_r_chnp2+ nz_chnp2 * tflux_TBorg_z_chnp2</td>
</tr>
<tr>
<td>nJ_chnp</td>
<td>Current density</td>
<td>A/m²</td>
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<td>Maxwell surface stress tensor (r)</td>
<td>Pa</td>
<td>-0.5 * (up(Dr_es) * up(Er_es)+up(Dz_es) * up(Ez_es)) * dnr+(dnr * up(Dr_es)+dnz * up(Dz_es)) * up(Er_es)</td>
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<td>unTEz_es</td>
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<td>Pa</td>
<td>-0.5 * (up(Dr_es) * up(Er_es)+up(Dz_es) * up(Ez_es)) * dnr+(dnr * up(Dr_es)+dnz * up(Dz_es)) * up(Er_es)</td>
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<td>dnTEr_es</td>
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<td>Pa</td>
<td>-0.5 * (down(Dr_es) * down(Er_es)+down(Dz_es) * down(Ez_es)) * unr+(unr * down(Dr_es)+unz * down(Dz_es)) * down(Er_es)</td>
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<td>Pa</td>
<td>-0.5 * (down(Dr_es) * down(Er_es)+down(Dz_es) * down(Ez_es)) * unr+(unr * down(Dr_es)+unz * down(Dz_es)) * down(Er_es)</td>
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<td>dnTMz_es</td>
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<td>dVolbnd_es</td>
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8.1.2. Boundary 4, 6-9, 11, 13, 17

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<td>ntflux_Sraq_chnp</td>
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<td>mol/(m²*s)</td>
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<tr>
<td>ntflux_TBaq_chnp</td>
<td>Normal total flux, TBAq</td>
<td>mol/(m²*s)</td>
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</table>
ncflux_TBaq_chnp \quad \text{Normal convective flux,} \quad \text{TBaq} \quad \text{mol/(m}^2\text{s)} \quad nr_chnp * cflux_TBaq_r_chnp+ nz_chnp * cflux_TBaq_z_chnp

nmflux_TBaq_chnp \quad \text{Normal electrophoretic flux,} \quad \text{TBaq} \quad \text{mol/(m}^2\text{s)} \quad nr_chnp * mflux_TBaq_r_chnp+nz_chnp * mflux_TBaq_z_chnp

ntflux_TBaq_chnp \quad \text{Normal total flux,} \quad \text{TBaq} \quad \text{mol/(m}^2\text{s)} \quad nr_chnp * tflux_TBaq_r_chnp+nz_chnp * tflux_TBaq_z_chnp

unTEr_es \quad \text{Maxwell surface stress tensor (r)} \quad \text{Pa} \quad -0.5 * \left( \text{up(Dr}_{es}) \times \text{up(Er}_{es})+ \text{up(Dz}_{es}) \times \text{up(Ez}_{es}) \right) * \text{dnr}+ (\text{dnr} * \text{up(Dr}_{es})+\text{dnz} * \text{up(Dz}_{es}) ) * \text{up(Er}_{es})

unTEz_es \quad \text{Maxwell surface stress tensor (z)} \quad \text{Pa} \quad -0.5 * \left( \text{up(Dr}_{es}) \times \text{up(Er}_{es})+ \text{up(Dz}_{es}) \times \text{up(Ez}_{es}) \right) * \text{dnz}+ (\text{dnr} * \text{up(Dr}_{es})+\text{dnz} * \text{up(Dz}_{es}) ) * \text{up(Ez}_{es})

dnTEr_es \quad \text{Maxwell surface stress tensor (r)} \quad \text{Pa} \quad -0.5 * \left( \text{down(Dr}_{es}) \times \text{down(Er}_{es})+ \text{down(Dz}_{es}) \times \text{down(Ez}_{es}) \right) * \text{unr}+ (\text{unr} * \text{down(Dr}_{es})+\text{unz} * \text{down(Dz}_{es}) ) * \text{down(Er}_{es})

dnTEz_es \quad \text{Maxwell surface stress tensor (z)} \quad \text{Pa} \quad -0.5 * \left( \text{down(Dr}_{es}) \times \text{down(Er}_{es})+ \text{down(Dz}_{es}) \times \text{down(Ez}_{es}) \right) * \text{unz}+ (\text{unr} * \text{down(Dr}_{es})+\text{unz} * \text{down(Dz}_{es}) ) * \text{down(Ez}_{es})

unTr_es \quad \text{Exterior Maxwell stress tensor (u), r component} \quad \text{Pa} \quad \text{unTEr}_{es}+ \text{unTMr}_{es}

unTMr_es \quad \text{Exterior magnetic Maxwell stress tensor (u), r component} \quad \text{Pa} \quad 0

unTz_es \quad \text{Exterior Maxwell stress tensor (u), z component} \quad \text{Pa} \quad \text{unTEz}_{es}+ \text{unTMz}_{es}

unTMz_es \quad \text{Exterior magnetic Maxwell stress tensor (u), z component} \quad \text{Pa} \quad 0

dnTr_es \quad \text{Exterior Maxwell stress tensor (d), r component} \quad \text{Pa} \quad \text{dnTEr}_{es}+ \text{dnTMr}_{es}

dnTMr_es \quad \text{Exterior magnetic Maxwell stress tensor (d), r component} \quad \text{Pa} \quad 0

dnTz_es \quad \text{Exterior Maxwell stress tensor (d), z component} \quad \text{Pa} \quad \text{dnTEz}_{es}+ \text{dnTMz}_{es}

dnTMz_es \quad \text{Exterior magnetic Maxwell stress tensor (d), z component} \quad \text{Pa} \quad 0

