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For my parents, to whom I will always be indebted
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Thank You.
UNIVERSITI MALAYA

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Abstract

The electrochemical behaviour of sodium p-sulfonatocalix[4]arene (s-psc₄) was studied. In this study ionic liquid/water mixtures were used as electrolyte, namely, [BMIM][BF₄]/water mixture and [BMIM][OTf]/water mixture ([BMIM] = 1-butyl 3-methyl imidazolium, BF₄ = tetrafluoroborate, OTf = trifluoromethanesulfonate). S-psc₄ can be oxidised at 0.84 V and 0.83 V in [BMIM][BF₄]/water and [BMIM][OTf]/water respectively. The reaction is an irreversible process for both systems. The number of electron transferred in this electrochemical process is one electron and the diffusion coefficient, \(D\) for both systems was 1.15 x 10⁻⁸ cm² s⁻¹ and 1.67 x 10⁻⁸ cm² s⁻¹ respectively. The anodic potentials were affected by temperature and the activation energy, \(E_a\) was 18.18 kJ mol⁻¹ and 18.78 kJ mol⁻¹ in [BMIM][BF₄]/water mixture and [BMIM][OTf]/water mixture respectively.

Sodium ion, (Na⁺) on s-psc₄ has been replaced with bigger ion, N₁₄₄₄⁺ (tributyl ammonium ion) in order to fully dissolve it in pure ionic liquid. The electrochemistry of the prepared calixarene namely, (N₁₄₄₄)SO₃calix[4]arene, was done in pure ionic liquid, [BMIM][BF₄]. Two oxidation peaks were observed at 0.20 V and 1.20 V and were assigned as the oxidation of phenolate and phenol ion.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>xii</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xvi</td>
</tr>
</tbody>
</table>

## CHAPTER 1 : INTRODUCTION

1.1 Background of the research................. 2
1.2 The structure and rational of the dissertation................. 2
1.3 Objectives..................................... 4

## CHAPTER 2 : LITERATURE REVIEW

2.1 Calixarenes..................................... 6
2.2 Calix[n]arene.................................... 7
2.3 Structural characteristic and conformation properties of calix[n]arene. 8
2.4 Water-soluble calixarene.............................. 10
   2.4.1 *para*-sulfonatocalix[4]arene.................... 10
2.5 Synthesis of calixarene............................ 14
   2.5.1 The one-step synthesis of calixarene.............. 14
      2.5.1.1 Acid-catalysed one-step synthesis................ 14
      2.5.1.2 Based-catalyed one-step synthesis................ 15
   2.5.2 Convergent condensation synthesis of calixarene...... 15
2.6 Modification of calixarene...................... 18
2.7 Electrochemistry of calixarene.................. 19
2.8 Ionic liquid.................................... 22
   2.8.1 Introduction to room temperature ionic liquids (RTILs)........ 23
CHAPTER 3 : RESEARCH METHODOLOGY

3.1 Chemicals

3.2 Analytical equipment and theory

3.2.1 Nuclear magnetic resonance spectroscopy

3.2.1.1 Chemical Shift

3.2.2 Electrochemical study

3.2.2.1 Cyclic voltammetry

3.2.2.2 Electrochemical cell

3.3 Experimental methods

3.3.1 Synthesis of sodium p-sulfonatocalix[4]arene

3.3.1.1 Synthesis of p-tert-butylcalix[4]arene

3.3.1.2 Synthesis of calix[4]arene

3.3.1.3 Synthesis of sodium p-sulfonatocalix[4]arene

3.3.2 Synthesis of (N\textsubscript{1444})SO\textsubscript{3}calix[4]arene

3.3.2.1 Synthesis of HSO\textsubscript{3}-calix[4]arene

3.3.2.2 Synthesis of (N\textsubscript{1444})SO\textsubscript{3}-calix[4]arene

3.3.3 Synthesis of ionic liquids

3.3.3.1 Synthesis of [BMIM][Br]

3.3.3.2 Synthesis of [BMIM][NTf\textsubscript{2}]

3.3.3.3 Purification of [BMIM][BF\textsubscript{4}] and [BMIM][OTf]

3.3.4 Synthesis of lanthanide salts

3.3.4.1 Synthesis of gadolinium(III) bistriflimide [Gd(NTf\textsubscript{2})\textsubscript{3}]

3.3.4.2 Synthesis of ytterbium(III) bistriflimide [Yb(NTf\textsubscript{2})\textsubscript{3}]

3.3.5 Synthesis of tetraphenylphosphonium trifluoromethanesulfonate [Ph\textsubscript{4}P(OTf)]

3.3.6 Electrochemical studies

3.3.6.1 Preparation of [BMIM][NO\textsubscript{3}]/AgNO\textsubscript{3} reference electrode (ILRE)

3.3.6.2 Electrochemical experiment (Part 1)

3.3.6.3 Electrochemical experiment (Part 2)
### CHAPTER 4: RESULT AND DISCUSSION

#### Part 1 The electrochemical study of sodium p-sulfonatocalix[4]arene (s-psc₄) in ILs/water mixture

4.1 Characterization of sodium p-sulfonatocalix[4]arene (s-psc₄).............. 61
4.3 Number of electron (n) and diffusion coefficient (D).......................... 65
4.4 Temperature dependence...................................................................... 76

#### Part 2 Characterization and electrochemical study of modified calixarene (N₁₄₄₄)SO₃calix[4]arene) in pure ILs

4.5 Characterization of (N₁₄₄₄)SO₃calix[4]arene................................. 82
4.6 Characterization of Ph₄P(OTf)......................................................... 87
4.7 Electrochemical study of (N₁₄₄₄)SO₃calix[4]arene in ionic liquid....... 88
4.8 The electrochemistry of (N₁₄₄₄)SO₃calix[4]arene with phosphonium and lanthanide ions................................................................. 90

### CHAPTER 5: CONCLUSION........................................................................ 93

LIST OF REFERENCES.................................................................................. 97
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Melting point and density of some RTILs</td>
<td>26</td>
</tr>
<tr>
<td>2.2</td>
<td>Conductivity and viscosity of selected ionic liquids</td>
<td>27</td>
</tr>
<tr>
<td>2.3</td>
<td>Electrochemical stability window of ionic liquids</td>
<td>29</td>
</tr>
<tr>
<td>3.2</td>
<td>Chemicals used in the synthesis of ionic liquids</td>
<td>40-41</td>
</tr>
<tr>
<td>3.3</td>
<td>Chemicals used in electrochemical studies</td>
<td>41</td>
</tr>
<tr>
<td>3.4</td>
<td>Samples for electrochemical study</td>
<td>59</td>
</tr>
<tr>
<td>4.1</td>
<td>Cyclic voltammogram data for the oxidation of s-psc4 at glassy carbon electrode (A= 0.071 cm²) (a) s-psc4 in [BMIM][BF₄]/water mixture and (b) s-psc4 in [BMIM][OTf]/water mixture</td>
<td>68</td>
</tr>
<tr>
<td>4.2</td>
<td>Data from plot of ( I/A ) versus ( \nu^{1/2}/\nu^{1/2} )</td>
<td>72</td>
</tr>
<tr>
<td>4.3</td>
<td>Steady state voltammogram data and the value of ( n ) and ( D )</td>
<td>75</td>
</tr>
<tr>
<td>4.4</td>
<td>Data for temperature dependence studies</td>
<td>80</td>
</tr>
<tr>
<td>5.1</td>
<td>Result from Part 1</td>
<td>96</td>
</tr>
<tr>
<td>5.2</td>
<td>Result from Part 2</td>
<td>96</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>A calix[4]arene</td>
<td>8</td>
</tr>
<tr>
<td>2.2</td>
<td>Conformation of calix[4]arene</td>
<td>9</td>
</tr>
<tr>
<td>2.3</td>
<td>Bowl like p-sulfonatocalix[4]arene and the hydrophilic-hydrophobic bilayer</td>
<td>11</td>
</tr>
<tr>
<td>2.4</td>
<td>Interplay of phosphonium cations (Ph₄P⁺ and Ph₃BzP⁺) with p-sulfonatocalix[4]arene involving lanthanide metal cations at different molar ratio as reported by Mohamed Makha</td>
<td>12</td>
</tr>
<tr>
<td>2.5</td>
<td>An example of back-to-back arrangement of p-sulfonatocalix[4]arene, phosphonium cation and ytterbium (lanthanide).</td>
<td>13</td>
</tr>
<tr>
<td>2.6</td>
<td>The cyclic voltammogram of 5.0x10⁻⁴ M p-sulfonatocalix[4]arene + 0.05M CH₃COOH + 0.05 M CH₃COONa at different scan rates, 25°C : (1) 0.01 (2) 0.02 (3) 0.05 (4)0.10 (5) 0.20 (6) 0.50</td>
<td>21</td>
</tr>
<tr>
<td>2.7</td>
<td>Cations and anions for ionic liquids</td>
<td>22</td>
</tr>
<tr>
<td>2.8</td>
<td>Voltammogram for [BMIM][PF₆] at glassy carbon, platinum and gold macro disk as working electrodes. The scan was carried out at 100 mV/s versus the Ag wire quasi-reference electrode</td>
<td>31</td>
</tr>
<tr>
<td>2.9</td>
<td>Cyclic voltammetry of Yb(NTf₂)₃ in [BMPyrr][NTf₂] at glassy carbon, 10 mV/s</td>
<td>33</td>
</tr>
<tr>
<td>2.10</td>
<td>Cyclic voltammetry of Al deposition on mild steel substrate in [EMIM][Cl]/AlCl₃ (40/60 mol %) at room temperature with scan rate of 10 mV/s</td>
<td>34</td>
</tr>
<tr>
<td>2.11</td>
<td>Cyclic voltammetry during the synthesis of poly(o-phenylenediamine) in RTIL</td>
<td>35</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Examples of eleven different resonance signals for different compounds</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Proton chemical shift range</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>AUTOLAB Potentiostat/Galvanostat (PGSTAT 12/30/302)</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Reversible cyclic voltammogram using glassy carbon as working electrode and Ag/AgCl as reference electrode</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>A three-electrode cell set-up</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>The voltammograms of blank [BMIM][BF₄] (red) and [BMIM][OTf] (blue) at 100 mV/s versus ILRE</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>FTIR spectrum of s-psc₄</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>¹H-NMR of s-psc₄</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>At 25°C, the voltammogram of 0.12 M of s-psc₄ in (a) [BMIM][BF₄]/water mixture and (b) [BMIM][OTf]/water mixture at scan rate ranged from 10 mV/s to 400 mV/s, GC versus SCE</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>At 25°C, the plot of Eₚ versus ln ν of 0.12 M of s-psc₄ in (a) [BMIM][BF₄]/water mixture and (b) [BMIM][OTf]/water mixture</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>Plot of Iₚ versus ν¹/² for (a) s-psc₄ in [BMIM][BF₄]/water mixture, (b) s-psc₄ in [BMIM][OTf]/water mixture</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>Cyclic voltammogram of s-psc₄ in (a) [BMIM][BF₄]/water mixture (b) [BMIM][OTf]/water mixture at 0.012 M, 0.12 M and 1.2 M, 25°C, 100 mV/s, GC versus SCE</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>The steady state voltammogram of s-psc₄ in (a) [BMIM][BF₄]/water mixture and (b) [BMIM][OTf] on a GC electrode ν = 5 mVs⁻¹</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>Cyclic voltammogram of s-psc₄ in (a) 0.12 M [BMIM][BF₄]/water mixture (b) 0.12 M [BMIM][OTf]/water mixture up to 60°C, 100 mV/s, GC versus SCE</td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>Plot of log D versus 1/T(K⁻¹)</td>
<td></td>
</tr>
<tr>
<td>4.10</td>
<td>$^1$H-NMR spectrum of HSO$_3$-calix[4]arene.............</td>
<td>83</td>
</tr>
<tr>
<td>4.11</td>
<td>$^1$H-NMR spectrum of (N$_{1444}$)SO$<em>3$-calix[4]arene with excess of N$</em>{1444}$OH. ..........................</td>
<td>84</td>
</tr>
<tr>
<td>4.12</td>
<td>$^1$H-NMR spectra of (N$<em>{1444}$)SO$<em>3$-calix[4]arene. (a) 50 µL of N$</em>{1444}$OH added, (b) 200 µL of N$</em>{1444}$OH added, (c) 300 µL of N$_{1444}$OH added ................................</td>
<td>86</td>
</tr>
<tr>
<td>4.13</td>
<td>$^1$H-NMR and $^{19}$F-NMR for Ph$_4$P(OTf)................</td>
<td>87</td>
</tr>
<tr>
<td>4.14</td>
<td>The cyclic voltammetry of (N$_{1444}$)SO$_3$-calix[4]arene (0.06M) in [BMIM][BF$_4$] at 100 mV/s versus ILRE, GC.................................................................</td>
<td>89</td>
</tr>
<tr>
<td>4.15</td>
<td>Cyclic voltammogram of Ph$_4$P(OTf) in [BMIM][BF$_4$] (0.06 M) at 100 mV/s versus ILRE, GC.............................................................</td>
<td>90</td>
</tr>
<tr>
<td>4.16</td>
<td>Cyclic voltammogram of Gd(NTf$_2$)$_3$ in [BMIM][BF$_4$] (0.2 M) at 100 mV/s versus ILRE, GC........................</td>
<td>91</td>
</tr>
<tr>
<td>4.17</td>
<td>Cyclic voltammogram of (N$_{1444}$)SO$_3$-calix[4]arene in [BMIM][BF$_4$] in the absence (red) and presence (blue) of Ph$_4$P(OTf) in [BMIM][BF$_4$] at 100 mV/s versus ILRE, GC..........................</td>
<td>92</td>
</tr>
</tbody>
</table>
# LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Synthesis of ladder polymer by condensation reaction of resorcinol and butanedial</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>One-step synthesis of single bridge bis-calix[4]arene with oligooxyethyleneethyl spacers</td>
<td>16</td>
</tr>
<tr>
<td>2.3</td>
<td>Convergent synthesis for unsymmetrical calixarene, 3+1 and 2+2 strategy</td>
<td>17</td>
</tr>
<tr>
<td>2.4</td>
<td>Reaction of bis-carbene complex (1) with bis-proparyl benzene (2) to form Fisher carbine complex (3)</td>
<td>17</td>
</tr>
<tr>
<td>2.5</td>
<td>Synthesis of germylated calixarene</td>
<td>19</td>
</tr>
<tr>
<td>2.6</td>
<td>Proposed reaction sequence for three-electron reduction process. A = Benzaldehyde, B= radical anion, C= dianion species, D= anion-radical anion dimerization</td>
<td>36</td>
</tr>
<tr>
<td>3.1</td>
<td>The route for the synthesis of sodium p-sulfonatocalix[4]arene</td>
<td>49</td>
</tr>
<tr>
<td>3.2</td>
<td>Synthetic route for (N\textsubscript{1444})SO\textsubscript{3}calix[4]arene</td>
<td>53</td>
</tr>
<tr>
<td>3.3</td>
<td>Synthetic route for [BMIM][Br]</td>
<td>54</td>
</tr>
<tr>
<td>3.4</td>
<td>Synthetic route for [BMIM][NTf\textsubscript{2}]</td>
<td>55</td>
</tr>
<tr>
<td>3.5</td>
<td>Chemical equation for the synthesis of Gd(NTf\textsubscript{2})...</td>
<td>56</td>
</tr>
<tr>
<td>3.6</td>
<td>Chemical equation for the synthesis of Yb(NTf\textsubscript{2})\textsubscript{3}...</td>
<td>56</td>
</tr>
<tr>
<td>3.7</td>
<td>Chemical equation for the synthesis of Ph\textsubscript{4}P(CF\textsubscript{3}SO\textsubscript{3})...</td>
<td>57</td>
</tr>
<tr>
<td>4.1</td>
<td>Proposed electrochemical oxidation of s-psc\textsubscript{4} in [BMIM][BF\textsubscript{4}]/water and [BMIM][OTf]/water...</td>
<td>64</td>
</tr>
<tr>
<td>4.2</td>
<td>Metathesis reaction of Ph\textsubscript{4}P(OTf). Reproduced from scheme 3.7...</td>
<td>87</td>
</tr>
<tr>
<td>4.3</td>
<td>The reaction of ($N_{1444}$)SO$_3$calix[4]arene with ionic liquid $IL = [BMIM][BF_4]$</td>
<td>89</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

