# Electrochemical investigation of Fe<sup>2+</sup>: trioctylphosphine oxide coordination reaction at a micro liquid|liquid interface

By

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## Abstract

Dissolved Fe is an important micronutrient for marine biota in the worlds' oceans that typically exists at sub-nanomolar concentrations. Many microorganisms such as phytoplankton have evolved specialized ligands for Fe uptake. Thus, spatiotemporal oceanic mapping of dissolved Fe and understanding Fe-ligand binding are critical areas of research. Herein, we have employed the micro ( $25 \mu m$  in diameter) interface between two electrolyte solutions (ITIES) as a platform to investigate Fe<sup>2+</sup> coordination with trioctylphosphine oxide (TOPO) via an electrochemically controlled facilitated ion transfer reaction. Based on established thermodynamics and using differential pulse voltammetry, the metal ion:ligand stoichiometry was determined to be ~15, and overall binding coefficient ( $\beta$ ) of Fe<sup>2+</sup>-TOPO was calculated 4.4×10<sup>45</sup>, respectively. It is speculated that the high stoichiometry may be owing to the generation of pseudo-micelle since *n* greatly exceeds the typical Fe-ligand stoichiometry. Na<sup>+</sup> and K<sup>+</sup> binding towards TOPO were also examined since they are major electrolyte components in seawater. However, they demonstrated high binding affinities through much lower Na<sup>+</sup>: TOPO or K<sup>+</sup>: TOPO stoichiometries of roughly 1.18 and 2.52 as well as  $\beta$ 's of 3.3×10<sup>14</sup> and 2.4×10<sup>15</sup>, respectively.

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## List of Abbreviations

Abbreviation	Description
AAS	Atomic absorption spectroscopy
AdSDPV	Adsorptive stripping differential pulse voltammetry
ACSV	Adsorptive cathodic stripping voltammetry
ASV	Anodic stripping voltammetry
SiO <sub>2</sub> -APTES	(3-Aminopropyl) triethoxysilane modified-silica particles
ACT	Aqueous complexation followed by the complex's transfer
BiABE	Bismuth bulk annular band electrode
BPY	Bipyridine
CSV	Cathodic stripping voltammetry
CE	Counter Electrode
CIC	Chelaion ion chromatography
CV	Cyclic voltammetry
Cu-HS	Copper-binding humic substances
CNS	Carbon nanosphere
DPV	Differential pulse voltammetry
DOM	Dissolved organic matter
DME	Dropping mercury electrode
DPSV	Differential pulse stripping voltammetry
DPASV	Different pulse anodic stripping voltammetry
DCE	1,2-Dichloroethane
EIS	Electrochemical impedance spectroscopy
EDX	Electron diffraction X-ray spectroscopy

EC'	Electrochemical-catalytic mechanism
EDTA	Ethylenediaminetetraacetic acid
ET	Electron transfer
FIT	Facilitated ion transfer
Au–Bi/ITO	Gold-bismuth/indium tin oxide electrode
AuND	Gold nano dendrites
GCE	Glassy carbon electrode
HMDE	Hanging mercury drop electrode
HHQ	4-Hydroxy-2-heptylquinoline
HMI	Heavy metal ion
IC	Ion chromatography
IL-rGO	Ionic liquid-reduced graphene oxide
IL	Ionic liquid
IT	Ion transfer
ITIES	Interface between two immiscible electrolyte solutions
LA-ICPMS	Laser ablation inductively coupled plasma mass spectrometry
LOD	Limits-of-detection
MWCNT	Multiwalled carbon nanotube
MOF	Metal-organic framework
NEP	N-ethylpentylone
N2N	1-Nitroso-2-naphthol
СМРО	Octyl(phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide
PDMS	Polydimethylsiloxane
PEDOT	Poly(3,4-ethylenedioxythiophene)

PUREX	Plutonium uranium extraction
Phen	1,10-Phenathroline
PC	Phthalocyanine
PQS	Pseudomonas quinolone signal
PAN	1-(2-Pyridylazo)-2-naphthol
PPW	Polarized potential window
RSM	Response surface methodology
RE	Reference Electrode
rGO/LMB/PtNPs	Reduced graphene oxide/leucomethylene blue/platinum nanoparticle
SWV	Square wave voltammetry
SEI	Solid electrolyte interphase
SIB	Sodium-ion batteries
SPM	Suspended particulate matter
SEM	Scanning electrochemical microscopy
SAL	Salicylaldoxime
SEM	Scanning electron microscopy
SnBiE	Tin-bismuth electrode
TBP	Tributylphosphate
TRUEX	Trans uranium extraction
TIC	Transfer by interfacial complexation
TID	Transfer by interfacial decomplexation
TOC	Transfer followed by organic phase complexation
LiTB	Tetrakis(pentafluorophenyl)borate lithium etherate
ТОРО	Trioctylphosphine oxide

## P<sub>8888</sub>TB Tetraoctylphosphonium tetrakis(pentafluorophenyl)borate

- TAC 2-(2-Thiazolylazo)-p-cresol
- UME Ultramicroelectrode
- WE Working electrode

## List of Symbols

Zi	Charge of species i
С	Concentration
C′	Catalytic
$\mathcal{C}_{M^{z^+}}$	The bulk metal ion concentration
$\mathcal{C}_{\mathrm{ML}_n^{z+}}$	The bulk metal complexation concentration with n ligands bound with metal ion
$c_L$	The bulk ligand concentration
$\mathcal{C}_L^*$	The initial concentration of a ligand
R <sup>2</sup>	Coefficient of determination
D	Diffusion coefficient
A	Electrode surface
Е	Electrochemical
F	Faraday's constant
$\Delta_o^w \phi_{i^{z_i}}^{o'}$	Formal ion transfer potential of ion, $i$ with charge z
$\Delta_o^w \phi$	Galvani potential difference across a water (w) oil (o) interface
R	Gas constant
$\Delta_o^w \phi_{1/2}$	Half-wave transfer potential
i	Ionic species
L	Litre
n	Ligand stoichiometry
L	Ligand
μm	Micrometer
mg	Milligram

μg	Microgram
mM	Millimolar
ms	Millisecond
μΜ	Micromolar
mV	Millivolt
$M\Omega$ cm	Megaohm centimeter
$ML_n^z$	Metal ion and ligand complex with a stoichiometry of n and charge z
nA	Nanoampere
nM	Nanomolar
β	Overall complexation constant
Rs	Ohmic solution resistance
$\Delta_o^w \phi_{max}$	Potentials at current maximum
$\Delta E$	Pulse amplitude
M	Refers generally to a metal ion
S	Second
Т	Temperature in degrees Kelvin
V	Voltage
w DCE	Water 1,2-dichloroethane
w CHCl <sub>3</sub>	Water chloroform
w o	Water oil

## Chapter 1

### **1** Introduction

### **1.1 Metal Cations in the Ecosystem**

#### 1.1.1 The importance of Fe in ocean ecosystems

Photosynthetic organisms are a crucial part of the global photosynthetic carbon fixation process.<sup>1</sup> Thus, their presence is essential for understanding global climate cycles. The biological carbon pump is influenced by phytoplankton productivity through several important mechanisms: carbon sequestration,<sup>1,2</sup> photosynthesis,<sup>3</sup> biological pumps, and nutrient cycling. The evolution of marine organisms, which make up the oceanic food chain, often depend on iron (Fe) as a micronutrient.<sup>4–6</sup> Fe is a very important micronutrient for water systems that is often absent in surface waters, particularly in the oceans. This lack of Fe affects the growth of phytoplankton, which are important for the planet's productivity and carbon fixation.<sup>7</sup> The low concentration of Fe is owing to it's relatively rapid oxidation following the Haber-Weiss mechanism:<sup>8</sup>

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{-}$$
 (1.1)

$$Fe^{2+} + O_2^{\bullet-} + 2H^+ \rightarrow Fe^{3+} + H_2O_2$$
 (1.2)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^-$$
(1.3)

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-}$$
(1.4)

The (aq) designation has been left out of these equations for simplicity. Combining equations 1.1-1.4 with Fe<sub>2</sub>O<sub>3</sub> precipitate formation, as exemplified through the following half-reaction,<sup>9</sup>

$$Fe_2O_3(s) + 4H^+ + 2e^- \rightleftharpoons 2FeOH^+ + H_2O$$
  $(E^\circ = 0.16 V)$  (1.5)

with it's relatively low standard reduction potential, a more comprehensive, chemical view forms of why Fe concentrations are so low in natural waters. Thus, the distribution of Fe throughout the ocean is of particular interest as, owing to it's limited solubility and persistence, it appears to be a limiting factor for phytoplankton growth in some regions.

Voltammetry, spectrophotometry, and atomic spectrometry are just some of the analytical techniques employed in monitoring Fe levels in the open ocean and coastal areas that have been used to develop reliable long-term trends.<sup>10</sup> Electrochemical approaches, such as cathodic stripping voltammetry (CSV), are robust, high-sensitivity methods of identifying total Fe in seawater that are easily portable for ship-board monitoring/quantification and are ideal since they have a minimal instrument foot-print. These techniques can also aid experts in understanding how ligands affect Fe in the water by studying their strength and spread. Ligands are crucial as they help maintain dissolved Fe in seawater inhibiting Fe oxidation to solid, particulate forms (*i.e.*, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>).<sup>11</sup> This means that Fe's concentration in seawater is in the nanomolar range and more than 99% of is bound to ligands.<sup>12</sup> Ligands binding strength can vary, however, most coordinate weakly with Fe.<sup>13,14</sup> Oceanic Fe-ligands are thought to be siderophores sourced from bacteria, porphyrins, and humic substances - so-called 'dissolved organic matter' (DOM) - derived from terrestrial runoff, atmospheric sources, or from estuaries;<sup>15-17</sup> however, the chemical structure of most DOM responsible is poorly understood beyond some small molecules.<sup>17,18</sup> Electrochemistry at immiscible liquid|liquid interfaces can offer a method to directly measure binding strength as well as simultaneously offer a potential means of directly measuring Fe concentration in the ocean. Because this approach employs ligand themselves directly, to offer an analytical means for spatiotemporal monitoring of Fe in seawater, then this form of electrochemistry will need to overcome a serious bottleneck: other interfering ions in seawater. While some ligands have shown good selectivity for a particular metal, most bind indiscriminately. Two major interfering ions of interest owing to their high concentration are potassium (K<sup>+</sup>) and sodium (Na<sup>+</sup>) coming in at roughly 0.010 and 0.5 M in seawater, respectively.<sup>19</sup>

In this chapter, the importance of ligand chemistry, especially with respect to  $Fe^{2+}$ ,  $Na^+$ , and  $K^+$  in the environment will be discussed, then conventional analytical methods will be introduced. Subsequently, the fundamentals of electrochemistry at liquid liquid interfaces are

reviewed. These aspects are key to developing methods for interrogating metal ion-ligand interactions. Indeed, through facile electrochemical experiments, physical insight into metal ion-ligand structures and coordination mechanisms can be gained, which is important for biochemical processes in living systems.

