Electrochemically Controlled Metal Separation and Reduction at Polarized Liquid-Liquid Interfaces

Eemi Niemininen
Electrochemically Controlled Metal Separation and Reduction at Polarized Liquid-Liquid Interfaces

Eemi Nieminen

A doctoral thesis completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Engineering, at a public examination held at the lecture hall Ke2 of the school on 13 October 2023 at 13.

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Abstract

Hydrometallurgy and solvent extraction is a prevalent method to separate several metals from impurities of leached ores. In solvent extraction, the leached solution is brought into contact with an water-insoluble organic phase containing a selective ligand which extracts the desired metal, thus separating and purifying it. The interface between two immiscible electrolyte solutions can also be utilized as an easily reproducible template for biphasic metal deposition in which the electron donor is in the organic phase and the reducing metal cation in the aqueous phase.

In this thesis, electrochemically enhanced metal extraction and reduction reactions and their kinetics were investigated at these liquid-liquid interfaces. In practice, when two immiscible electrolyte solutions are brought into contact with each other and they contain a common ion, they establish an electrochemical equilibrium that is governed by the standard transfer potential characteristic to the common ion. This equilibrium determines a Galvani potential difference which can act as a driving force for ion transfer and reduction reactions. The extraction experiments showed that for certain metal-ligand pairs, only the introduction of the potential determining ions to the electrolyte solutions enabled the extraction of metals that otherwise would not be transferred and the transfer of which could not be detected in 4-electrode cyclic voltammetry.

Cu²⁺ reduction and nanoparticle nucleation at the liquid-liquid interface was studied by scanning electrochemical microscopy (SECM) and square-wave voltammetry (SWV) at a micro-interface established at the tip of a micropipette. In SECM, a Pt ultra\-micro\-_electrode was used to probe TCNQ⁻-mediated metal reduction taking place at the substrate interface and the redox reaction could be detected a positive feedback loop. In the SWV experiments, two steps of the coupled electrochemical reactions were detected as two separate waves that could not be easily distinguished by CV. By analyzing the experimental results of SECM and SWV with the finite element method simulations, the kinetic constants for the redox reaction could be quantitatively evaluated, which is valuable in understanding the mechanism of NP nucleation and potentially controlling their growth.

Keywords Liquid-Liquid Interfaces, electrochemistry, potential determining ions, SECM, micropipettes

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**Tekijä**
Eemi Nieminen

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Kemian teknikiann korkeakoulun

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During my time at Aalto University, I had the opportunity to meet and befriend with a large number of great individuals that were my colleagues, and naming and acknowledging them individually in this short paragraph would be an impossible task. I would like to thank them for the years I had the pleasure to spend together with, particularly Dr. Lauri Viitala, who had already instructed me in my Master’s thesis and continued to support and help me in the doctoral work. Of course I would also like to express my gratitude to my office mates, particularly Dr. Juhani Teeriniemi and Mr. Farhan Ali who made coming to the office all the more enjoyable. Dr.
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Lastly, I would like to thank my family, especially my mother, sister, and grandmother, for all the continuous support, love and encouragement I have received throughout the years.

Prague, August 27, 2023,

Eemi Nieminen
## Contents

**Preface**

**Contents**

List of Publications .......................... i

Author's Contribution .......................... iii

Errata ........................................... v

Abbreviations ................................... vii

Symbols ......................................... ix

1. Introduction .................................. 1

2. Theory ........................................ 5
   2.1 Distribution potential .................... 5
   2.2 Assisted metal transfer at ITIES .......... 6
   2.3 Kinetics of charge transfer at ITIES ........ 9
   2.4 Voltammetric techniques .................. 10
      2.4.1 Cyclic voltammetry ................. 10
      2.4.2 Square-wave voltammetry ............ 12
   2.5 Scanning electrochemical microscopy ...... 15
   2.6 Finite Element Method .................... 17

3. Experimental approaches .................... 21
   3.1 4-electrode cell voltammetry ............ 21
   3.2 Shake-flask experiments .................. 23
   3.3 SECM probe approach curves .............. 24
   3.4 Voltammetry at ITIES established at the tip of micropipette 26
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>On the stability of quasi-reference electrodes</td>
<td>27</td>
</tr>
<tr>
<td>3.6</td>
<td>Finite element method simulations for SECM and micropipette voltammetry</td>
<td>29</td>
</tr>
<tr>
<td>4.</td>
<td><strong>Results</strong></td>
<td>33</td>
</tr>
<tr>
<td>4.1</td>
<td>Cyclic voltammetry of assisted metal cation transfer</td>
<td>33</td>
</tr>
<tr>
<td>4.2</td>
<td>Electrochemically assisted metal extraction</td>
<td>34</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Electrochemically assisted reduction of Cu^{2+}</td>
<td>37</td>
</tr>
<tr>
<td>4.3</td>
<td>SECM measurements</td>
<td>38</td>
</tr>
<tr>
<td>4.3.1</td>
<td>FEM simulations of the approach curves</td>
<td>40</td>
</tr>
<tr>
<td>4.4</td>
<td>Cyclic voltammetry and square-wave voltammetry at μ-ITIES</td>
<td>41</td>
</tr>
<tr>
<td>4.4.1</td>
<td>FEM simulations of CV and SWV</td>
<td>44</td>
</tr>
<tr>
<td>5.</td>
<td><strong>Conclusions</strong></td>
<td>47</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>Publications</td>
<td></td>
<td>57</td>
</tr>
</tbody>
</table>
This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “Extraction of metals under Galvani potential control”

EN and LM defined the research plan. EN conducted the electrochemical measurements; EN, EA and HN conducted the shake-flask experiments. EN and LM analysed the experimental results. The preliminary metal reduction experiments and their Zeta-Sizer analyses were carried out by LM. EN compiled the manuscript and the work was supervised and reviewed by LM.

Publication II: “Probing TCNQ-mediated Metal Reduction Reactions at Liquid-Liquid Interface with SECM”

EN and LM defined the research plan. EN and NK prepared the ultramicroelectrodes. NK performed cyclic voltammetry measurements with the electrodes, EN conducted the SECM measurements. EN prepared the COMSOL model and conducted the FEM analyses with it. EN compiled the manuscript in its entirety and the work was supervised and reviewed by LM.

Publication III: “Kinetics of Cu^{2+} reduction and nanoparticle nucleation at micro-scale 1,2-dichlorobenzene-water interface studied by cyclic voltammetry and square-wave voltammetry”

EN and LM defined the research plan and EN manufactured the micropipettes and planned and conducted all electrochemical measurements. EN prepared the COMSOL model and conducted the FEM analyses with
Author's Contribution

it. The manuscript in its entirety was compiled by EN and the work was supervised and reviewed by LM.
Errata

Publication I

In Figure 6, the x axis is $c_{\text{TBACl}}$ instead of $c_{\text{TBATPB}}$; the anion PF$_4^-$ should be PF$_6^-$.  

Publication III

The electrochemical measurements were carried out with CHI900 workstation (CH Instruments, Austin, USA), not with Autolab potentiostat (PGSTAT100). The value for charge transfer coefficient $\alpha = 0.5$ was used throughout the simulations.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>1,2-DCB</td>
<td>1,2-dichlorobenzene</td>
</tr>
<tr>
<td>AAS</td>
<td>atomic absorption spectrometry</td>
</tr>
<tr>
<td>ACT</td>
<td>aqueous complexation followed by transfer to the organic phase</td>
</tr>
<tr>
<td>BA⁺</td>
<td>bis(triphenylphosphoranylidene)ammonium</td>
</tr>
<tr>
<td>BATB</td>
<td>bis(triphenylphosphoranylidene)ammonium(tetrakis(pentafluorophenyl))borate</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DMFc</td>
<td>decamethylferrocene</td>
</tr>
<tr>
<td>EE</td>
<td>two-step electrochemical reaction</td>
</tr>
<tr>
<td>FEM</td>
<td>finite element method</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma – optical emission spectrometry</td>
</tr>
<tr>
<td>ITIES</td>
<td>interface between two immiscible electrolyte solutions</td>
</tr>
<tr>
<td>L</td>
<td>ligand</td>
</tr>
<tr>
<td>M</td>
<td>metal</td>
</tr>
<tr>
<td>ML</td>
<td>metal-ligand complex</td>
</tr>
<tr>
<td>MIBK</td>
<td>methyl isobutyl ketone</td>
</tr>
<tr>
<td>PDS</td>
<td>potential determining salt</td>
</tr>
<tr>
<td>QRE</td>
<td>quasireference electrode</td>
</tr>
<tr>
<td>REE</td>
<td>rare earth elements</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SECM</td>
<td>scanning electrochemical microscopy</td>
</tr>
<tr>
<td>SWV</td>
<td>square-wave voltammetry</td>
</tr>
<tr>
<td>SX</td>
<td>solvent extraction</td>
</tr>
<tr>
<td>TATB</td>
<td>tetraphenyl arsonium tetraphenyl borate</td>
</tr>
<tr>
<td>TB⁻</td>
<td>tetrakis(phosphoranylidene)borate</td>
</tr>
<tr>
<td>TBATPB</td>
<td>tetrabutylammonium tetraphenylborate</td>
</tr>
<tr>
<td>TCNQ</td>
<td>7,7,8,8-tetracyanoquinodimethane</td>
</tr>
<tr>
<td>TEA⁺</td>
<td>tetraethylammonium</td>
</tr>
<tr>
<td>TIC</td>
<td>transfer by interfacial complexation</td>
</tr>
<tr>
<td>TOC</td>
<td>transfer followed by complexation in the organic phase</td>
</tr>
<tr>
<td>UME</td>
<td>ultramicroelectrode</td>
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Symbols

Latin Symbols

\( a \) activity
\( c \) concentration
\( c^b \) bulk concentration
\( c^s \) surface concentration
\( D \) diffusion coefficient
\( d \) distance between the SECM tip and the substrate
\( E \) potential
\( F \) Faraday constant
\( f \) \( \frac{F}{RT} \)
\( f_{sw} \) square-wave frequency
\( \Delta_G^0 \) standard Gibbs energy of transfer
\( H \) Heaviside step function
\( i \) current density
\( k^0 \) standard reaction rate coefficient
\( \bar{k} \) forward reaction rate coefficient
\( \bar{k} \) reverse reaction rate coefficient
<table>
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<th>Symbols</th>
<th>Description</th>
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<tr>
<td>$n$</td>
<td>number of electrons transferring in a redox reaction</td>
</tr>
<tr>
<td>$o$</td>
<td>organic phase (index)</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$r_0$</td>
<td>radius of ultramicroelectrode</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$w$</td>
<td>aqueous phase (index)</td>
</tr>
<tr>
<td>$x$</td>
<td>geometric constant</td>
</tr>
<tr>
<td>$z$</td>
<td>ion charge</td>
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<table>
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<th>Greek Symbols</th>
<th>Description</th>
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<tr>
<td>$\alpha$</td>
<td>charge transfer coefficient</td>
</tr>
<tr>
<td>$\Delta_o \phi^0$</td>
<td>standard transfer potential</td>
</tr>
<tr>
<td>$\Delta_o \phi'$</td>
<td>standard formal transfer potential</td>
</tr>
<tr>
<td>$\Delta_o \phi$</td>
<td>Galvani potential difference</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>dielectric constant</td>
</tr>
<tr>
<td>$\kappa^0$</td>
<td>dimensionless reaction rate constant</td>
</tr>
<tr>
<td>$\mu^0$</td>
<td>standard chemical potential</td>
</tr>
<tr>
<td>$\nu$</td>
<td>stoichiometric coefficient</td>
</tr>
<tr>
<td>$\chi$</td>
<td>driving force</td>
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1. Introduction

Rare earth elements (REE) are a group of 15 metals that are extremely scarce in the crust of Earth. The European commission has defined these elements in a recent study [1] as critical raw materials, i.e. materials with high economic importance and high supply risk. Furthermore, as the industrial demand for REE increases due to novel technological applications, their economic importance will increase while the depleting ores raise the supply risk. Therefore, finding new methods to extract and enrich these elements from scarce resources has become an increasingly relevant focus of research in the field of metallurgy [2].