\( \alpha \): The electron transfer coefficient

\( A \): The area of the surface electrode, cm\(^2\)

\( C^*_R \): Initial concentration of sample, mol dm\(^{-3}\)

\( C^0 \): Concentration in (mol cm\(^{-3}\))

\( D \): Diffusion coefficient, cm\(^2\)s\(^{-1}\)

\( D_0 \): Diffusion coefficient at infinite temperature, cm\(^2\)s\(^{-1}\)

\( E_p \): Peak potential, V

\( E^0 \): Formal standard potential, V

\( F \): Faraday constant, 96485 C eqv\(^{-1}\)

\( R \): Gas constant, 8.314 J mol\(^{-1}\)K\(^{-1}\)

\( I_p \): Peak current, A

\( n_a \): The number of electron transferred in the rate-determining step

\( n \): The number of electron transferred

\( r \): Radius, cm

\( T \): Absolute temperature, K
LIST OF ABBREVIATIONS

EMIM : Ethyl methyl imidazolium
BMIM : Butyl methyl imidazolium
EDMIM : Ethyl dimethyl imidazolium
PrMIM : Propyl methyl imidazolium
PrDMIM : Propyl dimethyl imidazolium
BMPyrr : Butyl methyl pyrrolidinium
BTMIN : Butyl trimethyl ammonium
PrTMIN : Propyl trimethyl ammonium
BMPy : Butyl methyl pyridinium
BF$_4$ : Tetrafluoroborate
OTf : Trifluoromethanesulfonate
NTf$_2$ : Trifluoromethanesulfonylimide (Bistriflimide)
PF$_6$ : Hexafluorophosphate
Cl : Chloride
F : Fluoride
NPF$_2$ : pentafluoroethylsulfonylimide
(CN)$_2$N : dicyanamide
AsF$_6$ : hexafluoro arsenate
(C(CF$_3$SO$_2$)$_3$) : Tris-trifluoromethanesulfonylmethylide
GC : Glassy carbon
Pt : Platinum
ILRE : Ionic liquid reference electrode
Ph₄P(OTf) : Tetraphenylphosphonium trifluoromethanesulfonate
CHAPTER I

INTRODUCTION
1.1 Background of the research.

This dissertation described work carried out on the electrochemistry of sodium p-sulfonatocalix[4]arene in [BMIM][BF$_4$] and [BMIM][OTf] as electrolyte. Two major chemistry fields, namely supramolecular and ionic liquid were combined in order to understand and develop a new branch of research field. The research mainly focussed on the electrochemical behaviour of calixarene by looking at the cyclic voltammogram.

Sodium p-sulfonatocalix[4]arene is a water-soluble electroactive species. The unique arrangement of sodium p-sulfonatocalix[4]arene and the ability to do a self-assembly chemistry with other metals had attracted researchers to study and understand the behaviour and characteristic of calixarene in different conditions and structural modifications. In this research we are interested in study the electrochemical behaviour of p-sulfonatocalix[4]arene. Some publications had been referred regarding the potentials and explanation on the behaviour of calixarene in different solvents. This work specifically focused on the electrochemical behaviour of the sodium p-sulfonatocalix[4]arene and (N$_{1444}$)SO$_3$calix[4]arene using [BMIM][BF$_4$] and [BMIM][OTf] as electrolyte.

Ionic liquids are known as green solvents and had been designed to be green to the environment. The purpose of using ionic liquid as electrolyte is because it has good physical and electrochemical properties. Ionic liquids can be a solvent and at the same time can be a supporting electrolyte for electrochemistry. Some of them have wide electrochemical window, which can be up to 6.0 V.
1.2 The structure and the rational of the dissertation.

This dissertation is divided into five main chapters, namely introduction, literature review, research methodology, result and discussion and conclusion.

Chapter I (Introduction)

This chapter represents a brief outline of the whole dissertation. It highlights the aim and focus of the research.

Chapter II (Literature Review)

Chapter II describes the previous work that had been done and published by other researchers as a reference throughout this study. Generally this chapter is divided into 2 parts: calixarene and ionic liquid. Each part discussed the brief history, properties, and example of previous study.

Chapter III (Research Methodology)

Chapter III gives details on the experimental work. This chapter is divided into three main subtitles. The first subtitle lists the details on the chemicals used in the experiments. The second subtitle discusses the theory of analytical concepts, such as potentiostat/galvanostat for electrochemical measurement and nuclear magnetic resonance spectroscopy for sample characterisation. Besides, this part will give the basic concept on characterisations and measurements. The last subtitle describes the experimental procedure for the synthesis of sodium $p$-sulfonatocalix[4]arene, $(N_{1444})SO_3$calix[4]arene, [BMIM][BF$_4$] and [BMIM][OTf]. The details about sample coding and descriptions will be introduced in this chapter.
Chapter IV (Results and Discussion)

The experimental data is analysed in this chapter. All works that had been done will be combined together in order to reach the objective of the study. This chapter is divided into 2 parts. The first part discusses the characterisation of samples of NMR study and the measurement of number of electron and diffusion coefficient of sodium p-sulfonatocalix[4]arene. The second part describes the electrochemical study of (\(N_{1444}\)SO\(_3\)calix[4]arene in [BMIM][BF\(_4\)].

Chapter V (Conclusion)

This chapter concludes the finding in the research.

1.3 Objectives

The main focuses of this work is to understand and investigate the electrochemical behaviour of sodium p-sulfonatocalix[4]arene in ionic liquids.

Ionic liquids composed of anion and cation, have wider electrochemical windows and inherently conductive thus allowing the stabilisation of unusual species. Therefore, in theory different electrochemical behaviour of sodium p-sulfonatocalix[4]arene can be observed in ionic liquids compared to other organic solvents.

This project is divided into 2 main sections. The first section is the preparation of complex and ionic liquids and the second section is the electrochemistry study. In the first section, the following:
1. Synthesis of water-soluble ionic

2. Characterise the ionic liquids using \(^1\)HNMR and electrochemistry by comparing the data with the literature.


In the electrochemistry section, the aims are:

1. To study the behaviour of \(p\)-sulfonatocalix[4]arene in water immiscible ionic liquids \([\text{BMIM}][\text{BF}_4]\) and \([\text{BMIM}][\text{OTf}]\).