#### 1.1.2 Ligand/coordination chemistry of Fe



**Figure 1.1:** Chemical structures of Fe-ligands with high known binding affinities, including 1,10-phenanthroline (phen), phthalocyanine (pc), and bipyridine (bpy), as well as two examples of stable Fe organometallic complexes,  $[Fe^{II}(phen)_3]^{2+}$  and  $[Fe^{II}(bpy)_3]^{2+}$ .

dThe thermodynamics of metal ion-ligand binding can be described generally using equation  $1.1.^{22-24}$ 

$$\beta_{\alpha,j} = \frac{c_{\alpha,\mathrm{ML}_{j}^{z+}}}{c_{\alpha,\mathrm{ML}_{j-1}^{z+}} \left(c_{\alpha,\mathrm{L}}\right)^{j}} = \prod_{k=0}^{j} K_{\alpha,k} = K_{\alpha,1} K_{\alpha,2} K_{\alpha,3} \dots K_{\alpha,j}$$
(1.6)

Whereby,  $\beta_{\alpha,j}$  is the overall complexation constant and  $c_{\alpha,M^{z+}} = c_{\alpha,ML_{j-1}^{z+}}$  when j-1=0; thus,  $K_{\alpha,k}$  are the individual, stepwise complexation constants and j is the ligand stoichiometry. Several small organic molecules demonstrate high binding affinities to Fe, including 1,10phenanthroline (phen), phthalocyanine (pc), and bipyridine (bpy),<sup>20,21,25</sup> see **Figure 1.1**; whereby, phthalocyanine is structurally similar to porphyrins. These ligands bind so strongly that they often generate stable Fe organometallic complexes that are capable of reversible electron transfer, for example,

Fe<sup>II</sup>(bpy)<sub>3</sub> Fe<sup>III</sup>(bpy)<sub>3</sub><sup>3+</sup> + 
$$e^-$$
 (1.7)

However, high binding affinity is not necessarily ideal for Fe quantification in seawater. Indeed, most investigations rely on ligands such as salicylaldoxime (SAL), 1-nitroso-2naphthol (N2N), and 2-(2-thiazolylazo)-p-cresol (TAC), see **Figure 1.2**, which have demonstrated only modest  $\beta$  values.<sup>26</sup> These weaker coordination strengths facilitate the electrodeposition of Fe<sup>0</sup> onto an electrode interface, particularly a hanging mercury drop electrodes (HMDE).<sup>27</sup> A deeper discussion of HMDE is given below.<sup>28</sup>



**Figure 1.2:** Chemical structures of 1-nitroso-2-naphthol (N2N), salicylaldoxime (SAL), and 2-(2-thiazolylazo)-p-cresol (TAC).

As shown in **Figure 1.1** and **1.2**, most Fe-ligands rely on imine functionality in order to coordinate to the Fe center. Ligands incorporating a phosphine oxide moiety are seemingly rare in comparison when it comes to Fe; however, they have been employed to improve ligand specificity. For example, octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) has been used to greatly enhance the extraction efficiency of Sr<sup>2+</sup> from spent nuclear fuels.<sup>29–32</sup> This prompted us to explore more fundamentally the coordination properties of the phosphine oxide functional group; thus, we chose to focus our efforts on trioctylphosphine oxide (TOPO). In this way, the P=O group is only linked to hydrophobic alkyl chains. TOPO is a strong neutral ligand with high electron-donating properties, making it highly effective in coordinating metal ions in aqueous environments. Metal ions may be effectively removed from aqueous solutions thanks to their capacity to form stable complexes, which improves selective

extraction and separation procedures.<sup>33,34</sup> By donating electron density to metal ions, TOPO forms stable adducts, increasing their solubility in organic solvents and improving their phase transfer efficiency.<sup>35,36</sup> TOPO acts as a ligand, stabilizing the Fe<sup>3+</sup> complex and increasing the Fe<sup>3+</sup>-TOPO complex partition rate between the organic and water phases and its solubility in the organic phase (TOPO prevents Fe<sup>3+</sup> from re-entering the aqueous phase). The extraction process is made faster by the presence of other complex-forming ligands, such as nitrate (NO<sub>3</sub><sup>-</sup>) and bromide ( $Br^{-}$ ), which create Fe(H<sub>2</sub>O)<sub>5</sub>X<sup>2+</sup> complexes that bind with TOPO more effectively to form FeX(TOPO) extracted species.<sup>33</sup> TOPO's capacity to bind with Fe<sup>3+</sup>, K<sup>+</sup>, and Na<sup>+</sup> allows it to form complexes with these metal ions. The high ionic radius and low charge density of K<sup>+</sup>, and Na<sup>+</sup> prevent them from forming strong complexes with TOPO. These alkali metals remain highly solvated in the aqueous phase, making their interaction with TOPO weak. In contrast,  $Fe^{3+}$  is a transition metal ion with a high charge density and strong complexation tendencies, allowing TOPO to interact with it through coordination bonds.<sup>33,34</sup> The liquid|liquid interface enables complex formation and separation by facilitating charge transfer reactions across immiscible electrolyte solutions. This approach allows for ion detection. This method is a sensitive and efficient technique for ion analysis and complex formation in two-phase systems.<sup>37,38</sup> Fe<sup>2+</sup> complex formation and transfer at the liquid liquid interface using electrochemical methods. By applying cyclic voltammetry (CV) and differential pulse voltammetry (DPV). I analyzed the stability and interaction of  $Fe^{2+}$  with TOPO.  $Fe^{2+}$  complexes displayed stronger ligand interactions than K<sup>+</sup> and Na<sup>+</sup> complexes. Na<sup>+</sup> and K<sup>+</sup> complexes with TOPO were analyzed for comparison of the structures, with the primary focus on the Fe<sup>2+</sup>-TOPO complex.

#### **1.2 Analytical Methods**

#### **1.2.1** Conventional Analytical Methods

Cation anion concentrations can be measured using a technique called Ion Chromatography (IC).<sup>39</sup> It separates ions based on their interaction with a stationary and mobile phase. IC can measure sodium levels up to 10,000 ppm and detect very small amounts of lithium and barium.<sup>40</sup> Chelation Ion Chromatography (CIC) is a useful method for detecting transition metals in high-salt matrices like fossil fuel wastewater. CIC integrates a chelation column (CC-1) to remove interfering salts, such as calcium, before measuring metals like Fe<sup>3+</sup>, Cu<sup>2+</sup>, and Mn<sup>2+</sup>. It consistently attains recovery rates of 87%-108% in a 10,000 mg/L CaCl<sub>2</sub> medium, compared to inconsistent 2%-323% recoveries in traditional ion chromatography. According to the calibration curve, overestimations (108% or 323%) occur due to calcium competing with metals for binding on the CC-1 column; this competition cause the measured metal concentration to appear higher. CIC is validated for complex, high-salt samples.<sup>41</sup>

The flame-photometric technique detects alkali metal ions like K<sup>+</sup> and Na<sup>+</sup> in ceramic materials. Ceramic materials are used to measure reliability by standardization. Hydrofluoric acid breaks down the samples during preparation, and fluoride ions are eliminated using sulfuric acid by creating insoluble molecules. A propane flame detects ions because it provides a more stable flame and fewer interferences than town gas, which contains methane as a major component. Sodium and potassium salts undergo excitation and release distinctive light when a sample solution containing these salts is placed into a flame at its high temperature. Flame photometry uses this light to identify alkali metal ions and differentiate them based on their distinct emission spectra.<sup>42</sup>

One method for identifying trace elements in complex media is Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). Elements and biological molecules in structure samples can be precisely and spatially identified using LA-ICPMS. The dispersion of alkali and alkaline-earth elements like sodium and potassium, as well as transition metals like Fe, in mouse heart cryosections, was observed using LA-ICPMS. The metal concentration of Fe was 360  $\mu$ g g<sup>-1</sup> on average, while 3000  $\mu$ g g<sup>-1</sup> of potassium and 700  $\mu$ g g<sup>-1</sup> of sodium were determined.<sup>43</sup>

Complexometric titration is a method that uses metal ion-selective electrodes or pH meters to form stable complexes with alkali metal ions. This method enables the detection of Fe and aluminium under non-equilibrium conditions, using fluoride ion solutions as titrants.44 Electrochemical techniques allow for the direct production and identification of metal coordination complexes.<sup>45,46</sup> Based on the ligand type (*i.e.*, carboxylates, and alkoxides) and applied voltage, this method accurately detects oxidation states and coordination environments, such as Ni<sup>2+</sup> and Co<sup>2+</sup>.<sup>45,47</sup> These transitions are confirmed by electrochemical efficiency values (the reaction is mostly dictated by the mole ratio, or mol/F, of the metal to the moles of electrons moving through the cell) such as 0.5 mol/F for complexes of metal ions ( $M^{2+}$ ) like Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> complexes.<sup>45,48</sup> Electrochemical methods are cost-effective since electrons can be added or removed without the associated complexities that come with adding redox reagents. The electrochemical technique is one of the most straightforward ways to conduct oxidation or reduction operations and direct methods for characterizing metal complexes (electrochemical reactions take place in an environment without the need to provide high and low temperatures), providing control over redox processes (the techniques simplify redox processes by providing precise control over the addition or elimination of electrons without the associated difficulties), compatibility with ligands, and simplified purifying (avoiding complex separation procedures).<sup>45,49,50</sup> In my work, electrochemical methods (Cyclic Voltammetry and Differential Pulse Voltammetry) were employed to detect metal complex samples.