Hydrometallurgy is one of the most prevalent methods of separating metals from ores. As the etymology of the term suggests, hydrometallurgy involves an aqueous phase into which the metal is dissolved (i.e. leached) from ore or metal scrap with strong acids. In order to separate the metal from impurities, it is extracted to an organic phase that contains a metal selective ligand. This is called solvent extraction (SX), and with a proper choice of ligand, it can be employed to purify almost any metal from the leach solution, and SX of REE has been an intensively researched subject [3–13].

In addition to SX, the interface between two immiscible electrolyte solutions (ITIES) offers a convenient platform for interfacial redox reaction in which one phase contains the reducing species that donates the electrons e.g. to a metal cation in the other phase which results in metal deposition at the ITIES [14–19]. This phenomenon has been studied since the 1970’s, when Guainazzi et al. [20] first discovered that metal cations could be reduced and deposited onto an ITIES when a direct current through it was applied. Also, at the same time, pioneering work in the research of charge transfer at a polarizable ITIES was carried out by the Czech research group by Koryta et al. [21–24] and also in France by Gavach et al. [25–27]
Electrochemical measurements at ITIES are mostly carried out with a four-electrode potentiostat that allows the interface to be treated as a “working electrode” at which the Galvani potential difference can be controlled and the detected currents represent ions transferring from one phase to another. However, instead of using external electrodes and a potentiostat to control the potential difference at ITIES, it can also be determined by the ions that are distributed to both phases. It has been shown that this distribution potential can act as a driving force in interfacial electrochemical reactions, e.g. electrocatalytic dehalogenation [28], hydrogen evolution reaction [29], biomimetic oxygen reduction [30] and separation of metals has also been studied by Schiffrin et al. [31]

In this thesis, various electrochemical tools were employed to investigate both metal extraction and reduction reactions at the ITIES. The main focus was to utilize the Galvani potential difference between the aqueous and organic phase established by a common ion as a driving force to bring about these reactions. The aim was to investigate the possibilities to utilize Galvani potential difference as a hydrometallurgical tool to enhance metal separation by SX or reduction of the metal cations.

In Publication I, ligand assisted metal cation transfer and its characteristic transfer potential from the aqueous to the organic phase was measured with a conventional 4-electrode cell cyclic voltammetry (CV), and extraction of various metals was attempted by using potential determining ions to fix the Galvani potential difference to a range which favours the extraction. It was found that for some metal-ligand pairs, the SX could be enhanced electrochemically.

In Publication II, scanning electrochemical microscopy (SECM) with a Pt disc UME as a probe was utilized to detect metal reduction at the ITIES and study the effect of the Galvani potential difference on it. The Galvani potential difference could be imposed on the ITIES externally with a fourth electrode or with the potential determining ions. By utilizing the SECM feedback method, the redox reaction at the substrate ITIES could be observed as an increasing current through the probe due to positive feedback. With the help of finite element method (FEM), kinetic parameters of the reaction could be obtained.

In the third publication, the ITIES was miniaturized to a micrometer scale by establishing the interface onto the tip of micropipettes that were manufactured with a pipette puller. Micropipettes have been used since the early 1990’s to study ion transfer [32–34] and more recently electrosynthesis of nanoparticles at the ITIES by Moshrefi et al. [18, 19, 35]
Interfacial redox and metal transfer could be studied at the \( \mu \)-interface, or it could be used as an SECM probe similarly to a solid Pt disc [36, 37]. Publication III focused on the former as kinetics of \( \text{Cu}^{2+} \) reduction and nanoparticle formation were investigated, which was also the main focus in Publication II. By miniaturizing the ITIES, two benefits can be achieved: as the currents flowing through decrease, the Ohmic loss also decreases. More importantly, the diffusion limited mass transfer is enhanced which allows determination of fast reaction kinetics.

Square-wave voltammetry utilized in the paper has been shown theoretically to be able to distinguish the steps of a two-step electrode reaction, \textit{i.e.} two subsequent electrochemical reactions (EE mechanism) [38], and by comparing the voltammograms obtained from the measurements with the finite element simulations, an estimation for the reaction rate constants for the NP formation could be provided.
2. Theory

2.1 Distribution potential

When two immiscible electrolyte solutions (organic $o$ and aqueous $w$) are brought into contact with each other, they assume a state of electrochemical equilibrium which is defined by distribution of a common ion $i$. At electrochemical equilibrium, the electrochemical potentials ($\tilde{\mu}$) of such an ion are by definition equal in both phases:

$$\tilde{\mu}_i^o = \tilde{\mu}_i^w \Rightarrow \mu_i^{0,o} + RT \ln a_i^o + z_i F \phi^o = \mu_i^{0,w} + RT \ln a_i^w + z_i F \phi^w$$  \hspace{1cm} (2.1)

where $\mu_i^0$ is the standard chemical potential of $i$ and $\phi$ is the electrostatic potential in the phase indicated by the superscript. The Galvani potential difference ($\Delta_w^o \phi$) can be simply derived from this equation, which leads to an equation similar to the Nernst equation:

$$\Delta_w^o \phi = \phi^w - \phi^o = \Delta_w^o \phi_i^0 + \frac{RT}{z_i F} \ln \frac{a_i^o}{a_i^w} = \Delta_w^o \phi_i^0 + \frac{RT}{z_i F} \ln \frac{c_i^o}{c_i^w}$$  \hspace{1cm} (2.2)

where $\Delta_w^o \phi_i^0$ is the standard transfer potential of ion $i$ and $\Delta_w^o \phi_i^0$ is its standard formal transfer potential which is $\Delta_w^o \phi_i^0$ to which the contribution of the activity coefficients is incorporated. Essentially, $\Delta_w^o \phi_i^0$ is the voltage scale expression of standard Gibbs energy of transfer:

$$\Delta_w^o \phi_i^0 = - \frac{\Delta_w^o G_i^0}{z_i F} = - \frac{\mu_i^{0,w} - \mu_i^{0,o}}{z_i F}$$  \hspace{1cm} (2.3)

In effect, $\Delta_w^o \phi_i^0$ describes the affinity of ion $i$ to the organic phase. For hydrophilic ions $\Delta_w^o G_i^0 < 0$, and for hydrophobic ions $\Delta_w^o G_i^0 > 0$. $\Delta_w^o G_i^0$ and therefore the $\Delta_w^o \phi_i^0$ can be obtained experimentally with various electrochemical methods if the transfer can be observed within the potential...
window [39–42]. $\Delta u^w \phi_i^0$ can also be estimated with Born’s model [43], which takes into account the valence and size of the ion and the dielectric constant of the aqueous and organic solvent ($\varepsilon_w$ and $\varepsilon_o$, respectively). Equation 2.2 can be rewritten to represent the distribution of ion $i$, as shown in equation 2.4:

$$\frac{c_i^o}{c_i^w} = \exp \left[ z_i f \left( \Delta_o^w \phi - \Delta_o^w \phi_i^0 \right) \right]$$  \hspace{1cm} (2.4)

The implication of equations 2.2 and 2.4 is that the Galvani potential difference at an ITIES is determined by the standard transfer potential of the common ion and its concentration ratio between the two phases. If there are more than one distributing ions, their contribution to the Galvani potential has to be taken into account. Combining mass balance equations, electroneutrality condition and the electrochemical equilibrium (which is expressed in equation 2.2) leads into following equation:

$$\sum_i \frac{z_i (c_i^w,0 + r c_i^o,0)}{1 + r \exp \left[ -z_i f (\Delta_w^o \phi - \Delta_w^o \phi_i^0) \right]} = 0$$  \hspace{1cm} (2.5)

where $r$ is the volume ratio of the two phases and $f = F/(RT)$. $\Delta_o^w \phi$ can be solved from this equation if all other parameters are known, including the $\Delta_w^o \phi_i^0$ for each distributing ion.

Most ions in aqueous solutions are extremely reluctant to transfer to an organic phase, and their contribution to $\Delta_o^w \phi$ can be neglected. Usually the potential determining ion is a bulky hydrophobic ion that is dissolved to the aqueous phase as a salt of a small counterion, and to the organic phase as a salt of a hydrophobic counterion. For example, bis(triphenylphosphorylidene)ammonium tetrakis(pentafluorophenyl)borate (BATB) (figure 2.1) is widely used as such a potential determining salt (PDS). As it dissolves easily to organic solvents used in liquid-liquid electrochemistry, it is also commonly used as a supporting electrolyte in electrochemical measurements to improve conductivity as the high standard transfer potentials of BA$^+$ and TB$^-$ enable wide potential windows.

### 2.2 Assisted metal transfer at ITIES

Assisted metal transfer at an ITIES relies on the interaction between the metal ion and a selective hydrophobic ligand (L) that remains in the organic phase. As the two phases come into contact with each other, the metal forms a complex with the ligand making it essentially more
Figure 2.1. Chemical structure of cis(triphenylphosphoranylidene)ammonium) tetrakis(pentafluorophenyl)borate (BATB), created with Avogadro [44].

hydrophobic. The theory has been discussed in the literature [45, 46]. Assisted ion transfer (IT) can follow a mechanism, in which the metal forms the complex in the aqueous phase and is then transferred into the organic phase, i.e. ACT (aqueous complexation followed by transfer to the organic phase). Alternatively, the ion can transfer into the organic phase and subsequently form the complex with the ligand, i.e. TOC mechanism (transfer followed by complexation in the organic phase). Thirdly, the complexation can take place directly at the ITIES (transfer by interfacial complexation, TIC). [32]

In case of the TOC mechanism, the complexation reaction can be formally written as two separate reactions, namely the ion transfer and the subsequent complex formation in the organic phase:

\[
\begin{align*}
M^{2+}(w) &\rightleftharpoons M^{2+}(o) \\
M^{2+}(o) + 2L(o) &\rightleftharpoons ML_2(o)
\end{align*}
\] (2.6)

In electrochemical equilibrium, equation 2.2 applies for the former reaction. For the latter, an equilibrium constant can be defined as shown in equation 2.7:

\[
K_{eq} = \frac{a_{ML_2}^o}{a_{M^2+}^o c_L^o} = \frac{c_{ML_2}^o (c^o)^2}{c_{M^2+}^o (c_L^o)^2}
\] (2.7)

Combining \(K_{eq}\) to equation 2.2 and defining \(\Delta^\omega\phi^0_{ML_2}\) results in equation 2.8
\[
\Delta_o^w \phi = \Delta_o^w \phi_{M^{2+}}^0 - \frac{RT}{2F} \ln K_{eq} + \frac{RT}{2F} \ln \frac{c_{ML2}^0 (c^0)^2}{c_{M^{2+}}^w (c_L^0)^2}
\]
\[
= \Delta_p^w \phi_{ML2}^0 + \frac{RT}{2F} \ln \frac{c_{ML2}^0 (c^0)^2}{c_{M^{2+}}^w (c_L^0)^2}
\]

(2.8)

where \(c^0\) is the standard concentration (1 M by definition). Equation 2.8 essentially shows that presence of a ligand in the organic phase decreases the transfer potential threshold of the metal cation [47].