2. To determine the number of electron transferred, diffusion coefficient and activation energy for the different systems.
CHAPTER II

LITERATURE REVIEW
2.1 Calixarenes

Calixarenes are a fascinating family of macrocyclic compounds composed of phenolic units connected by methylene bridges to form a hydrophobic cavity molecules that feature extensively in the field of supramolecular chemistry\textsuperscript{1,2}. This is related to their synthesis availability and ease of modification, coupled with the presence of cavities/clefts that are capable of binding a variety of species\textsuperscript{1,2,3}.

Leo Baekeland succeeded in making phenol-formaldehyde resins in 1902 under the trade name Bakelite. In this resins, phenol and formaldehyde are exhaustively condensed with each other to form heavily cross-linked polymers. The first attempt to control the reaction was made by Alois Zinke and Erich Ziegler in 1942. They employed para-substituted phenols which inhibits crosslinking and should result in linear polymers with formaldehyde. So, in 1944 \textit{p-tert}-butylphenol with formaldehyde and sodium hydroxide in linseed oil as a solvent to produced for the first time a crystalline solid with a high melting point rather than a resin. In the same year, Niederl and Vogel did similar experiments with a \textit{para}-substituted resorcinol and they were the first to propose a cyclic tetramer. In those days structure elucidation was limited to determination of molar mass by freezing-point depression and functional group analysis\textsuperscript{1,2,4}. In the fifties, the first commercial success came to calixarene when the company petrolite which had been consulted by David Gutsche, started a range of calixarene products as demulsifiers in oil industry.

The first calixarene was synthesized by Adolph Von Baeyer as a product of the reaction of phenols with aldehydes in the presence of strong acid (hydrochloric acid) although he didn't realise its potential and unable to determine the structure\textsuperscript{1,2,4}. In 1972, he mixed benzaldehyde and pyrogallol in the presence of hydrochloric acid
and observed a red-brown resin with a markedly increased viscosity. He also tried to use resorcinol and formaldehyde which he prepared himself from iodoform since there was no commercial grade of formaldehyde at that time.

Experiments carried out by John Cornforth (an Australian chemist working in Britain and obtained the Nobel Prize in 1975 for his work on enzyme-catalyzed reactions) in 1950s indicated that the Zinke product are actually mixtures. Cornforth and co-worker repeated the Zinke’s experiments with two $p$-substituted phenols and obtained two pairs of compounds, high and lower melting species. He elicited the services of Dorothy Crowfoot Hodgkin for structure elucidation by X-ray crystallography but with limited success. In 1984 the Lederer-Manasse hydroxyalkylation was invented as a synthetic tool for the preparation of hydroxymethylphenols. The introduction of this synthetic route makes calixarene easier to prepare. Then, starting in the mid-1980s and continuing to the mid-1990s the worked on calixarene becomes even more steeply ascending, now reaching a plateau with the publication of five or more papers per week$^{1,4}$.

### 2.2 Calix[n]arene

The term “calix[n]arene” ($n=4,5,6,7,8$) indicates a class of phenolic metacyclopahnes derived from condensation of phenols and aldehydes. The name was coined by Gutsche although the name did not appear in print before 1978$^4$. Calixarene derives from Latin words “calix” means vase and “arene” means aromatic rings. The bracket in between “calix” and “arene” indicates the number of aromatic rings. The phenolic units are linked to each other by methylene to form cavity/cleft and hence defines the size of the macrocycle$^{1,4,5}$. A calix[4]arene is illustrated in Figure 2.1.
2.3 Structural characteristic and conformation of calix[n]arene

Calixarenes are characterised as a group of polyphenolic by a three dimensional bowl, cup, bucket, cone or basket-shaped molecules with hydrophobic cavities. The cavities or clefts are capable of binding molecules with appropriate electronic and or steric complementarily. Specific properties of these molecules can be tailored by functionalised either the ‘upper rim’ or ‘lower rim’ of the calixarene framework. The lower rim contains phenolic group; while capped with anionic sulfonated groups. The increasing interest in this class of compound arises from the possibility of functionalization of both rims in region- and stereo-controlled ways. It has the flexibility to adjust the cavity’s dimension and the ability to form inclusion compound with ionic or neutral molecules such as fullerenes and lanthanide.

Calixarene can exist in different chemical conformations. For example, \( p\text{-tert}-\)butylcalix[4]arene can exits in four up and down conformations. Gutsche et. al
reported that the four designs are cone, partial cone, 1,2-alternate, and 1,3-alternate conformations as shown in Figure 2.2. This study had been supported by $^1$H-NMR in chloroform by Gutsche et al. The results showed that calix[4]arene prefers the cone formation but that inversion of the cone takes place fairly rapidly at room temperature$^2$.

![Conformations of calix[4]arene](image)

**Figure 2.2 Conformations of calix[4]arene**

The conformational flexibility of calixarenes carrying endo-annular hydroxyl groups is determined by the size of the macrocyclic ring, which in turn influences the nature of intramolecular hydrogen bonding. Gutsche et al. concluded that calix[4]arenes and calix[5]arenes adopt cone conformation; calix[6]arenes are postulated to adopt a winged or hinged conformation; calix[7]arene adopt a pseudo pleated-loop conformation and the calix[8]arenes are thought to exist in a true pleated-loop conformation.$^{1,2,4,17}$

### 2.4 Water-soluble calixarenes
Water-soluble calixarenes are readily accessible by functionalising either the upper or lower rim of the phenol macrocycle. Among their water-soluble derivatives, the para-sulfonatocalix[4]arenes are the most widely studied.\textsuperscript{13,14}

2.4.1 \textit{para}-sulfonatocalix[4]arenes

The structure of water-soluble \textit{p}-sulfonatocalix[4]arenes was resolved by Atwood in 1988\textsuperscript{18}. Research showed that \textit{p}-sulfonatocalix[4]arenes can complex with different species such as organic ions, amino acids, and aliphatic alcohols. However, \textit{p}-sulfonatocalix[4]arenes are well known as electroactive reagents.

\textit{p}-Sulfonatocalix[4]arenes are versatile tectons in supramolecular chemistry, forming a diverse range of structural motif. Highlights include nanoscale spheroids as potential inorganic viral mimics, tubules and more recently, a unique zeolite-like material formed from helically arranged chains of the supramolecule\textsuperscript{16}.

Atwood \textit{et. al.} pioneered the use of \textit{p}-sulfonatocalix[4]arenes in building up structures, initially as a bilayer arrangement with the calix[4]arenes arranged in an up/down fashion; for example the calix[4]arene in hydrophilic-hydrophobic bilayer structures with the positively charged species and included molecules between the layers\textsuperscript{16,19}. The clay or bilayer arrangement (\textbf{Figure 2.3}) comprised of hydrophilic layers of adjacent calixarene engaged in π-stacking interactions, and a hydrophilic domain between these layers containing water molecules, metal ions and various organic molecules such as crown ethers, amino acids, peptides and nucleic acids and bases.\textsuperscript{16,19}
A lot of modification of $p$-sulfonatocalix[4]arene was investigated in recent years due to the unique properties and demands on this supramolecule. For example, Figure 2.4 and 2.5 shown the studies done by Mohamed Makha et. al.\cite{10}.
Figure 2.4: Interplay of phosphonium cations (Ph₄P⁺ and Ph₃BzP⁺) with p-sulfonatocalix[4]arene involving lanthanide metal cations at different molar ratio of 1:1:3 and 1:3:1 as reported by M. Makha et. al.

A phenyl ring of a phenyl phosphonium cation occupied the cavity of p-sulfonatocalix[4]arene back-to-back arrangement
Figure 2.5: An example of back-to-back arrangement of $p$-sulfonatocalix[4]arene, phosphonium cation and ytterbium (lanthanide) cation.

These complexes were obtained by varying the molar ratio of the $p$-sulfonatocalix[4]arene to phosphonium cation [benzyltriphenylphosphonium ($\text{BzPh}_3\text{P}^+$), tetraphenylphosphonium ($\text{Ph}_4\text{P}^+$)] and lanthanide ions ($\text{Gd}^{3+}$, $\text{Yb}^{3+}$, $\text{Er}^{3+}$).

It was concluded that there is little structural impact of the $p$-sulfonatocalix[4]arene structure on substituting $\text{Ph}_4\text{P}^+$ with $\text{BzPh}_3\text{P}^+$. Overall work was highlighted the structural versatility of the $p$-sulfonatocalix[4]arene and the potential of the building material in catalysis and supramolecule devices$^{10,13,19,20}$.

2.5 Synthesis of calixarene

Multi-step methods had been exploited by researchers in order to synthesise calixarene. However, in recent years two general approaches are used to synthesise the unique basket shape calixarene, namely one-step synthesis and convergent condensation synthesis$^5$.

2.5.1 The one-step synthesis of calixarene

Acid-catalysed and base-promoted one-step synthesis provides the most powerful procedures to obtain symmetrically substituted calixarene having one type of phenolic unit in the cyclic array$^5$. 
2.5.1.1 Acid-catalysed one-step synthesis

The acid-catalysed reaction of resorcinol with aldehydes leads to cyclic tetramers which are grouped in the class of resorc[4]arenes (exo-calixarene). The reaction is quite general with respect to the aldehyde and to the starting resorcinol, which can bear several substituents in the 2-position. Niederl and Hogberg showed in typical example, the synthetic procedure by which an ethanolic solution of resorcinol, acetaldehyde and 37% hydrochloric acid maintained at 80°C for 16 hours, afforded 75% of the all cis-ethylresorc[4]arene⁵. A shorter reaction time leads to the ‘kinetic’ stereoisomer (trans, cis, trans, cis). This procedure is general for many aldehydes but the use of formaldehyde is limited to some special cases¹,⁵. Scheme 2.1 shows an example of a one-step acid-catalysed synthesis of ladder polymer by reacting resorcinol with butanediaid in the presence of concentrated HCl²¹.

Scheme 2.1: Synthesis of ladder polymer by condensation reaction of resorcinol and butanediaid²¹.

2.5.1.2 Based-catalysed one-step synthesis
In general, the base-catalysed condensation of a $p$-substituted phenol and formaldehyde yields a complex mixture of linear and cyclic oligomers and the outcome of the reaction is difficult to control. However, few reactions can be controlled when the starting phenol bears a bulky substituent at the $p$-position. The early procedures for their one-step preparation were not routinely reproducible and led difficulty to separate the mixtures until early 1980; the reliable procedures for preparing $p$-tert-butylcalix[n]arenes ($n=4,6,$ and $8$) were introduced. An example of a base-catalysed one-step synthesis is shown in Scheme 2.2\textsuperscript{22}. The scheme shows the reaction between $p$-tert-butylcalix[4]arene and ethylene glycol ditosylate in the presence of NaH and toluene. The main product was singly-bridge bis-$p$-tert-butylcalix[4]arene (49% yield) and 1,2-doubly bridge bis-calix[4]arene as by-product (5% yield).

![Scheme 2.2](image)

Scheme 2.2: One-step synthesis of singly-bridge bis-calix[4]arene with oligooxyethyleneethyl spacers\textsuperscript{22}. 
2.5.2 Convergent condensation synthesis of calixarene

Convergent stepwise syntheses (fragment condensation) are usually based on the condensation of two synthons from which calixarenes can be isolated in 10-25% yield. This strategy is complementary to the one-step procedure and also offers the advantage of obtaining calixarenes with different phenol rings incorporate in the molecular skeleton or having substituents at the methylene bridges. Scheme 2.3 and 2.4 show two examples of convergent stepwise syntheses of calixarene.