#### **1.2.2 Electrochemical Methods**

Electrochemical methodologies are relatively user-friendly, and low-cost,<sup>51</sup> often with the ability to scale up and be compatible with computer-assisted automation. The expansion of electrochemical testing capacity uses an automated system that can analyze simultaneously or individually modified electrode surfaces, such as gold electrodes with organosulfur on them. Automated sequential measurement of electrochemical current facilitates the expansion of testing capacity, and this measurement makes the process more efficient and faster through automated analysis.<sup>52</sup> On a boron-doped diamond electrode, CV, adsorptive stripping differential pulse voltammetry (AdSDPV), and DPV are efficient techniques for tracking Nethylpentylone (NEP) and recognizing different kinds of pesticides. These electrochemical techniques enable reliable, consistent on-site detection of NEP and pesticides, increasing the capabilities of analytical evaluations.<sup>53,54</sup> Electrochemical techniques such as CV and DPV are employed to monitor neurochemicals. These methods are combined with functional nanomaterials due to the electrodes' expansive active surface area in these methods and their enhanced detection performance. They are especially appealing because of their capacity to differentiate between several chemicals in complex examples of biology. This detection efficiency guarantees that these methods meet the requirements of clinical applications for precise analysis.55

Electrochemical sensors (electrochemical devices) are essential for analytical sciences. Sensitivity of modified electrodes enhance with nanomaterials, such as gold nanoparticles and carbon-based materials that improve sensor porosity due to their extensive surface area and conductivity. These properties like porosity, are necessary for accurate electrochemical detection. Metal oxides and their nanocomposites employed to identify significant biological analytes accurately are examples of nanomaterials with a large surface area that offer additional interaction sites for target molecules, and for improving sensor performance. Advanced electrodes coated with nanomaterials offer increased sensitivity (with additional sites on the surface) for identifying analyte traces.<sup>56</sup> These sensors offer miniaturization with a high surface area that allows for more active sites for reactions, more efficient electron transfer (high conductivity), and increased sensitivity in tiny sensors. This miniaturization makes sensors smaller without reducing their performance while increasing detection efficiency in environmental monitoring. This method was efficiently used to detect nitric oxide.<sup>56</sup> A network of pores in a sensor material is referred to as high porosity, which is efficient for electrochemical sensors. It improves the interaction between analytes and electrodes by increasing surface area, which increases the sensor's capacity to identify specific particles. A large surface area increases a sensor's ability to discriminate and separate chemical species by facilitating more analyte adsorption. Because of its quick response time and ability to identify concentrations in minute quantities, this arrangement of surface is used in medicine to conduct immediate tests and the detection of living specimens. An electrochemical method with a large surface area was applied detection of calcium phosphate nucleation.<sup>57,58</sup> The extreme porosity for of polydimethylsiloxane/multiwalled carbon nanotube (PDMS/MWCNT) composites enhances the efficiency of electrochemical sensors by permitting notable deformation under pressure and preserving stability at elevated pressures. By expanding contact sites and changing electrical resistance, their porous form makes it simple to compress them at low pressure and, reduce resistance and, allow more deformation under pressure and create more conductivity. The sensor can detect even very small pressures because of this change in resistance.<sup>59</sup> In a different context, CV and Electrochemical Impedance Spectroscopy (EIS) techniques are ideal for portable environmental assessments in detecting Pb<sup>2+</sup> ions in complex matrices like ocean water. A new electrochemical sensor, (3-Aminopropyl) triethoxysilane modified-silica particles (SiO<sub>2</sub>-APTES), based on silica nanoparticles, has been developed for Pb<sup>2+</sup> detection. This sensor achieves a low detection limit and shows potential for real-world water specimens.<sup>60</sup>

Adsorptive Cathodic Stripping Voltammetry (ACSV), a precise method, uses certain ligands that join to each oxidation state of Fe to distinguish between  $Fe^{2+}$  and  $Fe^{3+}$ . In this technique, an Fe-binding ligand is included to combine with Fe<sup>3+</sup>. This technique creates a complex that can then be evaluated using ACSV.<sup>10</sup> Additionally, chemiluminescence offers an efficient method for measuring  $Fe^{2+}$  in freshwater specimens, as it involves  $Fe^{2+}$  catalyzing the oxidation of luminol to produce light.<sup>61,62</sup> Both methods are crucial for long-term Fe monitoring in salt water because their ocean biogeochemistry is vital for climate change control.<sup>10</sup> Nanofibers, due to their large surface area and more porosity, are highly effective in electrochemical sensing applications. These characteristics enable them to be ideal for non-enzymatic sensing and analyte identification, as they have larger surface area than other nanostructures.<sup>63</sup> In another case, pyridoxine hydrochloride's electrochemical response was investigated using CV, DPV, and EIS, which reveal electron transfer kinetics and charge transfer efficiency on modified electrodes. These techniques provide enhanced sensitivity (greater peak current) and efficiency (fewer charge transfer resistance) owing to the improved electrode design (carbon paste electrode modified with oxo crown ether). These methods were accurately used to identify pyridoxine hydrochloride.<sup>64</sup> Graphene oxide electrodes were reduced chemically, and along with silver nanoparticles were employed to create a sensor to identify estriol in water. This method is suitable for recognizing estriol at low concentrations (21.0 nmol/L) because of the modified electrode,<sup>65</sup> and the electrodes' high surface area to volume ratio.<sup>66</sup> Since electrochemical sensors are effective in clinical diagnostics, modified electrodes enable miniaturized devices with advanced analytical capabilities and make advanced medical testing, like cholesterol tests, accessible to the public.<sup>67</sup> These electrochemical methods, like CV and DPV, effectively detect biologically relevant targets and early biomarkers like cancer with advanced nanomaterials. Amplification strategies improve electrochemical sensors' sensitivity by promoting signal results with nanomaterials, which make it possible to recognize trace amounts of analytes with stronger signals.<sup>68</sup> Two complementary methods for examining metalligand interactions in biphasic liquid|liquid systems are CV and DPV. These techniques reveal information about binding power and ligand coordination in addition to identifying facilitated ion transfer.<sup>26,69</sup> Background current impacts are eliminated, and sensitivity is increased by DPV.<sup>70</sup> CV and DPV are valuable for environmental and industrial applications, such as detecting trace metals or separating metals from complex solutions and identifying stoichiometric ratios of complexes like Fe(N2N)<sub>2</sub><sup>2+</sup>, Fe(TAC)<sub>6</sub><sup>2+</sup>, and Fe(SAL)<sub>6</sub><sup>2+</sup>.<sup>26,69</sup>

Electrochemical methods offer more affordable and easily transportable options than traditional techniques like Atomic Absorption Spectroscopy (AAS) for mercury detection for natural and organic specimens. Unlike AAS, which requires costly equipment and is difficult to use outside the lab, electrochemical methods are suitable for on-location examination and real-time monitoring. Additionally, the electrochemical method employing modified carbon paste electrodes with crown ethers and multi-walled carbon nanotubes (MWCNTs) provides improved detection capability, with results comparable in accuracy to AAS.<sup>71-74</sup>

#### **1.2.3 Hanging mercury drop electrode (HMDE)**

The Hanging Mercury Drop Electrode (HMDE) is employed in environmental monitoring because of low detection limits.<sup>75</sup> HMDE's remarkable sensitivity is especially suitable for identifying tiny quantities of metals (Cd, Pb, Cu, Zn, and Ni) in poison from honey bees, and it is helpful in environmental investigation.<sup>76</sup>

A quick overview of the Dropping Mercury Electrode (DME) is given below, as well as the factors that have led to the development of HDME. The first topic discussed about DME is polarography, a popular method for studying testing chemicals and identifying evidence of metals. The term "polarography" comes from the polarization of the DME versus a reference electrode.<sup>77,78</sup> When an amalgam forms, it can cause the metal ion under investigation to be lost within the liquid Hg phase, which makes it hard to get accurate results. The problem generally

arises when mercury is in touch with the liquid phase for a long time. To fix this problem, efforts are focused on enhancing the accuracy of the existing HMDE by optimizing its conditions and adding chelating agents like ethylenediaminetetraacetic acid (EDTA) which can mask the effect of interfering metals like copper and lead by forming stable complexes that do not adsorb on the HMDE as readily. The HMDE, along with ligands and a technique called Cathodic Stripping Voltammetry (CSV), are used to study an Fe complex on the mercury's surface.<sup>79,80</sup> In this method, an oxidizing agent is added to the solution in bulk to help with the process. Using the EC' mechanism (where E stands for electrochemical and C' stands for catalytic), the technique creates a catalytic current whereby the Fe<sup>3+</sup>-ligand complex is first attracted on the HMDE surface and then oxidized to Fe<sup>2+</sup> by means of an oxidizing agent; for example, Obata et al.<sup>81</sup> used BrO<sub>3</sub><sup>-</sup> as the oxidizer to detect very low levels of Fe at a HMDE.

Genovese et al.<sup>82</sup> studied Fe and organic ligands in Antarctic Sea ice using the ACSV technique with a HMDE as a working electrode. They found that Fe-free ligands could help the solubility and biological absorption of dissolved Fe in the ocean. The reduction of ocean ice could reduce the amount of biological absorption of dissolved Fe and free ligands.