The extraction fraction is defined as the ratio of the amount of metal extracted to the organic phase and the initial total amount of metal. Since all of the metal is initially in the aqueous phase and if the volumes of the aqueous and organic phase are equal and assuming that only a negligible amount of free metal ions are present in the organic phase in equilibrium, the extraction fraction \(X\) can be written as:

\[
X = \frac{n_{M^{2+}}^o}{n_{M^{2+}}^o + n_{M^{2+}}^w} = \frac{c_{M^{2+}}^o}{c_{M^{2+}}^o + c_{M^{2+}}^w} = \frac{c_{M^{2+}}^o}{[M^{2+}]^w} \approx \frac{c_{M^{2+}}^o}{[M^{2+}]^w} \approx \frac{c_{ML2}^0}{[ML2]^w}
\]

(2.9)

where \([M^{2+}]^w\) is the initial metal concentration in the aqueous phase. Combining equations 2.8 and 2.9, \(\Delta_o^w \phi\) can be presented as a function of \(X\):

\[
\Delta_o^w \phi = \Delta_o^w \phi_{ML2} + \frac{RT}{2F} \ln \frac{X (c^0)^2}{(1-X) ([L] - 2 [M^{2+}]^w X)}
\]

(2.10)

from which \(X\) can be easily solved numerically, when the initial concentration of the ligand and metal cation are known ([L] and \([M^{2+}]\), respectively). Figure 2.2 shows the behaviour of \(X\) as a function of \(\Delta_o^w \phi - \Delta_o^w \phi_{ML2}^0\) solved from equation 2.10 when \([L]^o = [M^{2+}]^w\) and the 1:2 stoichiometry shown in reaction 2.6 was assumed. Equation 2.10 also implies that \(\Delta_o^w \phi_{ML2}\) can be obtained if \(\Delta_o^w \phi\) is known for each \(X\). As previously demonstrated, \(\Delta_o^w \phi\) can be solved from equation 2.5.
2.3 Kinetics of charge transfer at ITIES

Assisted metal transfer is effectively a form of charge transfer that can be detected as a current through the interface. However, charge transfer at the ITIES can also take place as a biphasic redox reaction in which a reduced species (R(o)) is oxidized in the organic phase as it donates an electron to a metal cation in the aqueous phase:

\[ \nu R(o) + M^z(w) \rightleftharpoons \nu O(o) + M^{z-\nu}(w) \]  (2.11)

To approach the kinetics of electron transfer (ET) of this kind, a simple way to describe the reaction rate \( v \) is by equation 2.12 which simply states that \( v \) depends on the surface concentrations of the substrates and the products:

\[
v = \frac{i}{nF} = \bar{k} (c_{R}^{s,o}) c_{M}^{s,w} - \bar{k} (c_{O}^{s,o}) c_{M}^{s,w-\nu} \]

(2.12)

where \( i \) is the current density and \( c^s \) are the surface concentrations of the species denoted by the subscript in phase \( o \) or \( w \) (denoted by the superscript). \( \bar{k} \) and \( \bar{k} \) are the forward and reverse reaction rate coefficients that depend on \( \Delta w_o^\phi \) that and are shown in equations 2.13 and 2.13: [48]

\[
\bar{k} = k_0 e^{af(\Delta w_o^\phi - \Delta E^0)} \]

(2.13)

\[
\bar{k} = k_0 e^{-(1-a)f(\Delta w_o^\phi - \Delta E^0)}
\]

(2.14)
where $\alpha$ is the electron transfer coefficient and $E'^0$ is the difference of standard formal redox potentials of $M^z|M^{z-1}$ and $O(o)|R(o)$ against the same reference electrode. Combining equations 2.12, 2.13 and 2.14 leads to a Butler-Volmer type kinetics of second degree [49,50]:

$$
\frac{i}{nFk_0} = (c_R^{s,o}c_M^{w} e^{\alpha_f(\Delta_w \phi - \Delta E'^0)}) - (c_O^{s,o} c_{M^{z-1}}^{w} e^{-(1-\alpha_f)(\Delta_w \phi - \Delta E'^0)})
$$

(2.15)

The stoichiometry of reaction 2.11 obviously determines the amount of electrons transferred, i.e. $n = \nu$.

If $z = 2$, the metal reduction can also take place in two steps, i.e. in an EE reaction.

$$
R(o) + M^{2+}(w) \rightleftharpoons O(o) + M^{+}(w)
$$

(2.16)

$$
R(o) + M^{+}(w) \rightleftharpoons O(o) + M(ads)
$$

(2.17)

In this case, the Butler-Volmer kinetics can be written for both reactions separately and the total current is the sum of the two currents originating from the steps 1 and 2 (reactions 2.16 and 2.17, respectively). In practice, the Butler-Volmer equation is written for both steps with their characteristic electrode potentials, surface concentrations and kinetic constants.

### 2.4 Voltammetric techniques

#### 2.4.1 Cyclic voltammetry

Cyclic voltammetry (CV) is one of the fundamental tools of electrochemistry and it can be used to analyse various qualitative and quantitative features of electrochemical reactions, e.g. concentrations, diffusion coefficients, reversibility of the reaction, or its mechanics or the active surface area of the electrode. CV is more often applied to measure and analyse reactions taking place at a solid electrode, but with a suitable cell setup ion or electron transfer reactions through a liquid-liquid interface can also be studied.

In CV, the current flowing through the working electrode is recorded while the potential at it is swept at a constant sweep rate $v_c$ from an initial potential $E_{in}$ to a vertex potential $E_{vx}$, forming a potential cycle which can be repeated. i.e. the potential signal is a triangle function that is often expressed as a Heaviside step function $H$: 
Figure 2.3. A potential window with a charge transfer reaction in the middle, adapted from Publication I.

\[ E(t) = E_{in} + \nu_c t - 2H(t - (E_{ox} - E_{in})/\nu_c)\nu_c(t - (E_{ox} - E_{in})/\nu_c) \]  \hspace{1cm} (2.18)

where \( H(t - (E_{ox} - E_{in})/\nu_c) = 0 \) when \( t < (E_{ox} - E_{in})/\nu_c \) and \( 1 \) when \( t = (E_{ox} - E_{in})/\nu_c \). The theoretical current response to a triangle wave signal (the voltammogram) can be derived by combining equation 2.18 with Butler-Volmer equation, or Nernst equation in a case of a reversible reaction and by solving the surface concentrations from Fick’s second law, which leads to a convolution integral which can be solved numerically to derive the current-potential behaviour. The method has been described in more detail in literature [51,52].

Figure 2.3 shows a typical potential window at a macroscopic polarizable ITIES. It should be noted that instead of a conventional CV at a solid working electrode where currents represent redox reactions, in CVs at ITIES, the observed currents arise from ions transferring from one phase to another: the window is limited by the supporting ion that is most prone to transfer from one phase to another, and in the middle of the window the transfer of a studied ion generates a current wave with a characteristic duck shape that is also predicted by the theory. By convention, positive current can represent positively charged ion moving from the aqueous to the organic phase or negatively charged ion to the opposite direction, and vice versa for a negative current.

The shape of the wave, peak current and peak separation provide information on the reversibility and transfer potential of the reaction. An important diagnostic criterion for reversibility asserts that the separation of the forward and reverse peaks is \((56.5 \text{ mV})/n\) and the ratio of the peak currents is unity. Additionally, for a reversible reaction the peak current
density $i_p$ and its relation to the diffusion coefficient $D$ and $v_c$ follows the Randles-Ševčík equation:

$$i_p = 0.4463nFc^b\sqrt{\frac{nF}{RT}v_cD}$$  \quad (2.19)$$

I.e. the peak current is directly proportional to the bulk concentration $c^b$, $\sqrt{v_c}$, and $\sqrt{D}$. After the peak the current starts to decrease as the diffusion layer (the layer at the electrode’s surface where the concentration is substantially lower than the bulk concentration) grows because the diffusion of the reacting species is slower than the rate at which it reacts at the electrode, thus the current is limited by diffusion.

When the size of the electrode is decreased to a $\mu$m scale, the currents determined by the kinetics of the electrode reactions become so small that the diffusion is sufficient to transfer the reacting species onto the surface and mass transfer thus no longer limits the current. In practice, miniaturizing the electrode has the same effect as imposing a convection which prevents the diffusion layer from growing. As the thickness of the layer does not grow, the current does not have a local maximum but approaches the limiting current asymptotically.

### 2.4.2 Square-wave voltammetry

Square-wave voltammetry (SWV) is a differential voltammetric technique which utilizes a superimposed square-wave and staircase signal, and its theory has been widely discussed in literature [38, 53–55]. In practice, the technique has been used to analyse quantitative and qualitative electrochemical reactions: for example, Ikonen et al. measured partition of drugs at $\mu$-ITIES with SWV, and Mirčeski et al. [56] utilized the technique to quantify the kinetics of azobenzene and hexacyanoferrate reduction. Application of SWV in kinetic studies of biological/ enzymatic electrochemical processes has also been demonstrated [57, 58].

SWV is based on a potential signal that is characterized by the amplitude of the square wave $E_{am}$, step size $E_{st}$ and frequency $f_{sw}$. At each step, the square wave makes one cycle so that the potential is switched by $\pm 2E_{am}$ at every half-period. The square-wave potential signal can be thus represented as a sum of the initial potential $E_{in}$, step function $E_{st}$ and the square-wave function $E_{sw}$ as shown in equation 2.20:
\[ E = E_{in} + E_{st} + E_{sw} \]

\[ = E_{in} + \Delta E \text{ floor}((m(t) - 1)/2) \]

\[ + E_{am} \text{ SW}(m(t)) \]

where \( \Delta E \) is the potential step size and \( \text{SW} \) is a function that returns \(-1\) when \( m(t) \) is odd and \(1\) when it is even. \( m(t) \) is a function that discretizes \( t \) into integers in a way that first halves of the square wave period are represented by odd integers and the second halves by even ones:

\[ m(t) = \text{ceil}(2t f_{sg}) \]

The square wave signal is illustrated in figure 2.4. Instead of giving the current as an output as in cyclic voltammetry, in SWV the current is recorded twice at every cycle of a square wave, immediately before the potential is switched, and the output of SWV is the difference of currents between the forward (\( +E_{am} \)) and reverse (\( -E_{am} \)) potentials and it is plotted as a function of \( E - E_{SW} \).

A typical square-wave voltammogram is shown in figure 2.5 in which the transfer of \( \text{TEA}^+ \) through a \( \mu \)-ITIES generates a current response (blue line): the increasing current corresponds to accelerating current growth in CV whereas zero-current does not necessarily mean that the current is zero at the forward and reverse potentials but rather that the current does not change between them (\( i.e. \) steady-state current).

**Figure 2.4.** Square wave signal as a function of \( t/\tau \) (period) (blue line), created with MATLAB from equation 2.20. The black dashed line represents the \( E_{st} \) function which increases step-wise by \( \Delta E \) at the end of each period.

The theoretical approach for SWV is more complicated than in cyclic voltammetry although the principle is similar in both techniques. The
derivation of the current response to a SWV signal has been discussed in literature [53, 59, 60]. Similarly to CV, the square-wave potential function (equation 2.20) is incorporated to the Butler-Volmer equation which is combined to the diffusion equation (Fick’s second law) with the appropriate boundary values. The current as a function of $E$ can be solved numerically from the resulting equation.

Because of the differential nature of the technique, SWV is more sensitive to distinguish electrochemical reactions with redox potentials close to each other. SWV is also less sensitive to background noise such as capacitive charging current. The effect of these transients can also be minimized by decreasing $f_{sg}$. This will increase the time during which the signal remains at each potential, thus giving more time for the transients to dampen. $E_{am}$ is another parameter that can be varied and decreasing it also partly reduces the effect of the charging currents [61]. Furthermore, according to some studies [62], by running the SWV measurements at various amplitudes and by comparing the peak currents of the forward and reverse curves, kinetic information of the studied reaction can be obtained.