Scheme 2.3: Convergent synthesis for unsymmetrical calixarene. 3+1 and 2+2 strategies.
Scheme 2.4: Reaction of bis-carbene complex (1) with bis-propargyl benzene (2) to form Fisher carbone complex (3).

2.6 Modification of calixarene

The unique properties of calixarene such as the flexibility to adjust cavity dimension\textsuperscript{14} and the ability to form inclusion compound with ionic and neutral molecule\textsuperscript{14} have attracted many researches to explore more on calixarene chemistry. For example the modification of \textit{p}-tert-butylcalix[4]arene to become new ligand, namely 5,11,17,23-tert-butyl-25,27-dihydroxy-26,28-bis[(tetramethyldiamidophosphinyl)oxy]calix[4]arene\textsuperscript{24}. The work done by Videva \textit{et al.} discussed on the coordination ability of the ligand to bind alkali cations similarly to the calix[4]arene. Besides, many publications\textsuperscript{25} reported the modification of calixarene for different applications and study such as the modification of \textit{tert}-butylcalix[4]arene with germanium-containing side-chains at the lower rim (Scheme 2.5). In that research, the aimed was to synthesis new class of ditopic host. Although there was found to adopt cone conformation in solution, which is favourable for capturing cations, however these calixarenes failed to capture and transport cations. This is because of the poor cation capturing property of the calixarene moiety\textsuperscript{25}. 
Scheme 2.5 Synthesis of germylated calixarenes.


2.7 Electrochemistry of calixarene

+0.8 V versus SCE while an oxidation wave occurred at +1.40 V for $p$-tert-butylcalix[8]arene.

**Figure 2.6** shows the voltammogram of the solution containing $p$-sulfonatocalix[4]arene, acetic acid and sodium acetate as buffer. According to Nicholson for irreversible anodic reaction, the relationship between $E_p$ and ln $\nu$ is linear, and can be described by **Equation 2.1**. From this equation the number of electron and diffusion coefficient can be evaluated.

$$E_p = E^\circ + \frac{RT}{\alpha n_a F} [0.780 + \ln \left( \frac{D^{1/2}}{k^o} \right) + \ln \left( \frac{n_a F \nu}{RT} \right)^{1/2}] \quad \text{Equation 2.1}$$

The peak current $I_p$ for irreversible electrochemical reaction can be described by **Equation 2.2**:

$$I_p = -(2.99 \times 10^5)n(\alpha n_a)^{1/2}AC^*R^{1/2}D^{1/2}\nu^{1/2} \quad \text{Equation 2.2}$$

Guowang Diao et al. reported that the number of electrons transfer for $p$-sulfonatocalix[4]arene is two, and the diffusion coefficient is $3.1 \times 10^{-5}$ cm$^2$s$^{-1}$ while the anodic peak potential was observed at 0.83 V (versus SCE).
Figure 2.6: The cyclic voltammogram of $5.0 \times 10^{-4}$ M $p$-sulfonatocalix[4]arene + $0.05$ M CH$_3$COOH + $0.05$ M CH$_3$COONa at different scan rates, $25^\circ$C: (1) 0.01 (2) 0.02 (3) 0.05 (4) 0.10 (5) 0.20 (6) 0.50 Vs$^{-1}$

The same behaviour was also reported for $p$-sulfonatocalix[6]arene and $p$-tert-butylcalix[8]arene. The water soluble $p$-sulfonatocalix[6]arene showed an irreversible reaction which is similar to oxidation of phenol. The number of electron transferred in the electrochemical oxidation at pH 3.9 is one and the diffusion coefficient is $1.4 \times 10^{-6}$ cm$^2$s$^{-1}$ while at pH 10.6 the number of electrons transferred in the electrochemical oxidation is three and the diffusion coefficient is $1.1 \times 10^{-6}$ cm$^2$s$^{-1}$. The author concluded that as the pH increases, the oxidation of $p$-sulfonatocalix[6]arene was easier due to more hydrogen ions being released from the calixarene. The same behaviour was observed for the $p$-tert-butylcalix[8]arene. An irreversible electrochemical oxidation was observed due to the oxidation of $p$-tert-butylcalix[8]arene. The number of electrons transferred in the electrochemical reaction was determined as four and the diffusion coefficient was $2.8 \times 10^{-5}$ cm$^2$s$^{-1}$.
2.8 Ionic liquids

Recently, ionic liquids have been investigated extensively as possible replacement for common organic solvents due to their low vapour pressures and wide liquid temperature range. Because of the unique combination of cations and anions (Figure 2.7) and by simply changing the anion and functionality on the cation, the physical properties of the ionic liquids may be varied systematically, making them versatile engineering solvents and described as designer solvents\textsuperscript{30}. These room temperature ionic liquids (RTIL) are the subject of this review.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2_7.png}
\caption{Cations and anions for ionic liquids}
\end{figure}
2.8.1 Introduction to Room Temperature Ionic Liquids (RTILs)

Ionic liquids, also known as liquid organic, molten, or fused salts, are nonmolecular ionic solvents composed of ions with melting point below 100°C. Ionic liquids that are also liquids at room temperature are referred as Room Temperature Ionic Liquids (RTILs).

Ionic liquids have been known for many years. For instance ethylammonium nitrate, \([\text{EtNH}_3][\text{NO}_3]\) (m.p. 12°C), was first described at the beginning of 1914\(^{31}\). In the middle of 1948, the first RTIL based on chloroaluminate anion was patented. Fifteen years later (1963), a similar system, based on chlorocuprate anion, \(\text{CuCl}_2^-\) and tetraalkylammonium cation, obtained by mixing copper(I) chloride (\(\text{CuCl}\)) and tetraalkylammonium chloride, was described. In 1967 the application of tetrahexylammonium benzoate as a solvent was published. The class of ionic liquids, based on tetraalkylammonium cation and chloroaluminate anion, has been extensively studied since late 1970s, following the works of Osteryoung (1975-1979)\(^{32,33,34}\). In 1979, Ronald A. Caprio reported several N-alkylpyridinium halides and their mixture with aluminium chloride, and in the same year Hussey published his studies on chloroaluminate\(^{35}\). Systematic research on the application of chloroaluminate ionic liquids as solvent was performed in 1980s. The most extensively studied RTILs of this type seems to be dialkylimidazolium chloroaluminates\(^{36,37}\). Such RTILs are good solvents for conducting various reactions because aluminium trichloride (\(\text{AlCl}_3\)) in hydrochloric acid acts as a co-catalyst. However, ionic liquids based on aluminium halides are moisture sensitive. \(\text{AlX}_3\) can react with water to form halic acid, \(\text{HX} (X=\text{Cl or Br})\)\(^{37}\). The development of ionic liquids began to flourish when in 1990’s new ionic liquids were introduced based on 1-ethyl-3-methyl-imidazolium tetrafluoroborate, \([\text{EMIM}][\text{BF}_4]\)\(^{38,39}\) and 1-butyl-3-
methyl-imidazolium hexafluorophosphate, [BMIM][PF₆]. During the last decade an increasing number of new ionic liquids have been developed and used as solvent.

2.9 Properties of RTILs

RTILs have unique properties that might not be found in any convenient solvents. They have attracted much attention as novel nonaqueous solvent. The feature of ionic liquids is to be a liquids in a wide temperature range and moreover the vapour pressure is approximately zero and do not evaporate under high temperature. RTILs also can be custom-synthesised to be water-miscible or immiscible, extraordinarily high chemical and thermal stability, good conductivity, wide electrochemical windows, no requirement for additional supporting electrolytes, good dissolving capability, can undergo multiple solvation interactions with many types of molecules, and have been widely used in organic synthesis, liquid-liquid extraction, electrochemistry, and inorganic synthesis and also green to the environment. Anderson et al. gives the structural, physicochemical properties and synthetic route for few selected ILs, each representative a particular class. The wide range combination of anion and cation could provide over 10¹⁹ organic salts that might be potential RTILs.

2.9.1 Melting Points and Density

Melting point is one important aspects most reported in studying the behaviour of RTILs. Definition of the room temperature ionic liquid was characterized by their melting point. As the alkyl chain gets longer (butyl to octyl) the melting
point decreases until reach certain points. Beyond these points, the melting points will increases which are from tetradecyl to higher alkyl. This behaviour can be described as the longer chain decrease the symmetry of the cation and thereby interfere in efficient crystal packing. Since the columbic forces are responsible for much of the attractive forces in RTILs, therefore anything that interferes the packing should decreased the melting point. However, the attractive van der Waals forces of the alkyl chain hold the ions together, leading to a steady increase in the melting point.

Density is another property of ionic liquids. Imidazolium RTILs are denser than water. This means they have densities greater than 1.0. Table 2.1 summarises the melting point and density of selected ionic liquids that have been published in the literature.

<table>
<thead>
<tr>
<th>IONIC LIQUIDS</th>
<th>DENSITY (g/cm$^3$)</th>
<th>MELTING POINTS (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][BF$_4$]</td>
<td>1.17, 1.12</td>
<td>-82,-81</td>
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<tr>
<td>[BMIM][OTf]</td>
<td>1.29</td>
<td>16</td>
</tr>
<tr>
<td>[BMIM][NTf$_2$]</td>
<td>1.43</td>
<td>-4</td>
</tr>
<tr>
<td>[BMIM][PF$_6$]</td>
<td>1.36</td>
<td>-8</td>
</tr>
</tbody>
</table>
Table 2.1: Melting point and density of some ionic liquids.  

| [BMIM][Cl] | 1.10 | 65 |

2.9.2 Vapour Pressure

Purifying RTILs is not as simple as conventional solvents. Since RTILs are non-volatile or have no vapour pressure, the RTILs cannot be distilled and cannot be recrystallised. Determination of amount and impurity presents in RTILs can be difficult and need several steps and analysis.