As another example, a study utilized Response Surface Methodology (RSM) to optimize the efficiency of the analysis of a HMDE for detecting imidacloprid, a pesticide. Square Wave Voltammetry (SWV) was used to determine the ideal circumstances for precise detection, which led to low detection limits (3.65×10<sup>-8</sup> mol/L) and reasonable recovery rates for specimens taken from the water. As a result, SWV is a potential technology for environmental monitoring.<sup>75</sup> CSV is used to measure copper-binding humic substances (Cu-HS) in oceanic water, especially near the coast. A HMDE helps detect these Cu-HS complexes, which is important for understanding how copper exists in the ocean.<sup>83</sup> Using ultra-cathodic deposition potentials makes Anodic Stripping Voltammetry (ASV) with a HMDE, more sensitive by raising the signal by 5–10 times

for identification of metals such as  $Pb^{2+}$  and  $Cu^{2+}$  as opposed to older methods. The best results occurred at pH 4.8 with an acetate buffer, improving detection limits from 0.2 to 0.02  $\mu$ g/L.<sup>84</sup>

The catalytic DPV method uses a bismuth bulk annular band electrode (BiABE) to find low quantities of Fe<sup>3+</sup>. It adjusts parameters such as potential, duration, and electrolyte concentration to be most effective. This technique has been applied to actual water specimens (where the concentration of Fe<sup>3+</sup> varied from 1 to 476  $\mu$ g/L) and has a detection limit of 0.28  $\mu$ g/L of Fe<sup>3+</sup>. The aim was to quantify low Fe levels and determine the detection limit in water specimens. The performance of BiABE was compared to the HMDE, which is also useful for detecting Fe, although mercury is more poisonous.<sup>85</sup>

Modified electrodes are employed to identify metal ions such as Cd<sup>2+</sup> and Hg<sup>2+</sup> in seawater. The toxicity of mercury has prompted the investigation of alternatives to HMDE, replacing it with safer, more environmentally friendly options.<sup>86</sup>

#### **1.2.4 Modified Electrodes**

Modified electrodes in electrochemistry improve sensitivity by adjusting surface characteristics. Gold nano dendrites (AuNDs) and ionic liquid-reduced graphene oxide (IL-rGO) have been used in a new technique for measuring Fe. IL-rGO has an extensive specific surface area. IL-rGO facilitates the special building of AuNDs and gives them distinctive shapes. A cation transfer polymer assists the IL-rGO and AuNDs in sticking to the electrode, resulting in outstanding electrochemical qualities. The reduction peak electrical current and concentration display a straight-line relationship between the maximum current and the concentration of Fe<sup>3+</sup> with an extent of 0.30 to 100  $\mu$ molL<sup>-1</sup>, and the method recognizes Fe ions and the smallest quantity of Fe<sup>3+</sup> that can be detected, is 35 nmolL<sup>-1</sup>. This modified electrode makes it a suitable choice for measuring Fe ions in solution.<sup>87</sup> Another work details the creation of a modified electrode using an electron transmit process constructed of reduced graphene oxide, leucomethylene blue (LMB), and platinum nanoparticles (rGO/LMB/PtNPs). Methylene

blue (MB) dye is first taken onto graphene oxide (GO). Then, through electrostatic interactions, platinum hexachloride ions (PtCl62-) self-build onto the GO/MB compound. Platinum nanoparticles (PtNPs) are created when GO turns into rGO using a reducer (sodium borohydride (NaBH<sub>4</sub>)). A successfully manufactured rGO/LMB/PtNP electrode is the product of this technique, which also transforms MB to LMB. Due to the synergistic features of rGO and PtNPs, which improve electron transfer, this modified electrode has the advantage of having great sensitivity. Fe<sup>2+</sup> ions may be efficiently detected by this electrode; the smallest quantity of Fe<sup>2+</sup> that can be distinguished is 3 nM.<sup>88</sup> The existence of metals like Fe and copper in seawater requires precise monitoring due to their potential environmental impacts. Electrochemical methods, like stripping voltammetry, are useful because they are selective. These methods can quickly detect metals and help address some of their risks to human health and the environment. Researchers developed several different polymer-modified glassy carbon electrodes to test for metals in water specimens. The metals tested include cadmium, arsenic, and copper, using SWV. They found that poly(3,4-ethylenedioxythiophene) PEDOT-modified glassy carbon electrode worked well. This study also showed that all the modified electrodes reacted exceptionally well when testing commercial wastewater specimens, with results confirmed by separate analysis using atomic absorption spectroscopy.<sup>89,90</sup> Glassy carbon electrodes (GCEs) modified with polymers were created for the study's Differential Pulse Stripping Voltammetry (DPSV) metal detection. The PEDOT-modified electrodes showed the best sensitivity and lowest detection limits. Critical conditions like pH, potential, and deposition time were optimized for effective detection. The method is fast and suitable for environmental water analysis.<sup>90</sup> Environmentally friendly electrodes have been increasing in use in some research studies. One of their popular types is nanoparticle-modified carbon ink. Metallic surfaces formed of bismuth or mercury can enhance the detection of heavy metals. Heavy metals are identified using electrochemical methods, and they react with films or nanomaterials on inexpensive electrode substrates.<sup>91</sup> Alloy electrodes also influence development and electrochemical performance and facilitate electron transfer.<sup>92</sup>

#### **1.2.5 Alloy Electrodes**

Alloy electrodes enhance electrochemical performance by combining metal properties, resulting in improved conductivity,<sup>93,94</sup> and corrosion resistance.<sup>95</sup> A special method called Different Pulse Anodic Stripping Voltammetry (DPASV), used with an electrode made of silver alloy, helps find reactive Fe in estuaries and oceans. This method shows that at around -1.5 V (relative to a double-junction Ag/AgCl/3 M KCl reference electrode), Fe<sup>2+</sup> in solution converts to elemental Fe that accumulates onto the silver alloy. Then, the potential is swept back to -0.55 V (*vs.* Ag/AgCl) with an observed small peak for Fe, corresponding to the oxidation of elemental Fe to Fe<sup>2+</sup>. As the concentration of Fe<sup>2+</sup> increases from less than 1 to 14 nmolL<sup>-1</sup>, the peak size grows, measured over a 900-second plating time. This method can detect levels of Fe<sup>2+</sup> as low as 0.3 nmolL<sup>-1</sup>.<sup>96</sup> A tin-bismuth alloy electrode (SnBiE) was utilized to detect tiny levels of Fe using a ligand known as 1-(2-pyridylazo)-2-naphthol (PAN). Adsorptive cathodic stripping voltammetry is used to reduce the Fe<sup>3+</sup>–PAN complex to Fe<sup>2+</sup>–PAN at the SnBiE. Fe<sup>3+</sup> levels can be measured between 1 and 900 seconds, with a limit of detection (LOD) of 0.2 nmolL<sup>-1</sup>. A reliable measurement of Fe levels in seas can also be identified using this technique.<sup>97</sup>

Both saturated and diluted sodium bis (trifluoromethanesulfonyl) amide/ethylene carbonate + dimethyl carbonate solutions were employed by the researchers to evaluate carbon nanosphere (CNS) electrodes and their durability. They discovered that the concentration of lithium and sodium ions affects CNS electrodes by adding and removing these ions from the electrodes. According to this research, batteries with concentrated electrolytes have higher cycle durability compared with lower concentrations of ions due to strengthening Solid Electrolyte Interphase (SEI), reducing its breakdown.<sup>98</sup> Sodium and potassium-ion batteries are popular

due to affordability and availability. Anode structures based on metallic alloys provide proper energy-saving potential, but they often face problems such as significant structural instability because of the process of holding and releasing sodium or potassium ions during charge and discharge. Recent advancements in materials like bismuth enhance efficiency through structural development and modification techniques.<sup>99</sup> An alloy electrode is the magnesium alloy anode utilized in Mg-air bio-batteries. These batteries use a renewable magnesium alloy anode submerged in a phosphate-buffered saline electrolyte. This electrode's renewable properties suggest possible uses in renewable devices.<sup>100,101</sup> Nanomaterials like gold nanoparticles and carbon-based materials improve sensor surface properties. Nanomaterials with a wide surface area, like metal oxides, noble metals, and graphene-based materials, provide more interaction sites for target molecules and boost detection limits. The combination of high electrical conductivity and extensive surface area in these sensors allows for their miniaturization for various environmental applications. The electrodes can facilitate the transfer of electrons between different phases at the liquid|liquid interface.<sup>102</sup>

### **1.3 Liquid Liquid Electrochemistry**

Science and medicine depend on understanding electrochemical processes at immiscible liquid|liquid interfaces. For two-phase electrolysis, the electrical potential differences between the two liquids are essential. Charge transfer, durability and dispersion of ions are all impacted by the electrical potential in liquid|liquid systems, such as water|nitrobenzene or water|1,2-dichloroethane.<sup>103</sup> Nitrobenzene has a high inner-layer capacitance (the inner layer's ability to maintain electric charge), which makes it challenging to interpret interfacial characteristics; so, nitrobenzene is rarely employed.<sup>104</sup> Rosenfeld<sup>103</sup> proposed a double layer between two liquids in 1902. The charge scattering creates an electrical double layer at the interaction boundary between different systems (liquid|liquid systems). According to Verwey and Niessen's<sup>105</sup>

conducted research on the development of the electrical double layer forming at liquid interfaces, potential dips typically appear in phases with lower dielectric constants and ionic concentrations.