DVolbnd_es \quad \text{Volume integration contribution} \quad \text{m} \quad r

nD_es \quad \text{Surface charge density} \quad \text{C/m}^2 \quad \text{unr} * \text{(down(Dr}_{es})-\text{up(Dr}_{es})+\text{unz} * \text{(down(Dz}_{es})-\text{up(Dz}_{es})}

8.1.3. Boundary 5

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<td>Ionic conductivity ( S/m ) ( F_{chnp}^2 \cdot (z_{BAorg}^2 \cdot BAorg \cdot um_{BAorg} + z_{Srorg}^2 \cdot Srorg \cdot um_{Srorg} + z_{TBorg}^2 \cdot TBorg \cdot um_{TBorg}) )</td>
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<td>( \text{mflux}_{BAorg _r} _chnp2 )</td>
<td>Electrophoretic flux, ( BAorg, r ) component ( mol/(m^2 \cdot s) ) ( -z_{BAorg} \cdot BAorg \cdot um_{BAorg} \cdot F_{chnp} \cdot V^3z )</td>
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<td>( \text{BAorgr} )</td>
<td>Concentration gradient, ( BAorg, r ) component ( mol/m^4 ) ( (-z_{Srorg} \cdot Srorg \cdot TBorg) / z_{BAorg} )</td>
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<td>( \text{dflux}_{BAorg} _chnp2 )</td>
<td>Diffusive flux, ( BAorg ) component ( mol/(m^2 \cdot s) ) ( \sqrt{\text{dflux}<em>{BAorg _r}^2 + \text{dflux}</em>{BAorg _z}^2} )</td>
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<tr>
<td>BAorg</td>
<td>BAorg</td>
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<td>sqrt(cflux_BAorg_r_chnp2^2+cflux_BAorg_z_chnp2^2)</td>
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<td></td>
<td>(-z_Srorg_chnp2 * Srorg-z_TBorg_chnp2 * TBorg)/z_BAorg_chnp2</td>
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<td>Mean diffusion coefficient, BAorg</td>
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<td>r * (Drz_BAorg_chnp2 * f_chnp2 * V3r)+Drz_BAorg_chnp2 * f_chnp2 * V3z</td>
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<td>-Drz_Srorg_chnp2 * Srorgr-Drz_Srorg_chnp2 * Srorgz</td>
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\[
\begin{align*}
\text{Dr}_{\text{es}} &= \epsilon_{\text{es}} \epsilon_0 (\text{Er}_{\text{es}} + \epsilon_{\text{rz}} \text{Ez}_{\text{es}}) \\
\text{Dz}_{\text{es}} &= \epsilon_{\text{es}} \epsilon_0 (\text{Er}_{\text{es}} + \epsilon_{\text{zz}} \text{Ez}_{\text{es}}) \\
\text{epsilon}_{\text{es}} &= \epsilon_0 (\epsilon_{\text{rr}} + \epsilon_{\text{rz}} + \epsilon_{\text{zz}}) \\
\text{normE}_{\text{es}} &= \sqrt{\text{abs}(\text{Er}_{\text{es}})^2 + \text{abs}(\text{Ez}_{\text{es}})^2} \\
\text{normD}_{\text{es}} &= \sqrt{\text{abs}(\text{Dr}_{\text{es}})^2 + \text{abs}(\text{Dz}_{\text{es}})^2} \\
\text{normDr}_{\text{es}} &= \sqrt{\text{abs}(\text{Drr}_{\text{es}})^2 + \text{abs}(\text{Drz}_{\text{es}})^2}
\end{align*}
\]
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<td>$0.5 \times ((\text{Dr}<em>{es} + \text{Drr}</em>{es}) \times \text{Er}<em>{es} + (\text{Dz}</em>{es} + \text{Drz}<em>{es}) \times \text{Ez}</em>{es})$</td>
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### 8.2.2. Subdomain 2