2.9.3 Viscosity and Conductivity

According to Stokes-Einstein equation, the conductivity of ionic liquids depends on the ion mobility which is related to the viscosity. The conductivity of ILs inversely parallels their viscosity. Thus, lower viscosity RTILs exhibit higher conductivities and higher temperature while viscosity significantly increase when temperature decrease. The viscosity of ionic liquid is also influenced in the presence of impurities. In ionic liquid, water and halides are common impurities. The presence of water in ionic liquids decreases the viscosity while the presence of chloride increases the conductivity. This conclusion was reported by Seddon et. al. in 2000. Research by Zhang et. al. found that the conductivity of ionic liquids usually exhibit classical Arrhenius behaviour. Table 2.2 summaries the viscosity and conductivity of selected ionic liquids that had been reported in the literature.
Table 2.2: Conductivity and viscosity of selected ionic liquids.\textsuperscript{41-46}

![Table 2.2: Conductivity and viscosity of selected ionic liquids.](image)

2.9.4 Electrochemical windows

Table 2.3 was from literature by M. Galinski et al. in *Electrochimica Acta*\textsuperscript{43}. The table show the electrochemical windows of certain ionic liquids with variety of electrodes used. Due to their desirable properties in electrochemistry, which is high conductivity ($>10^{-4}$ S/cm) and large electrochemical window ($>1$ V), RTILs were considered versatile electrolytes for electrosynthesis, and the redox behaviour of electroactive substrates, as well as electroplating of base, rechargeable batteries, photoelectrical cells, and electrochemical devices\textsuperscript{41,43}. Impurities also influence the potential windows in ionic liquids. Schroder et al. has reported in 2000 that the presence of water in ionic liquids dramatically reduce their potential windows and the contamination by halide might narrow the potential as the halide is usually easier to be oxidised than the anion in ionic liquids\textsuperscript{49}. The application of electrochemical studies in ionic liquids is summarised on page 31.
<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Cathodic Limit (V)</th>
<th>Anodic Limit (V)</th>
<th>Electrochemical Window (V)</th>
<th>Working Electrode</th>
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<td>-2.3</td>
<td>3.4</td>
<td>5.7</td>
<td>Pt</td>
<td>Ag wire</td>
</tr>
<tr>
<td></td>
<td>-1.9</td>
<td>2.5</td>
<td>4.4</td>
<td>Pt</td>
<td>Pt</td>
</tr>
<tr>
<td>[BMIM][NTf₂]</td>
<td>-2.0</td>
<td>2.6</td>
<td>4.6</td>
<td>Pt</td>
<td>Pt</td>
</tr>
<tr>
<td>[EDMIM][NTf₂]</td>
<td>-2.0</td>
<td>2.6</td>
<td>4.4</td>
<td>Pt</td>
<td>Ag/Ag⁺ in DMSO</td>
</tr>
<tr>
<td>[PrMIM][NTf₂]</td>
<td>1.0</td>
<td>2.6</td>
<td>1.6</td>
<td>GC</td>
<td>Ag/Ag⁺ in DMSO</td>
</tr>
<tr>
<td>[PrDMIM][NTf₂]</td>
<td>-1.9</td>
<td>2.3</td>
<td>4.2</td>
<td>GC</td>
<td>I⁻/I₃⁻</td>
</tr>
<tr>
<td></td>
<td>-0.2</td>
<td>5.0</td>
<td>5.2</td>
<td>GC</td>
<td>Li/Li⁺</td>
</tr>
<tr>
<td>[PrDMIM][C(CF₃SO₂)₃]</td>
<td>0</td>
<td>5.4</td>
<td>5.4</td>
<td>GC</td>
<td>Ag wire</td>
</tr>
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</table>
Table 2.3: Electrochemical stability window of ionic liquids.

<table>
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<tr>
<th></th>
<th>0.7</th>
<th>5.0</th>
<th>4.3</th>
<th>GC</th>
<th>Li/Li⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PrDMIM][PF₆]</td>
<td>0.6</td>
<td>5.0</td>
<td>4.4</td>
<td>GC</td>
<td>Li/Li⁺</td>
</tr>
</tbody>
</table>

**Pyrroloidinium**

| [BMPyr][NTf₂] | -3.0 | 3.0 | 6.0 | Graphite | Ag/Ag⁺ |
| (BMPyr)[NTf₂] | -1.8 | 2.0 | 3.8 | Pt       | Ag/Ag⁺ in DMSO |

**Ammonium**

| [BTMIN][NTf₂] | -2.0 | 2.0 | 4.0 | Carbon | - |
| [PrTMIN][NTf₂] | -3.2 | 2.5 | 5.7 | GC     | Fe/Fe⁺ |

**Pyridinium**

| [BMPy][BF₄] | -1  | 2.4 | 3.4 | Pt       | Ag/AgCl wire |

2.10 Synthesis and purification of Ionic liquids.

There are numerous methods for the synthesis of ionic liquids; examples are alkylation of tertiary amines, reaction of a Lewis acid with a quarternary ammonium salt and anion exchange of ammonium or lithium salt by metathesis reaction

2.10.1 Alkylation reaction

RTILs are prepared by direct quaternisation of the appropriate amines and phosphines. Dialkylimidazolium and alkylpyridium cation-based ionic liquids are easily prepared by alkylation of the commercially available N-methylimidazolium or
pyridine with an alkyl halide to give the corresponding 1-alkyl-3-methylimidazolium or 1-alkylpyridinium halide respectively. Different anions have subsequently been introduced by anion exchange, although due to their non-volatile nature, they cannot be purified by distillation. Purification therefore is usually carried out by dissolving the ionic liquid in acetonitrile or tetrahydrofuran (THF), treating it with activated charcoal for more than 24 hours and finally removing the solvent in vacuo\textsuperscript{51}.

### 2.10.2 Metathesis reaction

Metathesis reaction is commonly used of introducing the anion to the ionic liquid. In general, 1-alkyl-3-methylimidazolium or 1-alkylpyridinium halide or 1-alkylammonium halide ionic liquid is mixed with lithium of sodium salts or acid which containing the anions such as tetrafluoroborate (BF\textsubscript{4})\textsuperscript{−}, bistriflimide (NTf\textsubscript{2})\textsuperscript{−}, trifluoromethanesulfonate (OTf)\textsuperscript{−}, or hexafluorophosphate (PF\textsubscript{6})\textsuperscript{−} in water and organic solvent. The metathesis reaction happen by changing the anions and the ionic liquid can be purified and dried under vacuum.

### 2.11 Applications of ionic liquids in electrochemistry

Due to their wide electrochemical windows and high conductivity, ionic liquids have received much attention in electrochemistry. Generally, the electrochemical study is determined by cyclic voltammetry (CV) three-electrode systems: working electrode (WE), reference electrode (RE) and counter electrode (CE). Glassy carbon (GC) and platinum electrode (Pt) are commonly used as WE. Figure 2.7 show an
example of cyclic voltammogram of [BMIM][PF₆] with different type of working electrode⁵².

Figure 2.8 : Voltammogram of [BMIM][PF₆] at glassy carbon, platinum and gold macro disk as working electrodes. The scan was carried out at 100 mV/s versus Ag wire.

Below are some application of ionic liquids in the field of electrodeposition⁵³,⁵⁴,⁵⁵, electrochemical devices⁵⁶, and electrosynthesis⁵⁷,⁵⁸ that had been reviewed.

2.11.1 Ionic liquids as electrolyte

Electrolytes for electrochemical devices should be resistant to electrochemical reduction and oxidation. Table 2.3 (pages 28-29) lists the electrochemical windows of certain ionic liquids that are usually used in electrochemical applications. The common ionic liquids that usually used as electrolyte are the bistriflimide ionic liquids⁵⁹,⁶⁰. These ionic liquids are favoured due to their moisture-stable property, wide electrochemical window, and high thermal stability⁵⁹. For example, Figure 2.9 shows the cyclic voltammetry of ytterbium(III) bistriflimide in [BMPyr][NTf₂]. It was
suggested that the electrode reactions of Yb(III)/Yb(II) couples at glassy carbon in [BMPyrr][NTf$_2$] are quasi-reversible or irreversible process due to the shielding effect of bistriflimide anion surrounding the redox center.

![Cyclic voltammetry of Yb(NTf$_2$)$_3$ in [BMPyrr][NTf$_2$] at glassy carbon, 10 mVs$^{-1}$.](image)

2.11.2 Electrodeposition

The development of RTILs has attracted researchers to explore the used of ionic liquids in electrodeposition of various metals and alloys, such as aluminium$^{53,54}$, manganese$^{55}$, and titanium$^{61}$. Due to their good features, ionic liquids prove good
quality of deposition because of the high conductivity and low reactivity against moisture\textsuperscript{62}. Figure 2.10 shows an example of electrodeposition of aluminium from aluminium chloride/1-ethyl-3-methylimidazolium chloride (AlCl\textsubscript{3}/[EMIM][Cl])\textsuperscript{63}. In this paper it was reported that mild steel can be coated by electrodeposition with adherent aluminium at room temperature in a first generation AlCl\textsubscript{3}/[EMIM][Cl] (60/40 mol %) ionic liquid. This type of ionic liquid only requires dry air, and aluminium can be employed as a sacrificial anode.

\[\text{Figure 2.10} \] Cyclic voltammetry of Al deposition on mild steel substrate in AlCl\textsubscript{3}/[EMIM][Cl] (60/40 mol %) at room temperature with a scan rate of 10 mV/s.

2.11.3 Electrosynthesis

Due to the good performance of ionic liquids, especially their electrochemical stability, the interest in electrosynthesis in ionic liquids began to flourish. However most of the literature is focused on the synthesis of polymer involve an aqueous, gel,
or polymer electrolyte. Zane et al. (2007) reported the electrosynthesis of poly(o-phenylenediamine) in RTILs (Figure 2.11). Poly(o-phenylenediamine) obtained by volumetric synthesis from ionic liquid electrolyte was a good candidate as substrate for enzyme amperometric biosensors\textsuperscript{56}.

![Cyclic voltammetry during the synthesis of poly(o-phenylenediamine) in RTIL.](image)

**Figure 2.11:** Cyclic voltammetry during the synthesis of poly(o-phenylenediamine) in RTIL.

Other example that might not involve polymer in electrosynthesis was the study reported by Doherty et al. on the electrosynthesis of benzaldehyde in room temperature ionic liquid\textsuperscript{58}. From the study they concluded that the overall electrochemistry is very similar to that found in conventional solvents, which is encouraging since it may indicate that the transition to RTILs may not be too problematic. **Scheme 2.6** was quoted from the literature\textsuperscript{57} on the proposed reaction sequence of benzaldehyde reduction in RTIL.
The reaction shows the conversion of a benzaldehyde (A) to an alcohol or alcholate (D) through several steps involving electron transfer and protonation.

- A benzaldehyde (A) undergoes a reduction to form an intermediate (B) which then undergoes another reduction to form an alcohol or alcholate (C).
- The intermediate (C) reacts with 2H⁺ to form an alcohol or alcholate (D).
- The alcohol or alcholate (D) can react with 2[BmPyr]+ to form another intermediate (E).
- The intermediate (E) can undergo an oxidation to form another intermediate (F) which can then react with 2[BmPyr]+ to form the final product.
**Scheme 2.6**: Proposed reaction sequence for three-electron reduction process. A = Benzaldehyde, B = radical anion, C = dianion species, D = anion-radical anion dimerisation.

### 2.11.4 Electrochemical devices

Rechargeable lithium batteries that employed lithium metal as anode and polymer electrolyte for charge transportation have received much attention as electrochemical devices. For example, Jae-Won et. al. (2007) reported that poly(ethylene oxide)-based polymer electrolyte incorporating RTIL for lithium batteries show good result on the modification of PEO-LiNTf$_2$ with [BMIM][NTf$_2$]. The result showed the increasing of ionic conductivity parallel to the increase in RTIL content. The study achieved faster lithium electrode stabilization, active material utilization of 82 % and stable cycling properties$^{64}$. Beside rechargeable lithium batteries, a lot of application of ionic liquids in electrochemical devices such as sensors, capacitors, solar cells and fuel cells had been reviewed in the literature$^{65}$. 
This chapter is divided into three main components.