In contrast to traditional solid electrodes, the Interface between Two Immiscible Electrolyte Solutions (ITIES) offers precise electric field control, which makes it perfect for enhanced sensing and catalysis.<sup>102,106</sup> **Figure 1.3** depicts the diagram of a micro-ITIES setup using a specialized holder and borosilicate glass pipette.<sup>107</sup> The liquid|liquid interface is critical for creating nanostructures, enabling dynamic processes and creating unique arrangements from organic materials to carbon materials. It helps molecules naturally organize into ordered structures through self-accumulation. This self-accumulation is important in material studies, especially in producing functional nanostructures like crystals.<sup>108</sup> A Y-Y-shaped microchannel was investigated to study the charge at the interfacial region of an insoluble decane-saline solution. The findings supported a negative surface that rose with pH, which was attributed to hydroxyl ions accumulating between the phases. The Y-Y-shaped microchannel allows the liquids to flow parallel to each other using separate routes, which decreases unstable conditions. This design reduces strain and produces a smooth interface by precisely setting the pressure to match the two liquids' flow speeds.<sup>109</sup>



**Figure 1.3:** Diagram of ITIES cell, where WE, CE, and RE stand for working, counter, and reference electrodes, respectively. Adapted from Moshrefi, R. et al., Simultaneous electro-generation/polymerization of Cu nanocluster embedded conductive poly(2,2':5',2''-terthiophene) films at micro and macro liquid|liquid interfaces, Scientific Reports, 2023, Springer Nature. Licensed under a Creative Commons Attribution 4.0 International License (CC BY 4.0).<sup>107</sup>

#### 1.3.1 Liquid liquid interface: several forms of charge transfer

The study of charge-transfer reactions by recording current signals within a certain potential range has identified four main mechanisms. These are simple ion transfer (**Figure 1.4A** and **B**), facilitated ion transfer (**Figure 1.4C**), photoinduced interfacial electron transfer (**Figure 1.4E**), and interfacial electron transfer (**Figure 1.4D**).<sup>102,110,111</sup> For example, palladium and platinum nanoparticle production at the liquid|liquid system by reducing their metal salts in the aqueous phase,<sup>112</sup> and using an electron donor in the oil phase results in the interfacial deposition of these nanoparticles and catalyzes hydrogen evolution-related reactions.<sup>113</sup>



**Figure 1.4:** Reactive mechanism for interfacial charge transfer at ITIES. Ion transfer (A and B), facilitated ion transfer (C), interfacial electron transfer (D), and photoinduced interfacial electron transfer (E). Adapted with permission from Scanlon, M. D.; Smirnov, E.; Stockmann, T. J., et al. Gold Nanofilms at Liquid|Liquid Interfaces: An Emerging Platform for Redox Electrocatalysis, Nanoplasmonic Sensors, and Electrovariable Optics. Chem. Rev. 2018, *118* (7), 3722–3751. Copyright 2018 American Chemical Society.<sup>102</sup>

#### **1.3.2 Simple Ion Transfer**

Ions move from one solvent to another due to variations in their solvation surroundings as they transfer across immiscible liquid surfaces. They must overcome energy barriers from desolation and solvation into another solvent, influenced by factors like solvent protrusions, which reduce contact and energy costs. Gibbs energy is crucial in ion transfer, affecting its ease. If the Gibbs energy difference between two liquids is minimal, ion transfer occurs without additional assistance like ligands. Thermodynamic barriers are less significant than kinetic factors in determining ion transfer rates. Rates are fundamentally determined by the kinetic process, especially where solvation, desolvation, and diffusion limitations significantly impact the transfer speed.<sup>114</sup>

#### **1.3.3 Facilitated Ion Transfer (FIT)**

Investigate the interface between two immiscible electrolyte solutions (ITIES) using electrochemical techniques, which has shown that the Galvani potential difference drives charge transfer and polarizes the interface. Facilitated ion transfer (FIT) is a crucial process at
ITIES, where ions are transferred across the interface with the assistance of complexing agents. This process allows for the selective transport of ions across liquid-liquid interfaces.<sup>115</sup>

The separation techniques Plutonium URanium EXtraction (PUREX) and TRans URanium EXtraction (TRUEX) depend on the FIT of uranyl ions utilizing tributylphosphate (TBP) and octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl-phosphine oxide (CMPO) ligands, which are essential in nuclear fuel. The research calculates complexation stoichiometries and constants using micro-ITIES. The research finds that CMPO and TBP strongly bind with uranyl ions differently. This research identifies multiple stoichiometries, with CMPO and TBP showing strong complexation with uranyl ions. This technique can help create electrodes that select particular ions. This technique is cheaper than some analytical methods, like inductively coupled plasma methods.<sup>116</sup> As another example of FIT, this mechanism is observed when the interactions between Fe<sup>2+</sup> ions and various ligands at a w/DCE interface occur. FIT emphasizes how ligands like 1,10-phenanthroline assist in ion transfer across the interface, which aids in the analysis of the ion-ligand complexes' binding, strengths and stoichiometries.<sup>26</sup>

Because of the ion's more considerable Gibbs energy at the liquid|liquid interface, it is impossible to study ion transfer peaks directly. The Gibbs energy of an ion can be decreased by dissolving a ligand in the opposite phase. Ion transfer (IT) is the most straightforward charge transfer process involving the movement of ions across an interface due to an externally applied potential difference until reaching equilibrium.<sup>37,117</sup> FIT at liquid|liquid interfaces can optimize separation in many chemical processes. IT is a process where ions move between two immiscible liquids, like water and an organic solvent, due to a potential applied across the interface. This movement highly depends on the Gibbs energy difference between the two phases, as ions naturally move to minimize this difference. For example, a cation in the aqueous phase can move into the organic phase. FIT is a process that lowers the energy barrier by creating a complex between an ion and a ligand. This ligand stays in the organic phase and

binds to the ion, reducing the Gibbs transfer energy.<sup>118</sup> According to Reymond's work,<sup>119</sup> FIT is distinguished between four processes of enhanced ion transfer: the ACT, TIC, TOC and TID. FIT is used to assess stoichiometry of structures.

**Figure 1.5** shows mechanisms of FIT, including aqueous complexation followed by the complex's transfer (ACT), transfer by interfacial complexation (TIC), transfer by interfacial dissociation (TID), and transfer followed by organic phase complexation (TOC). The third CT process, electron transfer (ET), is the interaction between redox species in either phase. ITIES has various application and has been studied by researchers.<sup>37,120</sup>



**Figure 1.5:** Mechanisms for three types of charge transfer processes: (a) simple ion transfer (IT), (b) facilitated/assisted ion transfer (FIT), and (c) electron transfer (ET). TIC/TID = transfer by interfacial complexation/decomplexation; ACT = aqueous complexation followed by transfer; and TOC = transfer followed by organic phase complexation. Adapted from Islam, G. J.; Zannah, S. Scope of Electrochemistry at Liquid|Liquid Micro-Interfaces. Dhaka Univ. J. Sci. 2022, 69 (3), 186–193. Licensed under a Creative Commons Attribution 4.0 International License (CC BY 4.0).<sup>120</sup>

FIT is a mechanism where a ligand (*L*) facilitates ion transfer across the ITIES,<sup>121</sup> as described in equation 1.1,<sup>29,122</sup>

$$i_{w}^{z_{i}} + nL_{o} \rightleftharpoons iL_{n,o}^{z_{i}} \tag{1.1}$$

Where n is the stoichiometric coefficient of the ligand, i is the hydrophilic ionic species of interest, and L is the ligand.

Reymond et al.<sup>119</sup> demonstrated that a linear relationship may be calculated when the ligand is hydrophobic and in excess concentration relative to the metal ion, meaning that the TIC or TOC (see **Figure 1.5**) mechanism is preferred. It is described in equation 1.2,

$$-\frac{zF}{RT} \left( \Delta_{o}^{w} \phi_{1/2, iL_{n}^{z_{i}}}^{z_{i}} - \Delta_{o}^{w} \phi_{i^{z_{i}}}^{o'} \right) = n \ln(c_{\mathrm{L}}^{*}) + \ln(\beta)$$
(1.2)

The initial concentration of a ligand  $(c_{\rm L}^*)$  determines the half-wave transfer potential  $(\Delta_o^w \phi_{1/2,iL_n^{z_i}})$  of a metal ion-ligand complex. The formal ion transfer potential for a free metal ion is denoted by " $\Delta_o^w \phi_{i^{z_i}}^{o'}$ ". The total complexation constant ( $\beta$ ) can be determined using the y-intercept of equation 1.2. In this equation, the slope is *n*, and concentrations of ligands are variable.

## **1.4 Scope of This Thesis**

The aim of this study was to assess the potential of the liquid|liquid interface as an electroanalytical system for determining total dissolved Fe<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> ions in oceans and coastal areas. In Chapter 2, there are tests at a water|1,2-dichloroethane (w|DCE) microinterface, with Tetraoctylphosphonium tetrakis(pentafluorophenyl)borate (P<sub>8888</sub>TB) as a supporting electrolyte in the oil phase. The interaction between Fe<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> ions in the water phase and the trioctylphosphine oxide (TOPO) ligand in the oil phase is efficiently studied in this research to calculate the stoichiometry of metal ions to ligands and overall complexation constants ( $\beta$ ). Finally, Chapter 3 will summarize the state of the field's research and its future directions.

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## Chapter 2

# Electrochemical investigation of Fe<sup>2+</sup>: trioctylphosphine oxide coordination reaction at a micro liquid|liquid interface

## 2.1 Co-authorship Statement

This chapter includes preliminary research on " Electrochemical investigation of Fe<sup>2+</sup>: trioctylphosphine oxide coordination reaction at a micro liquid|liquid interface": B. Bastan and T.J. Stockmann (2024) In-preparation. Experimental design by TJS. Experiments performed and analyzed by BB. First draft was prepared by TJS. Edited by BB and TJS; finalized by TJS.