In SWV, the sweep rate $v_c$ can not be given as a parameter similarly to CV because it is determined by $f_{sg}$ and $\Delta E$ by equation 2.22.

$$v_c = f_{sg} \Delta E$$

(2.22)

\_i.e. increasing either $f_{sg}$ or $\Delta E$ also increases the sweep rate.\_
2.5 Scanning electrochemical microscopy

Since the introduction of scanning electrochemical microscopy in the late 1980’s by Bard et al. [63] the technique has rapidly increased in popularity as a versatile electrochemical analytical tool to study e.g. the kinetics of interfacial reactions [64–67], biological imaging [68–71] and photocatalysis [72–75]. A simple Google Scholar search (figure 2.6) shows the steadily grown interest in SECM technology during the last three decades.

![Google Scholar search results for articles with "scanning electrochemical microscopy" and/or "SECM" in their titles since the 1980’s.](image)

In essence, SECM is a microscopical technique which—instead of light and lenses or electrons and magnets—is based on the electrochemical interaction between an electrode (probe) and the substrate (the surface that is being investigated). The instrumentation consists of a PC-operated bipotentiostat that is connected to the reference/counter electrode, to the substrate if needed, and to a micrometer scale probe that can be a solid ultramicroelectrode, e.g. Pt disk UME, or a micropipette with a μ-ITIES established at its tip [36]. The probe is in contact with an electrolyte solution that contains the oxidized form of a redox couple (O) that is reduced at the probe:

\[
O + e^- \rightleftharpoons R \quad (2.23)
\]

The potential at the probe should be at a regime where it can support a steady-state current characteristic to UMEs that is governed by equation 2.24 [52]:

\[
15
\]
\[ i_{ss} = x n D_0 F r c_0 \] (2.24)

where \( r \) is the radius of the UME and \( x \) is a constant that depends on the geometry of the UME. For example, for a hemispherical electrode \( x = 2\pi \) and for disk-shaped UME \( x = 4 \) [52]. \( x \) also depends on the \( RG \) value, which is the ratio of the radius of the tip including the insulating sheath and \( r \): as the sheath becomes less thick, the oxidized species in the bulk becomes more accessible to the electrode, thus increasing \( x \). Increasing the thickness would result in \( x \) approaching 4.

The probe itself is attached to a piezoelectric-motorized holder that enables positioning of the probe at high resolution and in all directions, which allows scanning and approaching the substrate. As the probe is set to approach the substrate while it releases R at a constant current, the interactions between substrate and the redox pair cause the current to deviate from the current at bulk determined by equation 2.24. SECM is based on these interactions [76].

SECM can be operated in a number of modes, most important of which are the feedback mode, substrate generation/tip collection (SG/TC) and tip generation/substrate collection (TG/SC) modes. Other SECM modes have been discussed in literature [76]. In feedback mode, the probe is brought close to the substrate at a potential in which the current is at steady state, the properties of the substrates affect the probe, which can be detected as changes in current. If the substrate is not conductive, its geometric properties hinder the access of the redox couple onto the probe, resulting in decreasing current (negative feedback), whereas conductive substrates have an opposite effect as the reduced species donates the electron to the substrate triggering a positive feedback loop. 2.7.
Instead of a solid insulating/conductive substrate, SECM can be utilized to probe liquid-liquid interfaces and redox/ion transfer reactions taking place at it. This has been first proposed by Shao and Mirkin [77,78] who used the micropipettes as probes to measure facilitated K\(^+\) transfer from inside a micropipette to the bulk organic phase and from the organic phase into the aqueous substrate phase.

SECM can also be used to probe electron transfer at ITIES [65,79,80]. The species that is reduced at the UME can donate the electron to a cation in the substrate phase and subsequently be reduced again at the UME, which results in a positive feedback loop. If no such electron transfer takes place, the ITIES behaves like an insulating substrate, and is thus detected as negative feedback.

The probe approach curves are a good method to detect redox and ion transfer reactions at an ITIES. The shape of the curves can also provide valuable information on the reaction kinetics. This can be achieved by comparing them to theoretical approach curves that are obtained by solving the diffusion problem at various distances from the substrate. Numerical models do this have been developed by Wei et al. [65] or Barker et al. [81] whose model has been later applied in several SECM studies (e.g. [82–84]).

### 2.6 Finite Element Method

As the computational capacity of personal computers has been constantly improving, finite element (FEM) simulations provide a useful tool to conduct kinetic analyses of voltammetric and SECM measurements. For
example, FEM simulations of CV and SWV at $\mu$-ITIES [85, 86] and also SECM [87–89] have been carried out. In this thesis, FEM models were developed for both SECM and CV/SWV at $\mu$-ITIES and they were used to extract kinetic parameters from the experimental measurements.

FEM is a simulation tool in which relevant physics are applied on a geometry that mimics the cell and electrode used in the experiments. Building an FEM model consists of defining the 1) geometry, 2) mesh, 3) parameters and physics and 4) study. The geometry is made to resemble the size and shape of the used cell or other subject of study to a reasonable accuracy. Depending on the symmetrical features of the target, it can be modelled in one, two or three dimensions. For example, in a case of large planar electrodes or interfaces, 1D modelling is sufficient. In figure 2.8, the geometry is axisymmetrical, which allows the cell to be modelled in two dimensions which decreases the computation time.

The geometry is divided into domains that correspond to different phases of the cell, namely the organic bulk and aqueous substrate phase. If micropipettes are modeled, the aqueous phase inside the pipette constitutes its own domain. The domains are separated from each other by boundaries and variables and physics (e.g. concentrations, diffusion coefficients, fluxes) can be assigned to each of the domains and boundaries separately.

![Diagram of FEM simulation process](image)

**Figure 2.8.** Summary of the FEM simulations, starting from defining the geometry and the mesh making the geometry into 3D using the axial symmetry, simulating the concentration profile and current at the electrode at various distances from the ITIES, and finally compiling the simulations into approach curves.

The domains are further discretized into meshes consisting of finite el-
elements that interact with each other based on the applied physics which generate a group of partial differential equations that are solved numerically. In order to produce accurate results in FEM simulations, creating a good mesh is crucial. If the mesh is too sparse, the accuracy of the model will suffer, but if it is excessively dense, the calculations will become time consuming. It is therefore reasonable to vary the density depending on the relevance of the simulated area: in the periphery of the model in which no reactions take place, the mesh can be set very sparse, whereas in the vicinity of the interfaces/working electrode, the density should be higher.

The electrode reactions and charge transfer at ITIES can be modeled as transport of dilute species at the boundary. With this module, the transport is defined by a flux at the boundary and it can be set to follow the desired kinetics, for example the discussed Butler-Volmer kinetics (equation 2.15) for reaction 2.11. For the reaction taking place at a UME (reaction 2.23), the steady state boundary condition can be established by setting a constraint that surface concentration of O to 0 and the surface concentration of R to the initial bulk concentration of O. A more accurate method would be to use first degree Butler-Volmer kinetics in equation 2.25, which is derived in a similar fashion as equation 2.15:

\[
\frac{i}{nFk^0} = c_R e^{a f (E-E_{O|R}^0)} - c_O e^{-(1-a) f (E-E_{O|R}^0)} \tag{2.25}
\]

where \(E_{O|R}^0\) is the standard redox potential of O/R and \(E\) is an arbitrary potential which is negative enough to support reduction of O to R at steady state current.

Depending on the nature of the problem, FEM simulations can be run by different studies, for example time-dependent or steady state. The former takes into account the time dependent transients in the equations that the physics are governed by, whereas the latter is applicable to a system which does not have variables that change in time, i.e. the equations representing the desired physics will be generated without the time derivatives. For example in the case of transport of dilute species which is utilized in this work, the time-dependent study corresponds to Fick’s second law and steady state to Fick’s first law.

In conjunction with the studies, parametric sweeps are often carried out. In other words, the simulation can be run multiple times by varying any parameter. For example, a probe approach curve can be achieved most easily by running a parametric sweep on the distance of the probe from the substrate \(d\); or the kinetic parameters can be swept in SECM, CV and
SWV simulations. The implementation of FEM modelling in this thesis will be discussed in more detail in the following chapter.
3. Experimental approaches

3.1 4-electrode cell voltammetry

4-electrode voltammetry is an elementary tool that has been used to measure charge transfer at the ITIES since the 1970’s [23, 90]. The setup consists of two reference electrodes and two counter electrodes that provide the current, one in the aqueous and one in the organic phase. The organic reference electrode was inserted to a separate aqueous phase with a liquid-liquid junction at which the potential drop is determined by equation 2.2.

In Publication I, 4-electrode cyclic voltammetry was used to measure the potential range at which ligand-assisted metal transfer takes place. Diphenylthiocarbazone (Dithizone, figure 3.1) was selected as a ligand. It is known to form hydrophobic complexes with several metal cations, Cu$^{2+}$ being one of them [91]. The aqueous phases in contact with Dithizone should be sufficiently acidic which prevents Dithizone from deprotonating and becoming hydrophilic.

The composition of the cell used in 4-electrode cell measurements in Publication I is shown in scheme 3.1. The experiments were carried out with both sulphate and chloride salts of the metal cations. Scheme 3.1 shows the sulphate setup: if chloride salts were used, LiCl was used as the supporting electrolyte and the pH was adjusted with HCl. Additionally, Ag|AgCl electrode was used instead of Pt. LiCl/Li$_2$SO$_4$ and bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BATB) were used as a supporting electrolyte in the aqueous and organic phase, respectively. BATB was formed by metathesis from bis(triphenylphosphoranylidene)ammonium chloride (BACl) and lithium tetrakis(penta-
**Experimental approaches**

**Figure 3.1.** Diphenylthiocarbazone (Dithizone) [92], created with Avogadro.

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>AgCl</th>
<th>10 mM BATB</th>
<th>5 mM Li$_2$SO$_4$</th>
<th>5 mM H$_2$SO$_4$</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dithizone</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>MSO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Reference aqueous (w')</td>
<td>Organic (o)</td>
<td>Aqueous (w)</td>
<td></td>
</tr>
</tbody>
</table>

**Scheme 3.1.** Structure of the 4-electrode cell used in the measurements.

fluorophenyl)borate (LiTB). The salt was subsequently recrystallized in acetone, as instructed in literature [16].

The conversion of the cell potential to the Galvani potential scale can be calculated from the cell equation 3.1:

$$\Delta^{w}_{o} \phi = E_{cell} + E_{Ag[AgCl]}^{0} + \Delta^{w}_{o} \phi_{BA}^{0} - \frac{RT}{F} \ln \left( \frac{(c_{BA}^{0})^{2}c_{H}^{w}}{c_{o}^{0}c_{BA}^{0}} \right)$$

(3.1)

Another convenient method to determine the $\Delta^{w}_{o} \phi$ scale is to measure the half-wave potential ($\Delta^{w}_{o} \phi_{i,1/2}$) of transfer of an ion that has a known $\Delta^{w}_{o} \phi^{0}$. The relation between $\Delta^{w}_{o} \phi_{i,1/2}$ is given in equation 3.2: [47]

$$\Delta^{w}_{o} \phi_{i,1/2} = \Delta^{w}_{o} \phi_{i}^{0} + \frac{RT}{2z_{i}F} \ln \left( \frac{D_{i}^{w}}{D_{i}^{0}} \right)$$

(3.2)

It is reasonable to approximate that the second term of equation 3.2 is roughly 0, from which follows that $\Delta^{w}_{o} \phi^{0}$ roughly equals the half-wave potential. In the 4-electrode CV measurements of Publication I, transfer of tetraethylammonium (TEA$^+$, $\Delta^{w}_{o} \phi_{TEA}^{0} = 116$ mV) was measured to establish the $\Delta^{w}_{o} \phi$ scale.