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**Mathematical expressions**

\[
J_r\_chnp = \sqrt{J_{r\_chnp}^2 + J_{z\_chnp}^2}
\]

\[
kappa\_chnp = \frac{F_{\text{chnp}}^2 \left( z_{\text{NO3aq\_chnp}}^2 \cdot \text{NO3aq} \cdot um_{\text{NO3aq\_chnp}} + z_{\text{Sraq\_chnp}}^2 \cdot \text{Sraq} \cdot um_{\text{Sraq\_chnp}} + z_{\text{TBaq\_chnp}}^2 \cdot \text{TBaq} \cdot um_{\text{TBaq\_chnp}} \right)}{\sqrt{V_{2r}^2 + V_{2z}^2}}
\]

\[
\text{gradV\_chnp} = \sqrt{V_{2r}^2 + V_{2z}^2}
\]

\[
\text{J\_chnp} = \sqrt{J_{r\_chnp}^2 + J_{z\_chnp}^2}
\]

\[
kappa\_chnp = \frac{F_{\text{chnp}}^2 \left( z_{\text{NO3aq\_chnp}}^2 \cdot \text{NO3aq} \cdot um_{\text{NO3aq\_chnp}} + z_{\text{Sraq\_chnp}}^2 \cdot \text{Sraq} \cdot um_{\text{Sraq\_chnp}} + z_{\text{TBaq\_chnp}}^2 \cdot \text{TBaq} \cdot um_{\text{TBaq\_chnp}} \right)}{\sqrt{V_{2r}^2 + V_{2z}^2}}
\]

\[
\text{gradV\_chnp} = \sqrt{V_{2r}^2 + V_{2z}^2}
\]

\[
\text{J\_chnp} = \sqrt{J_{r\_chnp}^2 + J_{z\_chnp}^2}
\]

\[
kappa\_chnp = \frac{F_{\text{chnp}}^2 \left( z_{\text{NO3aq\_chnp}}^2 \cdot \text{NO3aq} \cdot um_{\text{NO3aq\_chnp}} + z_{\text{Sraq\_chnp}}^2 \cdot \text{Sraq} \cdot um_{\text{Sraq\_chnp}} + z_{\text{TBaq\_chnp}}^2 \cdot \text{TBaq} \cdot um_{\text{TBaq\_chnp}} \right)}{\sqrt{V_{2r}^2 + V_{2z}^2}}
\]
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Curriculum Vitae

Name: Thomas J. Stockmann

Education

Ph.D. Candidate, Physical, Electroanalytical Chemistry (2008-present)
The University of Western Ontario
ASPIRE Award
Queen Elizabeth II GSST
B.Sc. Honours Specialization in Chemistry (4 Year) (2005-2008)
The University of Western Ontario
Deans Honour List
The University of Western Ontario
Fanshawe College
John Labatt Award for academic excellence

Work Experience

Ph. D. Candidate, the University of Western Ontario, London Ontario (2008-present)
Senior Lab Manager; duties included hazardous waste handling
Chemical inventory, lab training, and safety auditing
Teaching Assistant in Analytical Chemistry lab course using:
High Performance Liquid Chromatography
Gas Chromatography
Electrochemical
Atomic Absorption and UV-Vis Spectroscopy

Administrative Assistant, Cargill Meats London, Ontario (2005-2008)
Performed Good Manufacturing Practices auditing
Processed quality assurance data with reporting to management

Quality Assurance Technician; Strathroy Foods, Ingersoll, Ontario (2002-2005)
Performed routine quality control in a manufacturing setting
Microbial testing and analysis

Tested new formulations for total fats and solids
Familiarized with LIMS and reporting to R&D divisions

Articles Published or Accepted


Stockmann, T. J.; Olaya, A. J.; Méndez, M. A.; Girault, H. H.; Ding, Z., (2011) Evaluation of Gibbs energy of dioxouranium transfer at an electrified liquid|liquid interface supported on a microhole. *Electroanalysis* 23 (11), 2677-2686


Stockmann, T. J.; Ding, Z., (2011) Uranyl ion extraction with conventional PUREX/TRUEX ligands assessed by electroanalytical chemistry at micro liquid/liquid interfaces. *Anal. Chem.* 83 (19), 7542-7549


**Submitted or In Preparation**

Stockmann, T.J.; Ding Z., (2012) Nernst-Planck model used to explore liquid|liquid interfacial ion transfer with no supporting electrolyte. *In preparation.*


**Oral Presentations**


Stockmann, T.J.; Zhang, J.; Wren, J.C.; Ding, Z., (2011) Hydrophobic ionic liquids for metal extraction in nuclear waste. 94th Annual Canadian Society of Chemistry Conference, Montreal, Quebec, Canada.


**Poster Presentations**

2011 3rd Georgian Bay International Conference on Bioinorganic Chemistry (CanBIC), Parry Sound, Ontario, Canada
2010 93rd Annual Canadian Society of Chemistry Conference, Toronto, Ontario, Canada
2010 Electrochemistry Conference, Fall Symposium, London, Ontario, Canada
2009 2nd Georgian Bay International Conference on Bioinorganic Chemistry (CanBIC), Parry Sound, Ontario, Canada
2009 92nd Annual Canadian Society of Chemistry Conference, Hamilton, Ontario, Canada

**Graduate Courses**

9754 Structural Chemistry of Solid Materials
9685 Seminar
9532 Analytical Instrumentation
9752 Bioanalytical Chemistry of Small Molecules
9704 Solar Energy Conversion
9572 Spectroelectrochemistry and Photoelectrochemistry