#### **2.2 Introduction**

Iron is an important micronutrient for phytoplankton as it is integral to the chlorophyll oxidation/reduction cycle in the form of the Fe-S containing protein, ferredoxin.<sup>1-3</sup> This often makes iron a limiting micronutrient in certain areas of the open ocean.<sup>4,5</sup> Indeed, the spatiotemporal mapping of dissolved iron in the open ocean has been a major endeavor of the GEOTRACES program,<sup>5</sup> which has accumulated >16,000 observations at a wider range of depths and across more regions than ever before. Oceanic mapping of dissolved iron and other trace elements provides insight into possible nutrient sinks/sources and how these may influence the behaviour of marine organisms. In turn, because the worlds' oceans are responsible for 50% of the global photosynthesis and carbon fixation, this gives insight into global carbon cycling which impacts research in climate science. Thus, dissolved iron is of critical importance. Indeed, experiments were even performed investigating fertilizing the ocean with iron to induce algal blooms and speed up overall carbon sequestration as a means of combatting climate change.<sup>6</sup>

While suspended particulate matter (SPM) is typically quantified using Scanning Electrochemical Microscopy (SEM) with coupled Electron Diffraction X-ray (EDX) spectroscopy, spatiotemporal characterization of dissolved iron is often performed using a select number of preferred analytical techniques, including AAS,<sup>7-8</sup> and electrochemistry.<sup>9-16</sup> In the latter, investigators often rely on CSV coupled with DPV to achieve the extremely low detection levels necessary, since iron is only present in seawater at sub-nanomolar levels.<sup>5, 9-10</sup> They also make use of ligands such as 1-nitroso-2-naphthol (N2N), 2-(2-thiazolylazo)-*p*-cresol (TAC), and salicylaldoxime (SAL),<sup>17</sup> to concentrate and maintain iron in solution. As we demonstrated recently,<sup>17</sup> most bind weakly to iron; however, this is likely a desirable physicochemical trait since irreversible ligand coordination may fundamentally alter iron's electrochemical behavior and inhibit detection. Thus, tailoring ligand binding strength can be a key strategy in selecting the best species for dissolved iron's quantification.

Most traditionally employed ligands incorporate amine/imine and hydroxyl moieties as electron rich coordination groups. While phosphine oxide functionalized compounds have often been used in metal separation methods, for example, towards spent nuclear fuel<sup>18-20</sup> as well as for improved catalysts.<sup>21-22</sup> Herein, the ligand binding efficiency of trioctylphosphine oxide (TOPO) towards Fe<sup>2+</sup> has been investigated electrochemically at the interface between two immiscible electrolyte solutions (ITIES) between the w|DCE interface. Thermodynamic analytical solutions for the following interfacial complexation reaction (equation 2.1) have been described by Mareček,<sup>23</sup> Kakiuchi,<sup>24</sup> and Girault's<sup>25</sup> groups; whereby, a metal ion (M<sup>z+</sup>) of charge *z* coordinates to a hydrophobic ligand (L) in the organic phase with a ligand stoichiometry of *n*,

$$M^{z+}(aq) + nL(org) \to ML_n^{z+}(org)$$
(2.1)

Whereby, the complexation constant ( $K_n$ ) for any distinct coordination event is described by equation 2.2,

$$K_n = \frac{c_{\mathrm{ML}_n^{Z^+}}}{c_{M^{Z^+}(c_{\mathrm{L}})}}$$
(2.2)

The overall complexation constant ( $\beta$ ) is defined by,<sup>25</sup>

$$\beta_n = \frac{c_{\mathrm{ML}_n^{Z^+}}}{c_{M^{Z^+}}(c_{\mathrm{L}})^n} = \prod_{k=0}^n K_k$$
(2.3)

where  $c_{L}$  is the bulk ligand concentration in DCE, and when n = 1,  $c_{ML_{n-1}^{z+}} = c_{M^{z+}}$ , *i.e.*, the concentration of bulk metal ions in the aqueous phase.

This electrochemical approach exploiting the liquid|liquid interface as a means of accessing ligand binding efficiencies has been successfully deployed by Kanoufi's group<sup>26</sup> at the micro water|chloroform (w|CHCl<sub>3</sub>) interface investigating phospholipid coordination with protons and metal ions. Meanwhile, Scanlon's group<sup>27</sup> combined this method with DFT calculations to characterize the facilitated ion transfer mechanism of *Pseudomonas aeruginosa* pathogenic bacteria small molecule virulence vectors at the w|DCE interface. They also established a proof-of-concept electroanalytical method for these small molecules with limits-of-detection (LOD) of 1.2 and 1.1  $\mu$ M for 4-hydroxy-2-heptylquinoline (HHQ) and 2-heptyl-3,4-dihydroxyquinoline, *i.e.*, pseudomonas quinolone signal (PQS), respectively.

Herein, it was discovered that TOPO is an indiscriminate ligand which binds strongly to the three metal ions investigated, including  $Fe^{2+}$ ,  $Na^+$ , and  $K^+$  with low specificity. An analytical detection method for  $Fe^{2+}$  in seawater could not be developed since the facilitated ion transfer signals for  $Na^+$  and  $K^+$  occur at the same potential as  $Fe^{2+}$ . However, valuable association constants for each metal ion were determined, along with their metal ion:ligand stoichiometries, which could prove useful in the development of metal separation technologies.

## 2.3 Experimental Section

Ultrapure water from a MilliQ filtering system was used to create aqueous solutions (18.2 M $\Omega$  cm) unless otherwise indicated. Other chemical species were used as received without additional purification. 1,2-dichloroethane (DCE,  $\geq$ 99.0%), iron (II) sulfate heptahydrate (FeSO4•7H<sub>2</sub>O,  $\geq$ 99%), trioctylphosphine (>97%), trioctylphosphine oxide (99%), and bromooctane (99%) were sourced from Sigma-Aldrich. Tetrakis(pentafluorophenyl)borate

lithium etherate (LiTB,  $\geq$ 99%) was obtained from Boulder Scientific. The IL P<sub>8888</sub>TB (tetraoctylphosphonium tetrakis(pentafluorophenyl)borate) was prepared as previously described.<sup>28</sup>

The CH Instruments potentiostat (Model CHI602E) was used for electrochemical studies in two electrode mode. Micropipettes were made as has been already explained,<sup>29</sup> and fabricated with a 25  $\mu$ m diameter pore at one end. The pipettes were installed inside a specialized pipette holder<sup>30,31</sup> with an integrated Ag wire connected to an SMA connector which was in turn coupled to the working electrode (WE) lead of the potentiostat. The pipette was back-filled with the aqueous electrolyte solution (see **Scheme 2.1** below). Water and an organic solvent (water|1,2-dichloroethane system) were used. The tip was immersed in the oil phase, and the w|DCE interface was positioned at the tip. A second Ag wire was immersed in the DCE phase and connected to the counter/reference electrode leads. A 12× zoom lens assembly (Navitar) equipped with an 18-megapixel CCD camera was used to monitor the position of the ITIES.

AgAg2SO4
$$5 \text{ mM FeSO4}$$
 $\begin{bmatrix} Y \text{ mM } L \\ 5 \text{ mM P}_{8888} \text{TB} \\ (DCE) \end{bmatrix}$ AgTBAg[Cell 1]AgAg2SO4 $5 \text{ mM } XCl \\ (aq) \end{bmatrix}$  $\begin{bmatrix} Y \text{ mM } L \\ 5 \text{ mM P}_{8888} \text{TB} \\ (DCE) \end{bmatrix}$ AgTBAg[Cell 2]

**Scheme 2.1:** Schematic of the electrochemical cells employed at a micro-pipette ITIES (25  $\mu$ m in diameter) between water|oil (w|o) in which Y mM is the ligand concentration ( $c_L$ ) that was dissolved in the 1,2-dichloroethane (DCE) phase. X has been used to represent either the Na<sup>+</sup> or K<sup>+</sup> dissolved in the aqueous phase in Cell 2. The double vertical bars have been used to highlight the polarizable liquid|liquid interface. The ionic liquid (P<sub>8888</sub>TB) has been employed as a supporting electrolyte in the DCE phase.<sup>29</sup>

Voltammetric potentials were referenced to the Galvani scale using the formal ion transfer potentials of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> transfer, or  $\Delta_o^w \phi_{SO_4^{2-}}^{o'} = -0.540$  V and  $\Delta_o^w \phi_{Cl^{-}}^{o'} = -0.479$  V, respectively.<sup>32</sup>

#### **2.4 Results and Discussion**

Figure 2.1 A and B depict the CV and DPV recorded using Cell 1 with no ligand added to the organic phase. CVs were recorded at a rate of 0.020 V s<sup>-1</sup>, while DPVs had pulse parameters of 50 mV, 50 ms, and 0.5 s amplitude, width, and period, respectively. For the CV, a sharp increase in current was observed when scanning in the positive direction at  $\sim 0.7$  V and this corresponds to the simple ion transfer of  $Fe^{2+}$  from water to oil (w  $\rightarrow$  o). When next moving towards negative potentials, a peak-shaped wave was recorded with a peak potential at roughly -0.680 V, which is likely the SO<sub>4</sub><sup>2-</sup> transfer from w  $\rightarrow$  o. However, once the scan direction was switched at -0.9 V and potentials were swept positively again, a sigmoidal wave was observed for the transfer of  $SO_4^{2-}$  back from  $o \rightarrow w$ . The signal asymmetry is brought about by the shape of the pulled micropipette.<sup>33</sup> Within the microchannel species undergo linear diffusion (see Figure 2.2 A and B), which elicits peak-shaped CV responses reminiscent of *i-V* curves recorded at a large electrode. However, ions crossing from  $o \rightarrow w$  in this configuration (*i.e.*, from outside to inside the capillary) experience hemispherical diffusion generating steady-state or 's'-shaped responses similar to those recorded at an inlaid disc ultramicroelectrode (UME). Thus, these results agree well with previous reports.<sup>27, 34-37</sup> This asymmetry can be exploited to help identify the ion undergoing transfer since a cation will always generate a positive peak when crossing from  $w \rightarrow o$ , if the aqueous phase is maintained within the capillary, and vice versa for an anion.



**Figure 2.1:** Cyclic voltammogram (CV) and (B) differential pulse voltammogram (DPV) obtained using Cell 1 with no ligand added to the DCE phase (*i.e.*,  $c_{\rm L} = 0$  mM). CV was performed at a rate of 0.020 V s<sup>-1</sup>, while the DPV was carried out at a pulse amplitude, width, and period of 50 mV, 50 ms, and 0.5 s, respectively. Gray dashed arrows indicate scan direction. Current signals have been labelled with the ion undergoing transfer inset.