The 4-electrode CV measurements were carried out at room temperature in aerobic conditions with a PGSTAT100 potentiostat (Echochemie, the Netherlands). The glass cell was provided by prof. Z. Samec from J. Heyrovský Institute of Physical Chemistry, Prague, Czechia.
The resistance of the organic phase is the main cause of Ohmic loss in the measurements, and minimizing it with the hydrophobic supporting electrolyte (BATB) and by connecting the reference electrode to the ITIES with a Luggin capillary does not remove it entirely. Therefore, $iR$ compensation is required and it can be done with a positive feedback loop method that has been described in the literature [93] and can be enabled in software operating the potentiostat.

3.2 Shake-flask experiments

The shake-flask experiments were carried out to measure the extraction fraction, i.e. the percentage of metal transferred to the organic while being in contact with it under vigorous shaking (equation 2.9) $\Delta_{\text{w}} \phi$ was fixed with a common ion: different common ions could be utilized to set the potential to a desired regime, and an exact value of the potential difference could be calculated with equation 2.5 if the initial and final concentrations are known.

The composition of the phases is shown in table 3.1. The Galvani potential difference at the ITIES could be manipulated by selecting a different common ion and varying its concentration. For example, standard transfer potential of TB$^-$ from DCB to water is ca 0.66 V [30], which gives the highest $\Delta_{\text{w}} \phi$ in our experiments. BA$^+$ on the other hand has a negative $\Delta_{\text{w}} \phi^0$, and therefore it could be used in stripping experiments, or if the extracted metal is in a negatively charged chlorocomplex, e.g. PtCl$_2$$^-$ . Additionally, the concentration ratio of the common ion in the organic and aqueous phase have a small effect on $\Delta_{\text{w}} \phi$, as shown by equation 2.2. Therefore the shake-flask experiments were repeated at various aqueous TB$^-$ concentrations. In the Ni$_2^+$ extraction experiments, TEA$^+$ and PF$_6^-$ were also used as the distributing ion, and their standard transfer potentials were obtained from literature (0.117 V and -0.33 V, respectively [30]).

The experiments were performed by bringing equal volumes of the organic and aqueous phases (5 ml each) into contact with each other and shaking heavily for 45 s. After the phases were separated completely, the aqueous phase was recovered. The initial and final metal concentrations in the aqueous phase were analysed with atomic absorption spectrometry (AAS) or inductively coupled plasma optical emission spectrometry (ICP-OES). The initial and final pH were measured with a commercial pH meter. The extraction capability of Dithizone depends on pH. The shake-
Experimental approaches

Flask experiments were therefore performed at several acid concentrations. However, to prevent Dithizone from deprotonating, the pH should not be higher than 5.

Table 3.1. The initial compositions of the organic and aqueous phases. The cations were either chloride or sulphate salts.

<table>
<thead>
<tr>
<th>Organic phase</th>
<th>Aqueous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>BATB</td>
<td>BACl/LiTB</td>
</tr>
<tr>
<td>Dithizone</td>
<td>H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>M&lt;sup&gt;2+&lt;/sup&gt;/PtCl&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;−&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Li&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Since TB<sup>−</sup> in the aqueous phase has surface-active properties, mixing organic phase with the aqueous phase that contains LiTB results in a quasistable microemulsion. I.e. the contact time with the phases is much longer, when the PDS is present in both phases. Therefore the shake flask experiments were repeated with a considerably longer mixing time (overnight) when LiTB was not used, if necessary.

In addition to the metal extraction experiments, a simple demonstration of Cu<sup>2+</sup> reduction and NP formation at the ITIES enhanced by the Galvani potential difference was also conducted. This was done by bringing aqueous H<sub>2</sub>SO<sub>4</sub>-CuSO<sub>4</sub> (both 5 mM) solution with either 0 or 5 mM LiTB into contact with an organic solution containing 0.1 mM BATB and 5 mM decamethylferrocene (DcMFc). The metal reduction could be seen as a change of color characteristic to DcMFc and DcMFc<sup>+</sup>. Additionally, light scattering experiments with Malvern Zeta-Sizer apparatus were conducted to detect NPs and estimate their size.

3.3 SECM probe approach curves

Whereas Publication I focused on facilitated metal cation transfer at the ITIES, in the last two publications, metal reduction as a result of interfacial electron transfer and the effect of Galvani potential difference on it was studied. The SECM measurements were carried out in Publication II to measure the kinetics of Cu<sup>2+</sup> reduction mediated by reduced form of 7,7,8,8-tetracyanoquinodimethane (TCNQ<sup>−</sup>) that was formed at the UME.

In the SECM experiments, Pt disk UME was used as the probing working electrode. These electrodes are sold commercially but they can be
Experimental approaches

fabricated in laboratory as described in literature [94]. In practice, a glass capillary is cut with a pipette puller and a Pt wire is passed through the resulting orifice, which is subsequently sealed with a Bunsen burner. To secure a seamless connection between the glass sheath and the Pt wire, the pipette was subjected to a vacuum while heating the sealed end. The Pt wire was connected with Ag paste to a larger conducting wire which connects the UME to the open end of the capillary where it can be connected to the potentiostat. The resulting UME was subsequently ground with sandpaper and polished with FiberMet Abrasive Disk until the Pt surface of the UME was as smooth as possible. The quality of the resulting UME was controlled with light microscopy and carrying out cyclic voltammetry with a redox pair with a known concentration.

The UME was set to approach the ITIES from the side of the organic phase. Therefore methyl isobutyl ketone (MIBK) was selected as the organic phase since it was less dense than water (MIKB). As in Publication I, BATB was used as a supporting electrolyte in the organic phase. The potential at the UME was set to a value that would favour reduction of the TCNQ (1 mM) to TCNQ⁻. As the probe approaches the ITIES, TCNQ⁻ generated at the UME can donate the electron to the metal that resides in the aqueous phase. Two possible mechanisms for this metal reduction reactions are shown in figure 3.2. In the heterogeneous reaction (a), only the electron is transferred through the ITIES while the reacting species remain in their corresponding phases, whereas in the homogeneous reaction (b), TCNQ⁻ is first transferred to the aqueous phase, in which the redox reaction takes place. In the measurements, the aqueous phase contained 5 mM CuSO₄, i.e. the metal cation concentration was in slight excess compared to 1 mM TCNQ.

The SECM cell setup consisted of three electrodes: the UME, Pt counter electrode and a Ag wire as a quasi-reference electrode. The SECM device was equipped with a bipotentiostat, which allowed the probe approach experiments to be performed against a substrate that was polarized with an additional fourth electrode instead of polarizing the interface with the potential determining ion. For this purpose, Pt wire was immersed into the aqueous phase without it to be in contact with the organic phase. Δ₀⁻φ at the ITIES could be then calculated from the cell equation between the aqueous Pt electrode and the reference electrode in the organic phase, as shown in equation (1) in the Publication II, and Δ₀⁻φ was converted to χ which is simply defined by equation 3.3:
Figure 3.2. Possible reaction mechanisms of metal reduction at the ITIES: a) heterogeneous reaction; b) homogeneous reaction. Published originally in Publication II, reprinted with permission from Wiley.

\[
\chi = \Delta_{w} \phi - \Delta E^{0}
\]  

(3.3)

where \(\Delta E^{0}\) is the difference of electrode potentials of \(\text{Cu}^{2+}\) and TCNQ against the same reference electrode. In the measurements \(\chi\) was varied between \(-0.4\) and \(0.2\) V. The probe approach curves were presented conventionally by non-dimensionalizing the distance between the tip and the substrate \(d\) by dividing it by the radius of the electrode \(r_{0}\).

### 3.4 Voltammetry at ITIES established at the tip of micropipette

In Publication III, voltammetric techniques at a microscopic ITIES were utilised to study the kinetics of \(\text{Cu}^{2+}\) reduction and nanoparticle formation. The most common ways to miniaturise ITIES is to establish the interface at a microhole or a tip of a micropipette [78, 95, 96]. Micropipettes have an asymmetric geometry and therefore the diffusion problem has different geometric constraints depending on whether the diffusion takes place inside or outside of the micropipette.

The micropipettes used in our work were prepared with a P-2000 pipette puller (Sutter Instrument, the USA). Since the external surface of the micropipette was in contact with the organic phase, it was made more hydrophobic by dipping it in trimethylchlorosilane while a constant flow of \(\text{N}_{2}\) was directed through the pipette in order to prevent the silane from
entering inside it. The procedure results in a type of micropipette shown in image 3.3.

The electrochemical measurements in Publication III were performed with the same SECM bipotentiostat as in Publication II. A simple two-electrode was used with a Pt wire working electrode inside the micropipette and a Pt quasi-reference/counter electrode in the organic phase.

In the measurements, the CuSO\textsubscript{4} concentrations were varied between 0–50 mM while the DcMFc concentration was kept at 4 mM. 1 mM BATB and 100 mM Li\textsubscript{2}SO\textsubscript{4} were used as the supporting ion in the organic and aqueous phase, respectively. In the CV, the scan rate was set to 25 mV/s. SWVs were run at several frequencies and amplitudes at higher and lower CuSO\textsubscript{4} concentrations.

3.5 On the stability of quasi-reference electrodes

In all measurements carried out with a UME or micropipette, the reference electrodes were needed to be placed into the organic phase. In practice, the reference electrode used in the measurements was a Pt or Ag wire which falls into the Bard-Faulkner definition of quasi-reference electrode (QRE) [52]. This has implications on the measurements that should be addressed.

A conventional reference electrode is an electrode at which a well-established redox reaction takes place that can be scaled to the standard hydrogen electrode (SHE) which has the standard electrode potential 0 V by definition [97]. In case of a QRE, no such reaction takes place from which follows that QRE can not be used to convert the working electrode
Experimental approaches

potential to SHE scale. QREs are often also unstable for this reason, i.e. the potential at the reference electrode is susceptible to e.g. reactions with impurities.

Nevertheless, QREs are often used in conjunction with organic solvents due to their convenience compared to well-defined organic reference electrodes that are difficult to fabricate and stabilize [30,98–100]. The currents at which the UME and micropipettes are operated are at nA scale which also justifies the use of QRE, since it is unlikely that the working currents affect the reference electrode potential even if a two electrode system is used.

Figure 3.4 summarizes how the QRE scale is converted to a well-known Ag|AgCl(w) scale (a) and $\Delta^w_0 \phi$ scale (b). In 3.4a, half-wave potential of TCNQ reduction was measured both vs. QRE and an Ag|AgCl with a liquid-liquid junction determined by standard transfer potential of a distributing ion ($BA^+$) which leads to cell potential:

$$E_{cell} = E_{TCNQ|TCNQ} - \Delta^w_0 \phi_{BA^+} + \frac{RT}{F} \ln \left( \frac{c_{BA^+}^0}{c_{BACl}^0} \right)^2 - E_{0}^{Ag|AgCl} \quad (3.4)$$

On the other hand, for QRE the cell equation is simply:

$$E_{cell} = E_{TCNQ|TCNQ} - E_{0}^{QRE} \quad (3.5)$$

When the difference between TCNQ reduction half-wave potentials at these two cells are known, the working electrode potentials could be converted from the QRE to the standard Ag|AgCl scale. This inner standard was also used to approximate the Galvani potential difference at the substrate ITIES, as shown in equation (1) in Publication II.

Figure 3.4. CV measurements to convert QRE potentials to standard scales:

a) reduction of TCNQ vs Ag QRE and vs aqueous Ag|AgCl used in Publication II; b) CV of TEA$^+$ transfer (black curve) matched to its FEM simulation with $\Delta^w_0 \phi_{TEA^+} = 0.116 \text{ V}$ (red dashed curve) (blue dashed curve: baseline). Published originally in Publication II, reprinted with permission from Wiley.