3.1 Chemicals

3.2 Analytical Equipments and Theory

3.3 Experimental Methods

3.1 Chemicals

All chemicals used in this project are listed in tables below. The chemicals were used without further purifications, unless otherwise stated.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Formula</th>
<th>Manufacturer</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-tert-butylphenol</td>
<td>C_{10}H_{14}O</td>
<td>Aldrich</td>
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</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>Fisher</td>
<td>98%</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>Sigma-Aldrich</td>
<td>≥ 97.0%</td>
</tr>
<tr>
<td>Phenyl ether</td>
<td>(C_{6}H_{5})_{2}O</td>
<td>Sigma-Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Toluene</td>
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<td>98%</td>
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</tr>
<tr>
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</tr>
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<td>Riedel-de Haën</td>
<td>98%</td>
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<td>sulphate</td>
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</tr>
<tr>
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<td>Sigma-Aldrich</td>
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<td>J.T Baker</td>
<td>98%</td>
</tr>
<tr>
<td>Acetone</td>
<td>CH₃COCH₃</td>
<td>J.T Baker</td>
<td>98%</td>
</tr>
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<td>N-butyl-methyl ammonium hydroxide</td>
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<td>Distilled deionized water</td>
<td>H₂O</td>
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</tbody>
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<table>
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<th>Formula</th>
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<td>Aldrich</td>
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**Table 3.2** Chemicals used in the synthesis of ionic liquids.
3.2 Analytical Equipment and Theory

3.2.1 Nuclear Magnetic Resonance Spectroscopy

Over the past fifty years magnetic resonance spectroscopy, commonly referred to as nuclear magnetic resonance (NMR), has become the pre-eminent technique for determining the structure of organic compounds. Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected. Although larger amounts of sample are needed than for mass spectroscopy, NMR is non-destructive, and with modern instruments good data may be obtained from samples weighing less than a milligram.

NMR is the most powerful technique for molecular characterization. It can provide three dimensional informations on any type of molecule as long as the compound in question possesses NMR active nuclei almost do. In order to understand the NMR characterization technique, it is necessary to understand the physical principles on which the methods were based.

The nuclei of many elemental isotopes have a characteristic spin (I). Some nuclei have integral spin (e.g. I=1, 2, 3…), some have fractional spin (e.g. I= 1/2., 3/2, 5/2…), and few have no spin, I=0 (e.g. $^{12}$C, $^{16}$O, $^{32}$S…). Isotopes of particular interest and use to organic chemists are $^1$H, $^{13}$C, $^{19}$F, and $^{31}$P, all of which have I=1/2. Since...
the analysis of this spin state is fairly straightforward, the next discussion of NMR will be limited to these and other \( I=1/2 \) nuclei.

### 3.2.1.1 Chemical Shift

NMR resonance signals are dependent on external magnetic field strength and frequency. Since no two magnets will have exactly the same field, resonance frequencies will vary accordingly and an alternative method for characterising and specifying the location of NMR signals is needed. Figure 3.1 illustrated examples of eleven different compounds and the resonance signals are distinct and well separated and Figure 3.2 shows proton chemical shift range for sample in deuterated chloroform (CDCl\(_3\)).

**Figure 3.1** Examples of eleven different resonance signals for different compounds.
3.2.2 Electrochemical Study

3.2.2.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the commonly used electrochemical methods as compared with other voltammetry technique, and is based on a linear potential waveform which is the potential change as a linear function of time. The rate of change of potential with time is referred to scan rate. CV is widely used for the study of redox processes, for understanding reaction intermediates, and for obtaining reaction products.

CV is an attractive method for illustrating a number of concepts in electrochemistry. Potentiometric measurement, which has similar technique, might be described as “passive” electrochemical analysis because the voltage of the system simply responds to changes in the concentration of one or more analytes. For example, H⁺ (acid) in the case of pH probes. Electrolysis, cyclic voltammetry,
amperometry and several other techniques might be described as “active”
electrochemical methods because the electron drives an electrochemical reaction
into a circuit and then controlling the reaction by circuit parameters such as voltage.

Figure 3.3 AUTOLAB Potentiostat/Galvanostat (PGSTAT 12/30/302).

CV is a versatile electroanalytical technique for the study of electroactive
species. CV consists of an electrode immersed in an unsterred solution while
measuring the resulting current. Thus, a voltammogram is a display of current versus
potential. The most useful aspect of this technique is an application to the qualitative
diagnosis of electrode reactions. This technique is based on varying the applied
potential at a working electrode in both forward and reverse directions (at some scan
rate) while monitoring the current. For example, the initial scan could be the negative
direction to the switching potential. At that potential the scan would be reversed and
run in the positive direction. Depending on the analysis, one full cycle, a partial cycle,
or a series of cycles can be performed as shown in Figure 3.4 for a reversible redox
system.

The important parameters in a cyclic voltammogram are the peak potentials
\((E_{pc}, E_{pa})\) and peak currents \((i_{pc}, i_{pa})\) of the cathodic and anodic peaks, respectively. If
the electron transfer process is fast compared with other processes (such as
diffusion), the reaction is said to be electrochemically reversible, and the peak separation is

$$\Delta E_p = E_{pa} - E_{pc} = 2.303 \frac{RT}{nF}$$  \hspace{1cm} \text{Equation 3.1}

**Figure 3.4** Reversible cyclic voltammogram using glassy carbon as working electrode and Ag/AgCl as reference electrode.

Thus, for a reversible redox reaction at 25°C with \( n \) electrons \( \Delta E_p \) should be 0.0592/\( n \) V or about 60 mV for one electron. In practice this value is difficult to obtain because of such factors as cell resistance. Irreversibility due to a slow electron
transfer rate results in $\Delta E_p > 0.0592/n$ V, greater than 59.2 mV for a one-electron reaction. The reduction potential ($E^0$) for a reversible couple is given by

$$E^0 = (E_{pc} + E_{pa})/2$$  \[\text{Equation 3.2}\]

For a reversible reaction, the concentration is related to peak current by the Randles-Sevcik expression (at 25°C)

$$I_p = (2.686 \times 10^5) n^{3/2} AD^{1/2} v^{1/2}$$  \[\text{Equation 3.3}\]

Where $I_p$ is the peak current in amps (A), $n$ is the number of electron, $A$ is the electrode area (cm$^2$), $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$), $C^0$ is the concentration in (mol cm$^{-3}$), and $v$ is the scan rate in V s$^{-1}$.

3.2.2.2 Electrochemical cell

![Electrochemical cell diagram](image)

**Figure 3.5** A three-electrode cell set up.

A typical electrochemical cell consists of the sample dissolved in a solvent, an ionic electrolyte, and electrodes. Cell (that is sample holder) comes in a variety of sizes, shapes and materials. The type used depends on the amount and the type of
Sample, the technique, and the analytical data to be obtained. The material of the cell (glass, Teflon) is selected to minimize reaction with the sample. In most cases the reference electrode should be as close as possible to the working electrode; in some cases, to avoid contamination, it may be necessary to place the reference electrode in a separate compartment. In this study, one small glass cell with Teflon cap was designed for the electrochemistry work. This is because the amounts of sample used in this study are ≤ 2 ml. Figure 3.5 illustrates the cell that was used in this study.

Reference Electrode: The reference electrode should provide a reversible half-reaction with Nernstian behavior, be constant over time, and be easy to assemble and maintain. The most commonly used reference electrodes for aqueous solutions are the calomel electrode, with potential determined by the reaction $\text{Hg}_2\text{Cl}_2 (s) + 2 \, \text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$, and the silver/silver chloride electrode (Ag/AgCl) with potential determined by the reaction $\text{AgCl} + \text{e}^- \rightarrow \text{Ag}(s) + \text{Cl}^-$. In this study the saturated calomel electrode (SCE), Ag wire and ionic liquid reference electrode (ILRE) were used. ILRE was made as described in page 57.

Counter Electrode: A counter electrode is used to complete the electrical circuit. In most voltammetric techniques, reactions at the electrode surfaces occur over very short time periods and rarely produce any appreciable changes in reduction and oxidation. Thus, isolation of the counter electrode from the sample is not normally necessary. Most often, the counter electrode is usually made of an inert material such as thin Pt wire, although Au and sometimes graphite have also been used. In this experiment the Pt wire was used as a counter electrode.

Working Electrode: The working electrodes are of various geometries and materials, ranging from small Hg drops to flat Pt disks. Mercury is useful because it displays a
wide negative potential range (because it is difficult to reduce hydrogen ion or water at the mercury surface), its surface is readily regenerated by producing a new drop or film, and many metal ions can be reversibly reduced into it. In this work, glassy carbon electrode or platinum electrode was used as a working electrode.3.3

Experimental Methods

The sodium \( p \)-sulfonatocalix[4]arene and ionic liquids were synthesised using the following methods.

3.3.1 Synthesis of sodium \( p \)-sulfonatocalix[4]arene

There are two common synthetic methods of sodium \( p \)-sulfonatocalix[4]arene which was described in Chapter II (2.5). In this study, the acid-catalysed and base-catalysed one-step promoted syntheses were chosen to synthesise the water-soluble sodium \( p \)-sulfonatocalix[4]arene.

Sodium $p$-sulfonatocalix[4]arene was synthesized using 4-$t$-butylphenol as a starting material. From this starting material, the $p$-tert-butylcalix[4]arene and calix[4]arene were formed as intermediate. Scheme 3.1 shows the route of the synthesis of sodium $p$-sulfonatocalix[4]arene.

3.3.1.1 Synthesis of $p$-tert-butylcalix[4]arene

To 155 ml of formaldehyde, 250 g of 4-$t$-butylphenol, and a mixture of 1.2 g of sodium hydroxide and 3 ml of water were added. The mixture was heated at 120°C under nitrogen gas with continuous stirring. After a few minutes ($\approx$10 minutes), the heterogeneous mixture turned to a homogeneous pale yellow solution. Then, the vapour was allowed to escape through the still head and then trapped by the water. The heat was turned off when the mixture became more viscous, and the stirring was stopped when a thick mass has formed. The reaction mixture was allowed to cool to room temperature.

To the solid mass, 2000 ml of phenol and 100 ml of toluene were added. Under the same conditions before the cooling process, the reaction mixture was reheated at 260°C. The vapour was allowed to escape the reaction mixture until the internal temperature reached 180 - 190°C. The heterogeneous light brown mixture was refluxed for 4 hours until it became a homogeneous and dark brown mixture.
The mixture was cooled to 60°C and 1500 ml ethyl acetate was added to it. The mixture was cooled at room temperature and was left to stir for additional hours. The pale brown crystals were filtered by suction and triturated with 200 ml acetic acid. The suspension was filtered. The crystal was washed with small portion of ethyl acetate (4 x 50 ml) and dissolved back by adding in small portions to 3000 ml of toluene and heated at 100°C in conical flask. The mixture was heated under reflux until complete dissolution had occurs. The solution was allowed to cool down to room temperature and the glistening crystal was separated by suction filtration. After drying, 175 g (55 % yields) of product were obtained as a 1:1 complex with toluene (m.p. 342 - 324°C).

3.3.1.2 Synthesis of calix[4]arene

All glasswares used in this reaction were dried at 120°C for 1 hour in an electric oven. 100 ml of toluene, 1.75 g of phenol and 10 g of \( \rho \)-tert-butylcalix[4]arene, were added to a flask under nitrogen gas and the mixture was stirred for 10 minutes. To the colourless heterogeneous mixture 10 g (75.02 mmol) of aluminium chloride was added at once. The mixture was vigorously stirred until it turned deep red. Within 30 minutes, a viscous deep-red sticky phase separated on the walls of the flask. The reaction was stirred at room temperature for about 2 to 3 hours. The reaction progress was monitored by TLC [hexane/ethyl acetate, (4/1)]. Once the reaction was completed, the reaction mixture was poured into 500 ml beaker containing 200 g of crushed ice. At this step, precaution was taken because of the formation of HCl. The reaction vessel was rinsed with 100 ml dichloromethane and another 100 g of crushed ice. The mixture was stirred with a glass rod and transferred into a separating funnel. Then, the mixture was extracted with 400 ml of
dichloromethane. The funnel was swirled and the organic phase separated was washed three times with HCl (1 M) and twice with water (100 ml). The washed organic phase was then dried in anhydrous sodium sulphate for 30 minutes. The sodium sulphate was filtered and the filtrate was collected in a 500 ml round bottomed flask. The solvent was removed under reduced pressure using a rotary evaporator. 50 ml of diethyl ether was added to the orange oily residue for the precipitation of calix[4]arene. The heterogeneous mixture was left for 1 hour at -15°C. The solid was collected by suction filtration on a Buchner funnel. The pale yellow solid was triturated with 100 ml of diethyl ether. After 1 hour at -15°C the powder was filtered by suction. The white powder of calix[4]arene (m.p. 315-318°C), was ready to be synthesized into sodium p-sulfonatocalix[4]arene.