FeSO<sub>4</sub> (aq) has been used as both supporting electrolyte and analyte. The former typically limits the width of the Polarizable Potential Window (PPW).<sup>17, 34-35</sup> However, as previously demonstrated by Ding's group<sup>34-35</sup> and by us,<sup>17</sup> it is possible to scan beyond the typical PPW using a micropipette installed within a specialized holder. The holder virtually eliminates electrophoretic movement of the ITIES, and combined with its small interfacial size, limits the current to the nanoampere (nA) range decreasing the ohmic solution resistance ( $R_s$ ), also known as the  $iR_s$  drop, *i.e.*,  $V = iR_s$ . The later generates signal interference at large (cm scale) liquid|liquid interfaces making the *i-V* recordings too resistive to obtain meaningful results. Moreover, one can further mitigate  $iR_s$  drop by using DPV.<sup>17, 34-35, 38</sup> Moreover, the analytical sensitivity of DPV is much higher than CV as well as most other pulse programs through mitigation of background currents, which emphasizes faradaic events of interest.<sup>39-41</sup> Exploiting these features, the DPV in DPV in **Figure 2.1B** was was obtained using Cell 1 with no ligand added to the DCE phase. The peaks with potentials at current maximums ( $\Delta_o^w \phi_{max}$ ) at -0.565 and 0.710 V correspond to respective simple SO4<sup>2-</sup> and Fe<sup>2+</sup> ion transfer.<sup>17</sup> The formal ion transfer potential ( $\Delta_o^w \phi^{o'}$ ) was then calculated through the following,<sup>17,42</sup>

$$\Delta_o^w \phi_{max} = \Delta_o^w \phi^{o'} + \frac{RT}{zF} \ln \sqrt{\frac{D_w}{D_o}} - \frac{\Delta E}{2}$$
(2.4)

In which  $D_w$  and  $D_o$  are the diffusion coefficients of the ion in either phase, while  $\Delta E$  is the pulse amplitude. If one assumes  $D_w \approx D_o$ , then equation 2.4 is greatly simplified. In this way,  $\Delta_o^w \phi_{Fe^{2+}}^{o'}$  was determined to be 0.71 V. This value agrees somewhat with the value previously determined by us of 0.66 V.<sup>17</sup> This latter value was used for all additional calculations.



**Figure 2.2:** (A) photograph taken using a 12× magnification lens assembly (Navitar) equipped with an 18megapixel CCD camera (AmScope) of the micropipette tip. (B) Diagram of the linear and hemispherical diffusion regimes that give rise to asymmetric voltammetric signals at micropipette supported liquid|liquid interfaces.

Next, TOPO was added to the DCE phase in incrementally increasing concentrations. **Figure 2.3** shows the DPV traces recorded when increasing TOPO from 25-90 mM. For the 25 mM case, there are still roughly two positive peak current signals; however, while the SO4<sup>2-</sup> transfer peak occurs at -0.565 V, the second signal is shifted to more negative potentials, appearing at  $\Delta_o^w \phi_{max} \approx 0.06$  V. Indeed, the second peak often appears to be multiple overlapping signals. In order to deconvolute these signals, the Multipeak fitting program in Igor Pro was employed (see **Figure 2.4**). As TOPO increases, the peak signal concomitantly shifts to more negative potentials. This agrees well with the thermodynamic theory of facilitated ion transfer developed by Mareček,<sup>23</sup> Kakiuchi,<sup>2,4</sup> and Girault's<sup>25</sup> groups; within which, three dominant mechanisms were proposed: (*i*) transfer by interfacial complexation/decomplexation (TIC/TID), (*ii*) transfer followed by organic phase complexation (TOC), and (*iii*) aqueous phase partitioning of the ligand followed by aqueous phase complexation and transfer (ACT).<sup>25</sup> TIC and TOC mechanisms cannot be distinguished voltammetrically. Since the TOPO ligand is likely very hydrophobic, the ACT mechanism was not considered. The following thermodynamic equation relating the ligand concentration ( $c_L$ ) and the measured half-wave potential ( $\Delta_o^w \phi_{ML_n^z}$ ) for the facilitated metal ion transfer was developed by Reymond *et al.*,<sup>25</sup>

$$-\frac{zF}{RT} \left( \Delta_o^w \phi_{\mathrm{ML}_n^z, 1/2} - \Delta_o^w \phi_{\mathrm{M}^{z^+}}^{o'} \right) = n \ln(c_{\mathrm{L}}) + \ln(\beta)$$
(2.5)

in which,  $\beta$  is the overall complexation constant and *n* is the metal:ligand stoichiometry.<sup>25</sup> Thus, the binding affinity of most ligands can be determined electroanalytically through this linear relationship. All the terms on the left-hand side of equation 2.5 are known constants except for  $\Delta_o^w \phi_{ML_m^z, 1/2}$  which is the half-wave potential for facilitated ion transfer signal and can be measured from the DPV using  $\Delta_o^w \phi_{max}$  along with equation 2.4.



**Figure 2.3:** DPV recorded using Cell 1 while changing the ligand concentration ( $c_L$ ) dissolved in the DCE phase from 25 mM (A) to 35 (B), 75 (C), and 90 mM (D). The gray, dashed arrow indicates scan direction. All instrument parameters were the same as described for Figure 2.1B.



**Figure 2.4:** An example of the Multipeak fitting analysis performed using Igor Pro 9.05 software to deconvolute the facilitated ion transfer signal towards positive  $\Delta_0^w \phi$ . The top, middle, and bottom panels are plots of the residual, DPV curve with the total fitting applied (blue trace); and a plot of the individual peaks obtained from program, respectively. The green curve in the middle panel shows the baseline correction, while the chi-square ( $\chi^2$ ) is shown in blue, inset.

**Figure 2.5** shows the plot of  $-\frac{zF}{RT} \left( \Delta_o^w \phi_{ML_n^z, 1/2} - \Delta_o^w \phi_{M^{z+}}^o \right)$  versus  $\ln(c_L)$ ; whereby, only the most negatively shifted facilitated Fe<sup>2+</sup> peaks were selected during Multipeak fitting (see **Figure 2.3** and **Figure 2.4**). Each ligand concentration was swept 3 times such that each data point in **Figure 2.5** represents an average of these 3 scans while the error bars are one standard deviation. A z = 2 was used in equation 2.5. The red trace in **Figure 2.5** shows the linear regression fitting performed in Igor Pro; from which, the slope and *y*-intercept were determined to be 15.4 and 105.1, respectively. This indicates an extreme metal:ligand stoichiometric ratio of roughly 1:15 with an equally large binding affinity of  $\ln(\beta) = 105.1$ , or  $\beta \approx 4.4 \times 10^{45}$ . While the R<sup>2</sup> for the linear regression analysis was 0.882, there is still a great deal of error owing to the Multipeak fitting approach and high degree of overlap for many of these signals. If a z = 1 is used instead, then an *n* value of ~7 and  $\beta \approx 2.5 \times 10^{22}$  can be calculated. The high stoichiometric ratios may be the result of a pseudo-micelle formation around the hydrated metal ion, or Fe<sup>2+</sup> coordination to a hydroxyl ligand forming Fe(OH)<sup>+</sup>, for example, reducing its perceived charge. In the case of the latter, the binding affinity is close to that determined for

CMPO towards strontium, which was found to have n = 2 and 3 with  $\beta = 4.5 \times 10^{19}$  and  $5.5 \times 10^{25}$ , respectively, by Ding and Girault's groups.<sup>18</sup> Additionally, Ding's group investigated TBP by this method and discovered two stoichiometries as well towards TBP's binding of UO<sub>2</sub>, with n = 3 or 4 and  $\beta = 3.2 \times 10^{11}$  and  $2.0 \times 10^{13}$ , respectively.<sup>19</sup> TOPO, CMPO, and TBP all utilize the phosphine oxide (R<sub>3</sub>P=O) moiety as a primary metal binding functional group; moreover, they all demonstrated high binding affinities.

We recently investigated four ligands often used to quantify the amount of iron in seawater as well as one other, which include 1,10-Phenathroline (phen), N2N, TAC, and SAL.<sup>17</sup> Phen demonstrated high binding affinity similar to TOPO for the z = 1 case, and 3 individual stoichiometries were observed. Meanwhile, N2N, TAC, and SAL showed very weak binding to iron. This may be a characteristic of a good ligand for analytical detection; since in this research condition, TOPO and phen likely bind irreversibly to the metal center generating at least in the case of phen a new redox active, molecular organometallic species, *i.e.*, Fe(phen)<sub>3</sub><sup>2+</sup> or ferroin.<sup>43,44</sup>



**Figure 2.5**: Plot of  $\delta = -\frac{zF}{RT} \left( \Delta_0^w \phi_{ML_n^z, 1/2} - \Delta_0^w \phi_{M^{z^+}}^o \right)$  versus  $\ln(c_L)$  from the differential pulse voltammetry (DPV) data shown in Figure 2.2 in which  $\Delta_0^w \phi_{ML_n^z, 1/2}$ , where obtained from the peak current maximums determined using Igor Pro software's Multipeak fitting program described in Figure 2.3. Error bars are for 1 standard deviation calculated from 3 replicate DPV scans.