In Publication III, similarly to the CVs in Publication I, $\Delta^w_0 \phi$ scale was
determined by measuring CV of TEA$^+$ transfer ($\Delta_{\phi}^0 \phi_{TEA^+} = 0.116$ V) from inside the micropipette into the bulk as a reference. However, instead of fixing the potential scale to the half-wave potential of transfer, the CV was compared to its FEM simulation. Both of these methods require that the standard transfer potential of the reference ion be known, which is not trivial and requires an extrathermodynamic assumption. Most widely used is the TATB assumption [101] which was first used in estimating single ion solvation in the late 1960’s [102]. Essentially, it asserts that the sum of standard transfer potentials of tetraphenyl arsonium (TPhAs$^+$) and tetraphenyl borate (TPhB$^-$) is 0 which effectively sets $\Delta_{\phi}^0 \phi = 0$ V in a potential window limited by TPhAs$^+$ and TPhB$^-$ transfer. Some discrepancy has been presented against the validity of the assumption [103] but it continues to be used to this day, and $\Delta_{\phi}^0 \phi_{TEA^+}$ used in this work is based on the TATB assumption [104].

3.6 Finite element method simulations for SECM and micropipette voltammetry

Finite element method simulations were performed in Publications II and III. In Publication II, FEM was used to analyse the approach curves of the SECM measurements and to extract kinetic information of Cu$^{2+}$ reduction at the substrate ITIES. In Publication III, the SWV and CV measurements were reproduced in the FEM simulations. In both papers, Butler-Volmer kinetics was assumed for all reactions.

The geometric features of the model, including the $RG$ value, were obtained from the microscopic images: the $RG$ value of the used tip was ca 19. Since the geometry of the probe and the ITIES was axisymmetric, the simulation could be run in a two dimensional geometry with the rotation axis running in the centre of the probe as shown in figure 3.5. Mesh density was set extremely high at the sites of high relevance, namely the surface of the electrode and the ITIES that the probe approaches. Especially the point which separates the electrode and the glass sheath which is a theoretical singularity [52], should be modelled with high precision.

The reactions were modelled as fluxes of dilute species, i.e. the boundaries where reactions takes place were set as a sink for the reacting species and source for the products, while the transport was governed by diffusive flux with no convection. The fluxes were defined by the assumed Butler-Volmer kinetics: reduction of TCNQ follows first degree Butler-Volmer
Experimental approaches

The TCNQ\textsuperscript{−} mediated metal reduction at the ITIES follows the second degree kinetics of equation 2.15, with \( \nu = 2 \) from which follows that \( n = 2 \). Irreversibility was also assumed and therefore the second term of the equation was omitted.

Figure 3.5. The used geometry and mesh of the probe approaching close to the ITIES that can be seen as the boundary with denser mesh, created with COMSOL.

The approach curves were reproduced by parametric sweeping the distance of the probe from the ITIES. At each distance, the fluxes at the ITIES and the probe were modelled in a steady state. The approach curves were obtained by extracting the TCNQ flux flowing "through" the probe and plotting them as a function of distance from the ITIES. The probe approach simulations were repeated at various \( \kappa \) which is defined as:

\[
\kappa^0 = 2k^0 e^{af(\Delta w_0\phi - \Delta E^0)} = 2k^0 e^{af\chi}
\]

If \( \Delta w_0\phi \) was determined by the common ion, its value was calculated from equation 2.5. Otherwise it was derived from the potential difference between the substrate electrode and the counter/reference electrode with the equations shown in the publication. By comparing the experimental and the computed approach curves at various \( \Delta w_0\phi \), an approximation for the reaction rate coefficient could be obtained.

In Publication III, since only reactions at an ITIES at a tip of a micropipette were investigated, the model contained only one reaction site. The geometry of the micropipette is slightly different from a UME. The \( RG \) value of micropipette is considerably smaller than that of UME, and from the microscopy images the exact value was difficult to measure accurately,
and it was approximated to be ca 0.1. Additionally, for micropipettes two domains have to be defined: the inside and outside of the pipette. All reactions take place at the boundary between these domains.

The measurements in Publication III were cyclic and square-wave voltammetry, which are inherently time-dependent methods and therefore all simulations were run in a time-dependent studies where the potentials were defined as a function of time by using equations 2.18 and 2.20 for CV and SWV, respectively. \(E(t)\) in the equations was shifted to represent \(\Delta w_\phi\) and it was incorporated to the kinetic equations. The reactions in the publication were modelled as a two-step EE mechanism, *i.e.* reactions 2.16 and 2.17 (steps 1 and 2, respectively): the kinetic equation could be written for both steps:

\[
i \frac{Fk_i^0}{Fk_i^0} = c_{s,w}^{O_i} c_{s,a}^{R_i} e^{a_i f(\Delta w_\phi - \Delta E_0^i)} - c_{s,w}^{R_i} c_{s,a}^{O_i} e^{-(1-a_i) f(\Delta w_\phi - \Delta E_0^i)}
\]  

(3.7)

where \(O_i\) and \(R_i\) are the oxidized and reduced aqueous species of step \(i\) (1 and 2), *i.e.* \(O_1\) and \(R_1\) are \(Cu^{2+}\) and \(Cu^{+}\), and \(O_2\) and \(R_2\) are \(Cu^{+}\) and \(Cu\), respectively. \(\alpha\) was assumed to be 0.5 in both reactions. The simulations were carried out at various ratios of \(k_0^1\) and \(k_0^2\). For the first step, the kinetic constant was expressed in a non dimensional form to facilitate the distinction between reversible, quasireversible and irreversible regimes:

\[
\kappa_i^0 = \frac{k_0^i c_{DcMFc}}{\sqrt{D_{DcMFc} f_{sg}}}
\]

It should be noted that the dimension of the kinetic constant depends on the stoichiometry. For this reason, \(c_{DcMFc}\) was incorporated to the equation.

The diffusion coefficients of the reduced and oxidized species of each component were assumed to be equal. This is not entirely true for \(Cu^{2+}\) and \(Cu^{+}\), and their respective diffusion coefficients depend on the system (concentration, other ions present in the electrolyte solution etc.) and many values have been determined for them [105,106]. Therefore the uncertainty of the diffusion coefficient can lead to some error in the simulations.
4. Results

4.1 Cyclic voltammetry of assisted metal cation transfer

Cyclic voltammetry at ITIES was utilized to detect metal cation transfer from the aqueous phase to the organic phase assisted by complexation reaction with Dithizone which is a ligand known to form hydrophobic complexes with several metal cations, Cu$^{2+}$ being one of them [91].

The effect of the presence of Cu$^{2+}$ in the aqueous phase with and without the ligand in the organic phase is shown in figure 4.1. As expected, without the ligand, the Cu$^{2+}$ has little to no effect on the CV, since its standard transfer potential is outside of the potential window. The uncharged ligand is obviously not detectable in the measurement, either, but it does facilitate the transfer of the supporting ion, which can be seen as a shrunk potential window on the negative side. Also the transfer wave of the reference TEA$^+$ shows an unusual peak separation less than the theoretical 59 mV, which may indicate ligand adsorption/film formation at the ITIES [52, 107].

When both Cu$^{2+}$ and the ligand are present in the cell, the assisted transfer of Cu$^{2+}$ can be detected as a current wave with a peak potential at $-190$ mV at $\Delta \phi$ scale. The transfer is irreversible but follows Randles-Ševčík dependency as shown in figure 4.2. Applying equation 2.19 would yield a low diffusion coefficient Cu$^{2+}$, $2.0 \cdot 10^{-7}$ cm$^2$/s when $n = 2$ was assumed, which is more than a decade smaller than the literature value, $5.4 \cdot 10^{-6}$ cm$^2$/s [52] and even with $n = 1$ the coefficient remains smaller than that, $1.6 \cdot 10^{-6}$ cm$^2$/s. The derivation of Randles-Ševčík equation assumes reversibility, and thus the irreversibility of Cu$^{2+}$ transfer may have resulted in error in the diffusion coefficient.

In the CV experiments in the publication, it was also found that the
Results

Figure 4.1. Cyclic voltammogram of 50 mM Cu$^{2+}$ transfer assisted by 5 mM Dithizone (solid red line). Dashed blue curve: baseline with 1 mM TEA$^+$ being transferred into the organic phase at $\Delta_{\phi}^{w} = 0.14$ V; dashed black curve: baseline with 50 mM Cu$^{2+}$ added to the aqueous phase, but no ligand in the organic phase. TEA$^+$ was present in all curves. The sweep rate was 50 mV/s. Published originally in Publication I, reprinted with permission from Research Trends.

choice of counterion and its concentration had considerable effect on the peak current. With SO$_4^{2-}$, the peak current increased from 20 to almost 50 µA/cm$^2$ as the concentration of the counterion was increased from 10 mM to 1 M. Conversely, increasing Cl$^-$ by the same amount decreased the peak current from 35 to less than 10 µA/cm$^2$. This could be expected since the chloride ions have a tendency to form stable chlorocomplexes with metal cations.

The potential of facilitated cation transfer depends on the affinity of the metal to the ligand, which on the other hand depends on the choice of metal and ligand. For example, the facilitated transfer of Ni$^{2+}$ nor Co$^{2+}$ could not be detected, which indicates that the transfer of these metals takes place outside of the potential window or does not happen at all.

4.2 Electrochemically assisted metal extraction

The shake flask experiments were carried out with the same metals as the CVs. Cu$^{2+}$, which according to the CV measurements was most prone to form a complex with the ligand, showed also in the extraction experiments almost complete extraction, regardless of the Cl$^-$ or HSO$_4^-$ concentration or the potential control with the common ion. In the CV of Cu$^{2+}$ transfer in figure 4.1, the half-wave potential of the transfer was very low and therefore a Galvani potential regime that favours the extraction could be reached without a distributing ion.
Figure 4.2. Dependency of the peak current of facilitated Cu\(^{2+}\) transfer on \(v_c\). Concentrations of CuSO\(_4\) and Dithizone were 1 mM and 5 mM, respectively. Published originally in Publication I, reprinted with permission from Research Trends.

By varying the ratio of the concentration ratio of the metal in the aqueous phase and the ligand in the organic phase, information on the stoichiometry of the complexation reaction could be obtained. For Cu\(^{2+}\) when there was an excess concentration of the ligand compared to the cation, the measured extraction fraction was virtually 100 %. When the ratio was decreased to 2:1, the fraction dropped to 50 %. This implies that each Cu\(^{2+}\) cation requires two ligands for complexation.

Figure 4.3. Extracted fraction of 5 mM Co\(^{2+}\) by 0 and 5 mM Dithizone (circles and diamonds, respectively) at various \(c_{L/TB}\). The volumes of the phases were equal. Published originally in Publication I, reprinted with permission from Research Trends.

Even though the assisted Ni\(^{2+}\) or Co\(^{2+}\) transfer could not be detected within the potential window in CV, the Galvani potential difference at the ITIES imposed by a common ion with high enough standard transfer
Results

potential was found to increase the extraction fraction. In case of both of these metals, the extracted fraction was hardly detectable when common ion was not present in either of the phases, but it increased significantly when $\Delta w_\phi$ was determined. For example figure 4.3 shows the dependence of the extracted fraction of Co$^{2+}$ on the LiTB concentration ($c_{LiTB}$): when the potential determining ion was present, the extracted fraction increased to up to 30%.

As figure 2.1 shows, TB$^-$ is a sizeable ion and it is possible that it can form a complex with the metal cation and increase it hydrophobicity. In figure 4.3, the shake-flask experiments were therefore repeated without the ligand to determine whether LiTB itself could extract the metal. TB$^-$ does indeed exhibit some tendency to extract Co$^{2+}$, but highest extracted fraction could only be obtained when both TB$^-$ and ligand were present.