3.3.1.3 Synthesis of sodium p-sulfonatocalix[4]arene

To 10 ml concentrated sulphuric acid (96 %), 3.0 g calix[4]arene (7.07 mmol) was added. The flask containing the mixture was immersed in an oil bath and heated at 60°C. While heated, the mixture was stirred for 4-5 hours. The flask was cooled in the refrigerator and white precipitate was filtered through the glass frit under vacuum until most of the sulphuric acid has been eliminated. The precipitate was dissolved in water in an Erlenmeyer flask. Barium carbonate (BaCO₃) and water were added slowly until the solution is neutral. When neutralised, the solution was stirred and gently heated. The resulting barium sulphate was filtered off. The first filtration was done through normal filtration. The second filtration was done through slow speed (speed ribbon) filter paper. The precipitate formed was washed carefully
with hot water. The aqueous filtrate was evaporated to dryness under reduced pressure. The residue was taken in water (15 - 20 ml) and the pH was adjusted to pH 8 with Na₂CO₃. The resulting carbonate was filtered off. 40 ml of methanol was added to the solution. The white precipitate was filtered using vacuum filtration. This precipitate consist of 4 - 5 g sodium p-sulfonatocalix[4]arene and impure with carbonate. The product was acidified with HNO₃ (0.1 M) to pH ≈ 3 and the solution was boiled. The solution was neutralised with dilute aqueous solution of NaOH and was left to concentrate under reduced pressure until a precipitate formed. 40 ml methanol was added slowly and after cooling, the purified product was filtered (m.p > 300°C) (45 % yield).

3.3.2 Synthesis of $(N\textsubscript{1444})SO\textsubscript{3}calix[4]arene$

The sodium $p$-sulfonatocalix[4]arene, prepared in 3.3.1.3, was used to prepared $(N\textsubscript{1444})SO\textsubscript{3}calix[4]arene$ as shown in Scheme 3.2.

![Scheme 3.2 Synthesis of $(N\textsubscript{1444})SO\textsubscript{3}calix[4]arene$](attachment:image.png)

3.3.2.1 Synthesis of $HSO\textsubscript{3}calix[4]arene$

A column was filled with 2 g of exchange resin (Dowex® 50WX2 hydrogen form). The resin was washed with 5 cm³ hydrochloric acid (37 wt % in H₂O) in 50 cm³ of
water and further washed with water until neutral (checked by pH paper). Sodium p-sulfonatocalix[4]arene (1 g, 12 mmol) was dissolved in water (100 cm$^3$), and the solution passed through the column. This process was repeated twice. The recovered solution was evaporated to remove the water. The pink solid obtained was dried under vacuum at room temperature for 12 hours. Yield 0.59 g (58.9%). $^1$H-NMR (D$_2$O, 300 MHz) $\delta$: 3.88 (s, 2H, Ar-CH$_2$), 7.43 (s, 2H, Ar).

3.3.2.2 Synthesis of (N$_{1444}$)SO$_3$calix[4]arene

The HSO$_3$calix[4]arene (0.58 g, 0.78 mmol) was dissolved in 5 cm$^3$ of water and neutralised with 4 equivalents of N$_{1444}$OH (t-butylmethylammonium hydroxide) (0.67 cm$^3$, 3.12 mmol). The mixture was stirred for 10 minutes and left in a rotary evaporator to evaporate the H$_2$O. A sticky brown-pink hygroscopic solid was obtained and was further dried in high vacuum. $^1$H-NMR (D$_2$O, 300 MHz) $\delta$: 7.39 (s, 2H, Ar), 3.5 (s, 1H, Ar-CH$_2$-Ar), 4.3 (s, 1H, Ar-CH$_2$-Ar), 3.05 (t, 2H, $^3$J$_{HH}$=8.4 Hz, NCH$_2$), 2.79 (s, 3H, CH$_3$), 1.53 (m, 2H, CH$_2$), 1.21 (m, 2H, CH$_2$), 0.75 (t, 3H, $^3$J$_{HH}$=7.2 Hz, CH$_3$).

3.3.3 Synthesis of ionic liquids

3.3.3.1 Synthesis of [BMIM][Br]

\[
\begin{align*}
\text{H}_3\text{C}-\text{N}-\text{N} & \quad + \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \quad \xrightarrow{\text{Reflux, 60$^\circ$C}} \\
\left(\text{H}_3\text{C}-\text{N}-\text{N}\right)\left(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\right)\text{Br}
\end{align*}
\]
Scheme 3.3 Synthetic route for [BMIM][Br].

To a vigorously stirred solution of 1-methylimidazole (112.4 g, 1.369 mol) in acetonitrile at room temperature, 1-bromobutane (281.4 g, 2.054 mol) was added dropwise. The solution was heated under reflux (at 60°C) for 48 hours, after which it was placed in a freezer for 12 hours. The white solid precipitated was recrystallised from acetonitrile and then repeatedly recrystallised from ethyl acetate to yield a white crystalline solid, which was dried under vacuum to give [BMIM][Br] in 85% yield and characterised by $^1$H-NMR. (CDCl$_3$, 300 MHz) $\delta$: 0.97 (t, 3H, $^3$J$_{HH}$=7.2 Hz, CH$_3$), 1.4 (m, 2H, CH$_2$), 1.7 (m, 2H, CH$_2$), 4.01 (s, 3H, CH$_3$-N), 4.37 (t, 2H, $^3$J$_{HH}$=7.2 Hz, N-CH$_2$), 7.57 (s, 1H, NCCH), 7.45 (s, 1H, NCCH), 10.12 (s, 1H, NCHN).

3.3.3.2 Synthesis of [BMIM][NTf$_2$]

\[
\begin{align*}
\text{Br} & \quad \text{LiNTf}_2 \\
\text{NTf}_2 & \quad \text{LiBr}
\end{align*}
\]
Scheme 3.4 Synthetic route for [BMIM][NTf₂].

[BMIM][Br] that had been prepared previously through the alkylation process was used. [BMIM][Br] [144.3 g, 0.66 mol] and CF₃SO₂NLiSO₂CF₃ [206.7 g, 0.72 mol] were dissolved in ultrapure water separately. The two solutions were mixed and left with continued stirring overnight. The solid was washed once with water and several times with dichloromethane until all the halide had been removed. The solvent was removed in a rotary evaporator and the resulting solution was further dried in high vacuum overnight yielding 200 g (0.48 mol, 65.8 %) of a colourless liquid.

3.3.3.3 Purification of 1-n-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] and 1-n-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][OTf]

[BMIM][OTf] and [BMIM][BF₄] were obtained from Merck and were purified before further use. [BMIM][BF₄] and [BMIM][OTf] were dissolved in dichloromethane. Each solution was passed through a short alumina column. The recovered solutions were left concentrated using a rotary evaporator. Then the ionic liquids were dried under high vacuum for 48 hours.

3.3.4 Synthesis of lanthanide salts

3.3.4.1 Synthesis of gadolinium(III) bistri fluorilimide [Gd(NTf₂)₃]

To 0.15 g (30.3 mmol) of Gd₂(CO₃)₃, 0.52 g (1.84 mmol) of (CF₃SO₂)₂NH was added. The Gd₂CO₃ reacted and carbon dioxide was released. The solution was left in
rotary evaporator to evaporate the H$_2$O. The white solid obtained was dried on high vacuum at 100°C. After drying, the resulting yield was 0.5 g (3.9 mmol, 38.9 \%).

$$\text{Gd}_2(\text{CO}_3)_{3.6}\text{H}_2\text{O} + 6(\text{CF}_3\text{SO}_2)\text{NH} \rightarrow 2 \text{Gd}[\text{N(}\text{CF}_3\text{SO}_2)\text{]_3} + 3\text{CO}_2\uparrow + 9\text{H}_2\text{O}$$

**Scheme 3.5** Chemical equation for the synthesis of Gd(NTf$_2$)$_3$.

### 3.3.4.2 Synthesis of ytterbium(III) bistriflimide [Yb(NTf$_2$)$_3$]

Yb[\text{N(}\text{CF}_3\text{SO}_2)\text{]_3} was prepared by reaction of Yb$_2$O$_3$ with H$_2$O. In a typical reaction, (\text{CF}_3\text{SO}_2)\text{NH} (0.42 g, 0.15 mmol) was added to a suspension of Yb$_2$O$_3$ (0.1 g, 2.54 x 10$^{-2}$ mmol) in H$_2$O with stirring until a clear solution was obtained. The solution was placed in vacuo to remove H$_2$O and any excess (\text{CF}_3\text{SO}_2)\text{NH}. The resulting yield was 0.4 g (1.97 mmol, 40\%).

$$\text{Yb}_2\text{O}_3 + 6(\text{CF}_3\text{SO}_2)\text{NH} \rightarrow 2\text{Yb}[\text{N(}\text{CF}_3\text{SO}_2)\text{]_3} + 3\text{H}_2\text{O}$$

**Scheme 3.6** Chemical equation for the synthesis of Yb(NTf$_2$)$_3$.

### 3.3.5 Synthesis of tetraphenylphosphonium trifluoromethanesulfonate [Ph$_4$P(OTf)]

Tetraphenylphosphonium bromide (2 g, 4.8 mmol) was dissolved in water at 30°C. Lithium trifluoromethanesulfonate (0.75 g, 4.8 mmol) was dissolved in water. Both solutions were mixed and a white solid precipitated. The solid was filtered and washed with hot ultrapure water. The washings were tested with AgNO$_3$ solution to make sure all bromide had been removed. The white solid was dried under high vacuum. The resulting yield was 1.46 g (3.84 mmol, 81\%). $^{19}$F-NMR: (CDCl$_3$, 300
MHz) δ: -79 ppm (s, 3F, CF$_3$S). $^1$H-NMR: (CDCl$_3$, 300 MHz) δ: 7.53-7.87 ppm (m, Ar-P).

\[
\text{Ph}_4\text{PBr} + \text{LiCF}_3\text{SO}_3 \rightarrow \text{Ph}_4\text{P(CF}_3\text{SO}_3) + \text{LiBr}
\]

**Scheme 3.7** Chemical equation for the synthesis of Ph$_4$P(CF$_3$SO$_3$).

### 3.3.6 Electrochemical studies

#### 3.3.6.1 Preparation of [BMIM][NO$_3$]/AgNO$_3$ reference electrode (ILRE)

[BMIM][Br] (3.5 g, 15.9 mmol) was mixed with AgNO$_3$ (2.71 g, 15.9 mmol) and the mixture was dissolved in H$_2$O. The AgBr precipitated was filtered and the filtrate concentrated in a rotary evaporator. The [BMIM][NO$_3$] obtained was dissolved in methanol and left in a freezer overnight. The solution was passed through a thick pad of aluminium oxide by suction filtration to remove residual AgBr. The filtrate was evaporated in a rotary evaporator to remove the methanol, and the ionic liquid obtained dried in high vaccum for 48 hours.