To investigate the selectivity of TOPO towards iron, particularly in a seawater environment, Cell 2 was employed. Either NaCl or KCl was used as analyte/supporting electrolyte in the aqueous phase, such that Figure 2.6 A-D and E-H show the respective DPVs recorded with changing TOPO. In either case, two fairly well resolved facilitated ion transfer signals were observed which shifted towards negative potentials with increasing TOPO. Their  $\Delta_o^w \phi_{ML_w^z,1/2}$ values were then determined without using the Multipeak fitting approach described above for Fe<sup>2+</sup> facilitated ion transfer. Again, the average  $\Delta_o^w \phi_{ML_n^z, 1/2}$  from 3 replicate scans was taken, and, using equation 2.5, the plots in Figure 2.7A and B were generated for the two peak signals. The formal ion transfer potentials for simple Na<sup>+</sup> and K<sup>+</sup> were  $\Delta_o^w \phi_{Na^+}^{o'} = 0.71 \text{ V}$  and  $\Delta_o^w \phi_{K^+}^{o'} = 0.63$  V, as determined by Ding's group.<sup>34</sup> For peak 1, there are good trends for both Na<sup>+</sup> and K<sup>+</sup> with *n* values of 1.18 and 2.52 as well as  $\beta$ 's of 3.3×10<sup>14</sup> and 2.4×10<sup>15</sup>, along with  $R^2$  values of 0.802 and 0.837, respectively. These data suggest that TOPO has a much stronger affinity for Na<sup>+</sup> and K<sup>+</sup> versus Fe<sup>2+</sup>, since facilitated ion transfer is achieved with far fewer equivalents of TOPO. Unfortunately, these data demonstrate that TOPO has very poor selectivity. The facilitated ion transfer peaks for Fe<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> all occur within the same potential region. Therefore, while this approach was successful towards determining the metalligand binding affinities, TOPO make a poor ligand as the basis for an electroanalytical, environmental sensor or separation system. Nevertheless, it does showcase the power of the phosphine oxide moiety within ligands for metal separation strategies. The R<sub>3</sub>P=O group, however, must be moderated by the functional groups stemming from it to enhance its selectivity such as the case for CMPO, which has demonstrated high selectivity towards Sr<sup>2+</sup>.<sup>18</sup>



**Figure 2.6:** DPVs obtained with Cell 2 with 5 mM of NaCl (A-D) or KCl (E-H) in the aqueous phase while increasing  $c_{\rm L}$  in DCE such that  $c_{\rm L} = 25$  (A), 35 (B), 55 (C), 75 (D), 25 (E), 35 (F), 40 (G), 75 mM (H). All other instrument parameters were the same as described described in Figure 2.2.



**Figure 2.7:** Plot of  $\delta = -\frac{zF}{RT} \left( \Delta_0^w \phi_{ML_n^z, 1/2} - \Delta_0^w \phi_{M^{z^+}}^{o'} \right)$  versus  $\ln(c_L)$  from the differential pulse voltammetry (DPV) data shown in Figure 2.6 in which  $\Delta_0^w \phi_{ML_n^z, 1/2}$ , where obtained from the peak current maximums determined using Igor Pro software's Multipeak fitting program described in Figure 2.3. Error bars are for 1 standard deviation calculated from 3 replicate DPV scans.

When analysing peak 2 (see **Figure 2.6** and **Figure 2.7**), however, the R<sup>2</sup> value determined from the linear regression was quite poor. Likely there are multiple competing mechanisms occurring within this potential region; particularly, since a large amount of the ligand in the vicinity of the ITIES may have been consumed before the potential reaches this level. Future work will combine *in situ* spectroscopic methods to help elucidate local ligand concentration changes as well as the appearance of possible irreversible coordination and the formation of molecular organometallic species.

#### **2.5 Conclusion**

Herein, trioctylphosphine oxide (TOPO) ligand coordination towards Fe<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> facilitated ion transfer was investigated electrochemically at a micro (25 µm in diameter) w|DCE interface. The metal ion:ligand stoichiometry (n) and overall binding coefficient ( $\beta$ ) were determined by tracking the change in  $\Delta_o^w \phi_{ML_n^z, 1/2}$  with increasing bulk ligand concentration  $(c_{\rm L})$  in the DCE phase. This approach is based on previously established analytical solutions derived from thermodynamic first principles.<sup>23-25, 45</sup> TOPO demonstrated poor selectivity through overlapping facilitated ion transfer signals in the same potential region for all three metal species tested. The Fe<sup>2+</sup>: TOPO ratio, using a z value of 2, was high at ~15 and a  $\beta$  value of 4.4×10<sup>45</sup>. If z = 1 was employed in the calculation, then an  $n \approx 7$  was determined; however, this is still high for Fe<sup>2+</sup> leading us to speculate that perhaps a pseudomicelle like forms to facilitate Fe<sup>2+</sup> transfer. Based on this high ligand stoichiometry, TOPO coordinates less strongly towards Fe<sup>2+</sup> than it does towards Na<sup>+</sup> or K<sup>+</sup>, which showed n and  $\beta$ values of 1.18 and 2.52 as well as  $3.3 \times 10^{14}$  and  $2.4 \times 10^{15}$ , respectively. Nevertheless, these data should be useful for fundamental physical chemists as well as by providing insight into phosphine oxide moieties coordination strength in the absence of other coordinating functional groups.

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## Chapter 3

## **3.1 Conclusions and Perspectives**

The results reported here result from a quantitative and comprehensive investigation of Fe<sup>2+</sup> coordination at w|DCE (DCE is oil phase) micro-ITIES interface. The objective was to determine if TOPO, a neutral ligand with a strong metal-binding capacity, could be used in a selective sensing setting where high quantities of Na<sup>+</sup> and K<sup>+</sup> are present along with Fe<sup>2+</sup>. To simulate saline environments like seawater, where alkali metals are present, amounts of iron were measured in laboratory-prepared samples. The first step was identifying how Fe<sup>2+</sup> ions move across liquid|liquid immiscible interfaces using a micropipette and electrochemical techniques called DPV and CV. It was found that TOPO helps this ion transfer, which is evident from the appearance of specific peaks and changes in the voltammetry signalled when TOPO was added. The tests indicated that about 15 TOPO molecules connect to each Fe<sup>2+</sup> ion, suggesting a specific type of bonding likely caused by the formation of larger structures like micelles in the DCE solvent. This was a significant discovery that provided appropriate knowledge on the behaviour of phosphine oxide ligands in low-polarity liquids. The quantitative analysis showed a  $\beta$  value for the Fe<sup>2+</sup>-TOPO complex of 4.4 × 10<sup>45</sup>, placing this interaction among the strong metal-ligand associations known in this study in the context of a liquid liquid interface. In contrast, although TOPO's interactions with Na<sup>+</sup> and K<sup>+</sup> were detectable, they were weaker by several orders of magnitude. The corresponding overall complexation constants of  $3.3 \times 10^{14}$  for Na<sup>+</sup> and  $2.4 \times 10^{15}$  for K<sup>+</sup> with TOPO confirm that although some complexations occur, it is significantly less favourable compared to  $Fe^{2+}$ . However, electrochemical signals at almost the same potentials as those of Fe<sup>2+</sup> were still produced by these weaker interactions. This conclusion was a critical finding of the project: TOPO, while strong in binding Fe<sup>2+</sup>, cannot be used analytically under these conditions due to a lack of selectivity.

This thesis shows  $Fe^{2+}$  may form powerful complexes with TOPO; when considering analytical applications, this method effectively quantified  $Fe^{2+}$  complexation stoichiometry and binding strength. The study of Na<sup>+</sup> and K<sup>+</sup> ions demonstrates that the method also provides insight into the comparison of competing ion complexations, which is useful for research associated with environmental chemistry and can be extended to other transition metals for comparative studies using the same approach.

These results suggest that while TOPO may not be appropriate for selective electroanalytical detection, it could still be investigated for its ability to bind Fe<sup>2+</sup> in procedures such as phase extraction from mixed-ion structures. Such applications would rely on the strength of complexation rather than on electrochemical resolution and thus may still benefit from the properties characterized in this work. Thus, this study has discovered that both thermodynamics and electrochemical resolutions must be jointly considered when designing sensors for trace metals. To achieve this, distinct electrochemical behaviour is needed; strong binding alone is insufficient. The framework here contributes to rationally developing more effective and selective sensing strategies for Fe<sup>2+</sup> in saline and complex aqueous systems. To summarize, this research confirms that TOPO binds Fe<sup>2+</sup> very strongly ( $\beta \approx 4.4 \times 10^{45}$ ; stoichiometry ~15:1) but lacks selectivity where Na<sup>+</sup> and K<sup>+</sup> are present as their corresponding stoichiometries (1.18 and 2.52) and overall complexation constant ( $\beta \approx 10^{14}$ –10<sup>15</sup>) show much weaker interactions.

These results should also be useful for fundamental physical chemists, as they offer a rare insight into the coordination strength of phosphine oxide moieties. TOPO is a good model to use for studying intrinsic metal-ligand interactions since it has donor groups.

Ligands incorporating structural elements such as rigid bidentate ligands (molecular structures that are inflexible and help in maintaining the forms of ligands) or multiple donor atoms (e.g., nitrogen or oxygen donors) could enhance selectivity by favouring octahedral coordination geometries commonly preferred by  $Fe^{2+}$ .<sup>1–3</sup> Simultaneously, electrochemical detection

techniques are essential; with the use of square wave voltammetry, it may be possible to identify transfer peaks in testing. This method might allow more accurate quantification and identification of ions in mixed systems.<sup>4,5</sup> Selectivity may also be affected by the organic phase selection. Exploring other solvents, including different ILs, could result in broader electrochemical windows and improved control over ion transfer. These solvents are proper for researching complex ion interactions because they often have low volatility and excellent stability under heat. Additionally, certain ionic liquids can suppress background current, allowing for more accurate detection of specific ion transfer processes under competitive conditions.<sup>6–11</sup>

Another key area is testing the developed system in real-world conditions. Assessing whether the technique continues to function in complicated matrix circumstances and high ionic strength would be done by simulating natural environments, such as saltwater or industrial brine.<sup>12</sup> Regarding the use of electrochemical methods for iron detection, although bimetallic gold-bismuth/indium tin oxide electrode (Au–Bi/ITO) electrochemical sensors have previously been used for Fe<sup>3+</sup> detection, as these sensors offer improved sensitivity and selectivity, enabling stronger and more accurate signals with very low detection limits.<sup>13</sup> Future research on natural water samples can explore adapting this approach for Fe<sup>2+</sup> detection. In order to better detect specific complexes and investigate metal-drug coordination, electrochemical methods may also be extended to pharmaceutical applications.<sup>14</sup>

Conclusion: (1) creating more selective ligands and (2) assessing system performance in practical settings in seawater samples should be the main goals of future research. The findings of this thesis can be transformed into practical and effective electrochemical sensor systems for the detection of trace  $Fe^{2+}$  using these techniques.

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