Out of the three studied metals, the extraction fraction of Ni$^{2+}$ was most impacted by Galvani potential control. Dithizone by itself could not extract Ni$^{2+}$ even when contact time with the phases was extended to 20 h. Same was true for the common ion TB$^-$: the extracted fraction of Ni$^{2+}$ remained under the detection limit at any TB$^{2+}$ concentration when no Dithizone was present in the organic phase, i.e. Ni$^{2+}$ did not show any affinity to the potential determining ions.

In figure 4.4, the extraction data of Ni$^{2+}$ with Dithizone in its entirety has been collected and converted to $\Delta w_\phi$ scale by solving it from equation 2.5. The data points form three distinct groups in the $\Delta w_\phi$ plot which is the result of the choice of potential determining ion: the most negative potentials were produced by BF$_4^-$ and the most positive ones by TB$^-$ whereas the potential regime around $\Delta w_\phi = 0.0$ V was obtained with TEA$^+$. The extraction fraction follows the $\Delta w_\phi$ dependency predicted in figure 2.2, and equation 2.10 could be fitted to the data and the value for $\Delta w_\phi^{\text{NiD}_2}$ was obtained (0.53 V).

In the calculation of the Galvani potential difference at various initial TB$^-$ concentrations, the final TB$^-$ concentrations could also be obtained. This analysis could result in extremely low or even negative TB$^-$ concentrations, specifically at the lowest initial TB$^-$ concentrations. This was attributed to the sensitivity of the bisulphate equilibrium to even a small error in the pH measurements. In the analysis, it was also assumed that the Li$^+$ and HSO$_4^-$ do not transfer to the organic phase, which is not necessarily true. This could have also resulted in the negative concentrations.

More research should be conducted on the interactions between the potential determining ions and the target metals. For example, some metals
that were investigated showed affinity to the potential determining anions and could be extracted without an additional ligand in the organic phase, which could be seen in case of Co$^{2+}$. In Publication I, hexachloroplatinate (PtCl$_6^{2-}$) extraction was also attempted with tetrabutylammonium tetraphenylborate (TBATPB) in the organic phase and tetrabutylammonium chloride (TBACl) in the organic phase: again, high extraction fractions could be obtained without ligand. It has been shown in literature that PtCl$_6^{2-}$ transfers to the organic phase without an additional ligand at ca −0.18 V [108], which nevertheless coincides with the $\Delta^w_0 \phi$ determined by TBA$^-$. It should be also noted that this affinity was later observed to complicate the AAS and ICP-OES metal analyses because of the lower solubility of the complex to water which may distort the quantitative analyses.

4.2.1 Electrochemically assisted reduction of Cu$^{2+}$

The shake flask experiments of Cu$^{2+}$ reduction by DcMFC were performed as a proof of concept that shows the effect of Galvani potential difference at the ITIES fixed by the common ion TB$^-$. Without the common ion, the organic and aqueous solutions could be in contact with each other overnight without notable reactions: the colour of the organic changed slightly from yellow to pale green, which can have been attributed to DcMFC reacting with atmospheric oxygen. Adding LiTB in the aqueous phase caused DcMFC to react immediately as the solutions were mixed. With the light-scattering experiments on the resulting aqueous phase,
particles of the size of ca 200 µm could be detected. This reaction was the focal point of research in the two last articles of this thesis.

4.3 SECM measurements

When the Galvani potential difference at the substrate ITIES was fixed with the common ion, its effect on the probe approach feedback was measured as a preliminary experiment in order to find a LiTB concentration regime where the feedback is negative. This effect is shown in figure 4.5 in which the approach curves were run against a substrate phase with varying LiTB concentrations. Unfortunately, TB\(^-\) concentration has a strong effect on the feedback. At 1.0 mM LiTB, feedback is already strictly positive. In the publication it was suggested that this behaviour was caused by deposition of a clearly visible film at the ITIES substrate. Knowing this, in all approach experiments in the publication, only the largest concentration that did not trigger a positive feedback was used (0.1 mM).

![Figure 4.5.](image)

Using the 0.1 mM LiTB concentration, approach curves shown in figure 4.6 were obtained. As in figure 4.5, the presence of LiTB alone could not generate a positive feedback. The feedback with Cu\(^{2+}\) in the aqueous phase generated a negative feedback, but as the UME approaches the interface, the feedback experienced a sudden change from negative to positive. This could be explained by spontaneous jumping of Cu\(^{2+}\) to the UME, which was also demonstrated in the publication as a positive feedback in the approach curve while no TCNQ was present in the organic phase.

When \(\Delta w\phi\) was fixed with the fourth electrode (the substrate electrode),
the feedback behaved similarly: as $\Delta \phi$ was increased (positive polarization of the aqueous phase), the feedback became positive. The positive feedback was observable only at the higher of the studied Cu$^{2+}$ concentrations, whereas at the lower Cu$^{2+}$ concentration increasing $\Delta \phi$ resulted into only slight changes in feedback which remained negative at all studied potentials.

Together with the SECM measurements in Publication II, the dependence of reduction of Cu$^{2+}$, Co$^{2+}$ or Ni$^{2+}$ on $\chi$ was also studied with a kind of TG/SC method which was done by bringing the UME to $ca 10 \mu m$ away from the substrate and measuring the current flowing through it at $-100 \text{ mV vs. Ag}|\text{AgCl}(w)$ while $\chi$ was varied. The results of these measurements are shown in 4.7 where the effect of the presence of Cu$^{2+}$ on the feedback is clear as $i/i_{lim}$ at the UME leaps from 0.8 to 1.4. For
Results

Co$^{2+}$ and Ni$^{2+}$, the potential had hardly any effect on the feedback. Only at the highest measured potential ($\chi = 0.2$ V), presence of Ni$^{2+}$ generated a positive feedback.

4.3.1 **FEM simulations of the approach curves**

The approach curves against ITIES with $\Delta_w^\omega \phi$ fixed by the substrate electrode were reproduced in the FEM simulations to extract kinetic parameters from them. Similarly to the experiments, the simulations were carried out in two CuSO$_4$ concentrations, 1 and 5 mM, and example of the fits for the latter are shown in figure 4.8. It was found that out of the two proposed mechanisms (figure 3.2), only the heterogeneous charge transfer provided approach curves that could be fitted to the experimental measurements. Additionally, for the lower concentrations, the computed approach curves could be fitted only when $\nu = 1$, but interestingly, for the higher concentrations only $\nu = 2$ produced approach curves that the experimental curves could be fitted to. In other words, comparing the experimental approach curves to the simulations suggests that the stoichiometry depends on the concentration ratio between Cu$^{2+}$ and TCNQ.

![Figure 4.8](image.png)

**Figure 4.8.** Fitted simulated approach for each experimental approach curve at different $\chi$. CuSO$_4$ concentration was 5 mM and in the simulations, $\nu = 2$. The $\kappa^0$ values were normalized to $\kappa_0 = 10^{-8}$ m$^7$/mol$^2$/s. Published originally in Publication III, reprinted with permission from Wiley.

By fitting the experimental approach curves to the simulations, kinetic constants of the reactions could be estimated. Since irreversibility and a single-step reduction with $\nu = 1$ or 2 was assumed (depending on the concentration), the Butler-Volmer equation could be simplified as shown in equation 4.1:
where $\kappa^0$ was defined in equation 3.6. In practice, each approach curve (at each $\chi$) was fitted to the simulated family of curves that were obtained by varying $\kappa^0$. As a result, $\kappa^0$ could be presented as a function of $\chi$ and the reaction rate coefficient can be calculated from the intercept of the line fitted for the $\ln(\kappa^0/\kappa_0)$ (as a function of $\chi$), and the $\alpha$ can be obtained from the slope. For $\nu = 1$ stoichiometry ($1 \text{ mM CuSO}_4$), the value for the reaction rate coefficient calculated this way was $2.2 \cdot 10^{-6} \text{ m/(s mM)}$.

4.4 Cyclic voltammetry and square-wave voltammetry at $\mu$-ITIES

The CVs of Cu$^{2+}$ reduction by 4 mM DcMFc at the $\mu$-ITIES at a tip of a micropipette are shown in figures 4.9a (Cu$^{2+}$ concentrations between 0.5–5 mM) and 4.9b (Cu$^{2+}$ concentrations between 10–50 mM). In the figures, the arrows indicate the sweep direction. At the lower Cu$^{2+}$ concentrations (2.5 and 5.0 mM in 4.9a), increasing the concentration increases the limiting/peak current ($i_{lim}$). The forward and reverse sweeps make a remarkable loop which is characteristic to particle nucleation. At higher concentrations this loop gradually decreases as DcMFc begins to limit the current. DcMFc limiting the current is evident due to two observations: doubling the Cu$^{2+}$ concentration from 25 mM to 50 mM does not double the limiting current as it should according to equation 2.24, but it reaches a plateau at $ca$ 25 mA/cm$^2$. The behaviour of the limiting current of the reverse sweep at all of the studied Cu$^{2+}$ concentrations is illustrated in figure 4.10 where current increases linearly at lower concentrations. Also the shape of the CV is characteristic to the CV of a redox reaction at a disc UME which has been shown in the literature [52].

![Figure 4.9](image)

**Figure 4.9.** Cyclic voltammetry of Cu$^{2+}$ reduction at micropipette ITIES: a) lower Cu$^{2+}$ concentrations; b) higher Cu$^{2+}$ concentrations. In each CV, $v_c = 25 \text{ mV/s}$. Published originally in Publication III, reprinted with permission from Wiley.
Results

Figure 4.10. Limiting currents ($i_{lim}$) at various $c_{Cu^{2+}}$ extracted from figure 4.9a and b.

Figure 4.11 shows the effect of frequency on the SWV sweep of 10 mM Cu$^{2+}$ reduction by 4 mM DcMFc. This concentration ratio corresponds to the black dotted curve CV in figure 4.9b, and the range of the frequencies (5 – 25 Hz) with the used potential increment size ($\Delta E$ of equation 2.20) 4 mV correspond to 20 – 100 mV/s. The cell potentials were converted to the $\Delta w_\phi$ scale by comparing the potential window to the one showing TEA$^+$ transfer, as demonstrated in figure 2.5. The forward and reverse sweeps were performed separately and are shown in figures 4.11a and 4.11b.

The SWV sweeps show two clearly distinguishable waves at all frequencies and at both sweep directions. These waves can be attributed to reactions 2.16 and 2.17: the peak potential of first (i.e. at more negative $\Delta w_\phi$) wave was ca −0.09 V and the peak potential of the following wave was ca 0.18 V. The behaviour of the peak currents ($i_p$) is illustrated in figures 4.11c and d for forward and reverse sweeps, respectively. For forward sweep, especially the second wave shows significant anomalous behaviour as $f_{sg}$ is increased to over 10 Hz even though the $i_p$ of the first wave increases relatively linearly. This phenomenon did not occur at reverse sweeps. The absolute values of $i_p$ at reverse sweeps were significantly larger than the corresponding values at the forward sweeps. The reasons for this were discussed in the simulations.

As it was discussed in the theory of SWV, as increasing $f_{sg}$ shortens the time how long the signal stays at each potential becomes, thus the currents arising from the transient phenomena, e.g. charging of the double layer, do not have enough time to dampen. Therefore, the sweeps at the lowest frequencies (up to 10 Hz) were likely to be most reliable. Therefore, SWV sweeps at the lowest frequency available in the potentiostat were carried out at various $E_{am}$. The resulting voltammograms are shown in figure 4.12a. The SWV sweeps can also be broken down into the forward and
Results

Figure 4.11. SWV sweeps with 10 mM CuSO₄ and 4 mM DcMFc at various frequencies (5, 10, 15, 20 and 25 Hz (blue, red, black cyan and magenta, respectively)), \( E_{am} = 25 \). The blue dashed line is the baseline without CuSO₄: a) forward sweep b) reverse sweep; c) and d) peak currents vs. \( f_{sg} \) at forward and reverse sweep, respectively (black: wave peaking at -0.09 V; red: wave peaking at 0.18 V). Published originally in Publication III, reprinted with permission from Wiley.

backward components of which the total current consists.

Figure 4.12. a) SWV sweeps with 10 mM CuSO₄ and 4 mM DcMFc at various \( E_{am} \) while \( f_{sg} = 1 \) Hz (10, 20, 30 and 40 mV (blue, red, black and cyan, respectively)); b) The SWV sweep at \( E_{am} = 40 \) mV (cyan in figure a): the total current and the forward and backward components of the sweep.

In Publication III, the behaviour of SWV sweeps at excess CuSO₄ concentrations was also investigated: for example, figure 4.13 shows SWV sweeps at various \( E_{am} \) while \( \text{Cu}^{2+} \) concentration inside the micropipette was 50 mM. Increasing \( E_{am} \) does not cause similar irregularities to \( i_p \) as \( f_{sg} \): the peak currents of each wave showed linear dependence on \( E_{am} \) which is also predicted in the theoretical approach of SWV [52]. Addition-

43
ally, as expected, as the current becomes limited by DcMFc, the two waves merge into one, which is in fact analogous to the CVs in figure 4.9b where one clear wave with can be seen at excess CuSO$_4$ concentrations. Also the peak current are reached already at potentials lower than 0.1 V probably because DcMFc is depleted already before the second reaction. The peak currents showed linear dependence on $E_{am}$, similarly as in figure 4.12a.

![Figure 4.13. SWV sweeps with 50 mM CuSO$_4$ at various $E_{am}$ (10, 20, 30, 40, 50 mV (blue, red, black cyan and magenta, respectively)), $f_{sg} = 10$ Hz.](image)

### 4.4.1 FEM simulations of CV and SWV

FEM simulations were carried out to provide an estimation to the kinetic parameters of the Cu$^{2+}$ reduction at the ITIES. Since the SWV sweeps were assumed to be most reliable at the low frequencies, the simulations were carried out at 5 Hz which corresponds to the blue curve in figure 4.11a. $E_{am}$ was set to 25 mV as in the experimental SWV. The values of the electrode potentials of Cu$^{2+}$|Cu$^+$, Cu$^+$|Cu and DcMFc$^+$|DcMFc were obtained from literature (0.156 V [109], 0.520 V [109] and 0.06 V [30], respectively).

In figure 4.14, to analyze the kinetics of the first step of the EE mechanism, the SWV was modeled while $k_1^0$ (as defined in equation 3.6) was varied between 0.001–10 which corresponds to $k_1^0$ values between $1.2 \times 10^{-8}$–$1.2 \times 10^{-4}$ m/(s mM). At each curve, the reaction rate constant of the second reaction $k_2^0$ was equal to $k_1^0$. The closest fit with the experimental SWV occurs when $k_1^0 = 1$ which corresponds to $k_1^0 = 1.2 \times 10^{-5}$ m/(s mM). As expected, when $k_1^0$ was increased to values greater than 10, no change in the peak potential or the peak current could be observed as large $k_1^0$ values represent a reversible reaction.

$k_1^0$ obtained from figure 4.14 was used in figure 4.15 where the effect
Figure 4.14. SWV simulations of reactions 2.16 and 2.17 at various $k_0^1$. At each curve $f_{sg} = 5$ Hz, $E_{am} = 25$ mV and $k_2^0 = k_1^0$.

Figure 4.15. SWV simulations with various $k_2^0$. For reaction 2.16, $k_1^0 = 1$ obtained from figure 4.14 was used. Of $k_2^0$ on the second wave was studied as it was varied between $k_2^0$ and $50k_2^0$ where $k_1^0 = 1.2 \cdot 10^{-5}$ m/(s mM). From the shape of the SWV and the ratio of the peak currents it is evident that the second step is fast: if the reaction rate constant is decreased to smaller values than that of $k_1^0$, the peak current of the second wave remains smaller than that of the first one. This did not happen in the experiments.

Figure 4.16. CV simulation of reduction of a) 10 mM b) 50 mM Cu$^{2+}$ by 4 mM DcMFC at various $k_2^0/k_1^0$ while $k_1^0 = 1$.

The FEM simulations of the CVs are presented in figures 4.16a and b at 10 and 50 mM Cu$^{2+}$, respectively, corresponding to the experimental measurements in figure 4.9b. Analogously to the SWV simulations in
figure 4.15, the ratio of \( k_2^0 \) and \( k_1^0 \) was varied while \( k_1^0 \) was kept constant. As expected, the value of \( k_2^0 \) had little to no effect on the CVs and at 50 mM Cu\(^{2+}\), the simulated voltammograms were practically identical. Only at 10 mM Cu\(^{2+}\) \( k_2^0 \) had a slight effect on the shape of second step wave.

The most interesting feature in the CV simulations, especially at the excess Cu\(^{2+}\) concentrations, was that the limiting current densities were consistently lower in the simulations compared to the experimental CVs. The likeliest explanation for this difference is the growth of the surface area due to the nucleation of Cu NPs. The expansion of the surface area was also speculated to have affected the half-wave potential: as the reaction surface area begins to expand due to the NP growth, the current also continues to increase which could be seen as a "shifting" half-wave potential.
In this thesis, several electrochemical techniques were utilized to study electrochemically enhanced metal cation transfer and reduction reactions at liquid-liquid interfaces. One of the main objectives was to investigate the effect of potential determining ions on these reactions. If e.g. metal extraction could be enhanced by imposing a Galvani potential difference between the aqueous and organic phases, the potential determining ions could provide a novel paradigm in industrial hydrometallurgical applications. Improving these metal separation technologies will become increasingly relevant as the reserves the critical materials deplete while their demand keeps increasing.

In Publication I, the effect of the potential determining ions on the extraction of several metal cations was studied, and the ligand assisted metal transfer was also investigated in cyclic voltammetry with a conventional four-electrode cell setup. The ability of the Galvani potential difference to enhance metal transfer was highly dependent on the choice of the metal-ligand pair. For example, if the ligand extracts the metal effectively, potential determining ions were unnecessary. For other pairs, the extracted fraction was strictly dependent on the Galvani potential difference, as was demonstrated for Ni$^{2+}$ and Dithizone. This was a proof of concept that for some metal-ligand pairs, Galvani potential difference can indeed enhance metal extraction.

However, some metal cations showed also affinity to the potential determining ions, i.e. some of the metals could be extracted with the common ion without having the ligand in the organic phase. Additionally, the affinity resulted in some complications in the metal analyses that have not yet been addressed. The interactions between the metal cations and the PDS is one of the topics that could be researched in more detail in the future.

Although stripping experiments were attempted in Publication I, they
Conclusions

were not successful due to strong affinity between the metal and the cation. The effect of the PDSs on the stripping reactions is another important aspect that can be studied. Also, in order to advance to an industrial level application, scale-up experiments should be carried out. In a larger scale utilization of potential determining ions, their price should be taken into consideration. The price of the salts used in our experiments is still relatively high, and thus the possibility of replacing them with cheaper alternatives should be investigated. The recyclability of the ions is also another topic that could be discussed in future research.

The potential determining ions set some requirements for the organic solvent. For example the dielectric constant should not be too low, which would prevent the salts from dissociating. Even the most hydrophobic salts such as BATB are not soluble to some of the widely used organic solvents (e.g. kerosene). If the dielectric constant was too high, however, the solubility to water would be likely to become a problem.

The last two publications of this thesis investigated Cu$^{2+}$ reduction at an ITIES by a reducing agent residing in the organic phase. Metal reduction at ITIES is not only important in hydrometallurgical applications, but ITIES can also be used as a platform for NP synthesis. Cu NPs usually supported on different carbon nanostructures have received a significant amount of interest due to their ability to catalyse e.g. CO$_2$ reduction to C-C hydrocarbons [110–115], and their catalytic properties for hydrogen evolution reaction has also been studied [17, 116, 117]. Therefore understanding the kinetics of the NP formations has become increasingly relevant.

In Publication II, the interfacial redox reaction was investigated by SECM where electron donor was formed at the SECM tip and the charge transfer to the metal cation could be detected as a positive feedback loop. In the final Publication, the ITIES was miniaturized to μm-scale by establishing it at the tip of a micropipette and metal reduction reaction was investigated at it.

In Publication II, some complications arose from the selection of the organic solvent, namely the precipitation of some salts which could be observed as a cloudy formation at the side of the aqueous phase; also a visible film layer could be observed directly at the interface, which may have had some effect on the measurements. This became more prevalent at higher LiTB concentrations. These complications were attributed to the interactions between MIBK and the PDSs. Furthermore, in some experiments where MIBK was in contact with an aqueous phase with BACl, it triggered a reaction apparently with the organic solvent itself,
turning it from transparent to black. For this reason, BACl was not used in experiments with MIBK as an organic solvent in Publication II.

MIBK was mainly selected for three reasons: 1. a high enough dielectric constant which enables dissociation of the hydrophobic salts but low enough that it is not soluble to water; 2. a density that is lower than that of water which was essential for the test set-up; and 3. a cheaper alternative to DCB/DCE that has been used in several commercial and industrial applications. The experiments could be run with DCB by immobilizing the aqueous phase with Agar which would allow the heavier organic phase to be placed on top of the aqueous phase. We tested this after publishing the second paper in conjunction with micropipette SECM experiments, which were attempted but never published.

Despite these complications, the electron transfer from TCNQ$^-\text{−}$ generated at the Pt UME to Cu$^{2+}$ in the aqueous substrate phase could be detected as a positive feedback when the ITIES was positively polarized. The Galvani potential difference at the ITIES was fixed either with a common ion or by utilizing a fourth electrode in the substrate phase. The positive feedback attributed to the electron transfer was detectable with both methods of polarization. The FEM simulations of the probe approach curves provided an estimation for the reaction rate constants of the Butler-Volmer kinetics.

The detection of Co$^{2+}$ and Ni$^{2+}$ reduction was also attempted with SECM. These cations have significantly lower electrode potentials. Because of this, it was expected that no positive feedback would be detected.

In Publication III, the CV and SWV measurements at $\mu$-ITIES at the tip of a micropipette provided a more detailed view on the Cu$^{2+}$ reduction by an organic electron donor. Specifically in the square-wave voltammograms, both reduction steps of Cu$^{2+}$ to Cu$^{+}$ and subsequently to Cu NPs could be observed as two distinct current waves. In CV measurement at macroscopic or microscopic electrodes, the two steps of the EE mechanism of Cu$^{2+}$ reduction are not readily distinguishable. However, due to the significant difference between the limiting current of the measured CVs and the simulations, the NP growth could be indirectly detected.

Compared to Publication II, the FEM simulations were carried out to a much greater detail in the final article. For example, the Butler-Volmer equation was modeled in its entirety, and no irreversibility was assumed. Also, both steps of the EE mechanism were modeled separately with their own kinetic equations and kinetic constants, whereas in Publication II, the entire reaction was represented by a single irreversible Butler-Volmer equation.
As mentioned earlier, the micropipettes could also be utilized as an SECM probe. For example, instead of having TCNQ be reduced at a Pt UME, it can receive the electrons via interfacial charge transfer from aqueous ferrocyanide inside the micropipette. This has been studied in by Solomon et al. [36] who could generate microscopic images with micropipette SECM. By utilizing micropipettes, which can be easily manufactured at different orifice diameters, the accuracy and resolution can be improved due to significantly lower $R_G$ values which also allow the probe to approach the substrate closer than when solid UME are used. Micropipette SECM has also been utilized to analyse ligand-assisted ion transfer [78], and by applying this method, more information regarding the kinetics of the facilitated Ni$^{2+}$ transfer shown in Publication I can be obtained in future studies.
References


References


53


References