0.01 M reference solution was prepared by adding AgNO$_3$ (2 mg, 1.18 µmol) to [BMIM][NO$_3$] (1.19 g, 5.4 mmol) and stirred for 2 hours.

The glass frit of the reference electrode was immersed in the pure [BMIM][NO$_3$] and the reference electrode body was filled with the same ionic liquid. The electrode was left overnight to make sure all the ionic liquid was absorbed into the tip. When there were no bubbles above the frit, most of the pure [BMIM][NO$_3$] was removed and replaced with the 0.01 M [BMIM][NO$_3$]/AgNO$_3$ solution. The ILRE was then ready to be used.
3.3.6.2 Electrochemical experiment (Part 1)

The following samples were prepared for electrochemical study (Table 3.4). Ionic liquids were used as supporting electrolyte while water was used as solvent. The potential range of ionic liquids is very sensitive to the presence of water. In this study a very minimum amount of water was used to dissolve the supermolecule of p-sulfonatocalix[4]arene. All the samples were deoxygenated by bubbling in nitrogen or argon gas for 5 to 10 min prior to perform or conduct the electrochemical measurements.

The electrochemical measurement was carried out using AUTOLAB POTENTIOSTAT / GALVANOSTAT. In this study the working electrode was glassy carbon 0.071 cm². This working electrode was polished to a mirror with alumina silica 0.3 µm aqueous slurry before being used. Saturated calomel electrode (SCE), Ag wire or ionic liquids reference electrode (ILRE) served as reference electrodes. The auxiliary electrode was Pt wire.

<table>
<thead>
<tr>
<th>p-sulfonatocalix[4]arene</th>
<th>WATER</th>
<th>IONIC LIQUID (ELECTROLYTE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mmol)</td>
<td>(g)</td>
<td>(ml)</td>
</tr>
<tr>
<td>12.0</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>12.0</td>
<td>0.1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.4 Samples for electrochemical study.
3.3.6.3 Electrochemical experiment (Part 2)

All electrochemical experiments were carried out in an AUTOLAB (PGSTAT12/30/302) with a three-electrode cell (Figure 3.1). A glassy carbon disc electrode (diameter: 3 mm) was used as working electrode. Platinum wire was used as the counter electrode. The reference electrode was an IL reference electrode. The glassy carbon working electrode was polished to a mirror with diamond slurry and rinsed with acetone before use. Then, the ionic liquids ([BMIM][BF₄] and [BMIM][OTf]) were scanned at glassy carbon with potential between -3 V and +3 V (versus ILRE) respectively. A stable reproducible voltammogram of the background was obtained for each ionic liquid. The result is shown in Figure 3.6. After the measurement of the background, the working electrode was polished again with diamond slurry and rinsed with acetone before continuing the electrochemical study of (N₁₄₄₄)SO₃calix[4]arene in [BMIM][BF₄]. For this, 0.05 g of (N₁₄₄₄)SO₃calix[4]arene was dissolved in 1.18 g of [BMIM][BF₄]. The mixture was left to stir for 10 minutes. The solution was bubbled with argon gas for 5 minutes.
Figure 3.6 The voltammograms of blank [BMIM][BF₄] (red) and [BMIM][OTf] (blue) at 100 mV/s versus ILRE.
CHAPTER IV

RESULT AND DISCUSSION


S-psc₄ was prepared as described in Chapter 3. Figures 4.1 and 4.2 show the FTIR and ¹H-NMR results of s-psc₄ respectively. The bands observed at 1641, 1593, 1471 and 1449 cm⁻¹ in FTIR spectrum was assigned to the phenyl plane bending vibrations. While the bands appear at 1100, 1052, and 629 cm⁻¹ were assigned to SO₃⁻ peaks¹⁵.

![FTIR spectrum of s-psc₄](image)

**Figure 4.1** FTIR spectrum of s-psc₄

The value of chemical shifts of s-psc₄ at 7.44 and 4.63 ppm in Figure 4.2 were referred to aromatic protons and methylene protons attached to phenyl ring respectively¹⁵. The broad peak observed for 3.92 ppm is due to the conformation¹²,⁶⁷,⁶⁸ of calixarene which had been discussed in Chapter 2.
4.2 Electrochemical behaviour of sodium \( p \)-sulfonatocalix[4]arene (s-psc\(_4\))

The solution of 0.12 M of s-psc\(_4\) was prepared in two different IL/water mixtures as mentioned in Chapter 3. The cyclic voltammogram of a solution containing 0.12 M of s-psc\(_4\) in \([\text{BMIM}][\text{BF}_4]\)/water mixture by using GC as WE and SCE as RE at 100 mV/s is shown in Figure 4.3 (a). There is one oxidation peak observed at 0.84 V and no cathodic peak was detected at the reversed scan. When the scans were repeated for few cycles, the current was decrease to a steady value, zero. This behaviour was expected where the electroactive species undergoing oxidation was depleted in concentration at the electrode surface and indicated that the electrochemical reaction was passivating the working electrode\(^{69}\). Therefore, the surface of working electrode was polished for every single scan. The same
behaviour of s-psc₄ was observed in [BMIM][OTf]/water mixture as one oxidation peak observed at 0.83 V and no cathodic peak detected on reversed scan (Figure 4.3 (b)). Therefore the same explanation was suggested for s-psc₄ in different electrolyte system of [BMIM][OTf]/water.

The oxidation peak observed was attributed to the oxidation on the GC surface ⁶⁹, which is well known and leads to the introduction of oxygen functionality to the surface and often used for the activation of such electrodes prior to electroanalysis. It has been shown that sodium p-sulfonatocalix[4]arene solutions can give rise one oxidation peak corresponding to the phenol ²⁶. Therefore, the peak was assigned to the oxidation of phenolic unit of the calixarene. Such electrochemical oxidation are produced by para coupling of the phenolate radicals generated at the electrode surface leading to the deposition of polyphenol or polyphenylene oxide on the electrode ⁷⁰. Scheme 4.1 shows the proposed electrochemical oxidation reaction of s-psc₄ in ionic liquid/water mixture.
Scheme 4.1: Proposed electrochemical oxidation of s-psc₄ in [BMIM][BF₄]/water and [BMIM][OTf]/water.
4.3 Number of electron \((n)\) and diffusion coefficient \((D)\)

In order to investigate the behaviour of s-psc₄ in IL/water mixture further, the scan rate dependent studies were done. When the potential scan rate ranged from 10 mV/s to 400 mV/s, both anodic peak potential, \(E_p\) and peak current, \(I_p\) are affected by scan rate as shown in Figure 4.3 (a) and (b). As the scan rate increase, the peak currents increase and the potential shifted to more positive potential. According to Nicholson for an irreversible anodic reaction, the relationship between \(E_p\) and \(\nu\) is

\[
E_p = E^* + (RT/\alpha n a F) [0.780 + \ln (D^{1/2}/k^*) + \ln (\alpha n a F \nu / RT)^{1/2}]
\]

Equation 4.1

By plotting \(E_p\) versus \(\ln \nu\) (Figure 4.4 (a) and (b)), the plot show a linear graph for s-psc₄ in both [BMIM][BF₄] and [BMIM][OTf] in water mixture. This behaviour obeys the Nicholson’s equation and confirmed that the electrochemical oxidation of s-psc₄ in ILs/water mixture in this experimental condition is totally irreversible. According to the slope of the straight line of \(E_p\) against \(\ln \nu\) the product of \(\alpha n a\) can be evaluated. Plot \(E_p\) versus \(\ln \nu\) (a) show the slope is \(1.3 \times 10^{-3}\) while (b) show the slope is \(1.1 \times 10^{-3}\). After simplifying the equation, the slope is \(RT/2\alpha n a F\). Therefore, the value of \(\alpha n a\) is 0.99 in [BMIM][BF₄]/water mixture and 1.17 in [BMIM][OTf]/water mixture.
Figure 4.3 At 25°C, the voltammogram of 0.12 M of s-psc₄ in (a) [BMIM][BF₄]/water mixture and (b) [BMIM][OTf]/water mixture at scan rate ranged from 10 mV/s to 400 mV/s, GC versus SCE.
Figure 4.4 At 25°C, the plot of $E_p$ versus $\ln (\nu)$ of 0.12 M of s-psc$_4$ in (a) [BMIM][BF$_4$]/water mixture and (b) [BMIM][OTf]/water mixture.
<table>
<thead>
<tr>
<th>$\nu / \text{Vs}^{-1}$</th>
<th>$\ln \nu$</th>
<th>$I_p / \text{A}$ (x10$^{-4}$)</th>
<th>$E_p / \text{V}$</th>
<th>$I_p / \text{A}$ (x10$^{-4}$)</th>
<th>$E_p / \text{V}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>-0.92</td>
<td>1.66</td>
<td>0.86</td>
<td>1.26</td>
<td>0.84</td>
</tr>
<tr>
<td>0.3</td>
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<td>1.33</td>
<td>0.87</td>
<td>1.10</td>
<td>0.83</td>
</tr>
<tr>
<td>0.2</td>
<td>-1.61</td>
<td>1.13</td>
<td>0.86</td>
<td>1.00</td>
<td>0.83</td>
</tr>
<tr>
<td>0.1</td>
<td>-2.30</td>
<td>-</td>
<td>-</td>
<td>0.74</td>
<td>0.82</td>
</tr>
<tr>
<td>0.5</td>
<td>-3.00</td>
<td>0.66</td>
<td>0.84</td>
<td>0.57</td>
<td>0.81</td>
</tr>
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<td>0.025</td>
<td>-3.69</td>
<td>0.52</td>
<td>0.83</td>
<td>0.44</td>
<td>0.81</td>
</tr>
<tr>
<td>0.01</td>
<td>-4.61</td>
<td>0.37</td>
<td>0.82</td>
<td>0.30</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Table 4.1. Cyclic voltammogram data for the oxidation of s-psc$_4$ at glassy carbon electrode ($A = 0.071$ cm$^2$). (a) 0.12 M of s-psc$_4$ in [BMIM][BF$_4$]/ water mixture (b) 0.12 M of s-psc$_4$ in [BMIM][OTf]/water mixture.
In addition, the peak current $I_p$ for an irreversible electrochemical reaction can be described by the following formula

$$I_p = (2.99 \times 10^5)n(\alpha n_a)^{1/2}AC*_{R,D}^{1/2} \nu^{1/2} \quad \text{Equation 4.2}$$

According to Equation 4.2, at a given concentration of s-psc$_4$, the plot of peak current, $I_p$ versus square root of the scan, $\nu^{1/2}$ should be linear passing through the origin. From the slope of the straight line, the value of $[n(\alpha n_a)^{1/2}AC*_{R,D}^{1/2}]$ can be evaluated (Figures 4.5 (a) and (b)). Linear plots of $I_p$ versus $\nu^{1/2}$ was obtained and the parameter of $[n(\alpha n_a)^{1/2}D^{1/2}]$ was calculated as $9.03 \times 10^{-5}$ cm$^{-1}$ s$^{-1}$ for [BMIM][BF$_4$] and $6.99 \times 10^{-5}$ cm$^{-1}$ s$^{-1}$ for [BMIM][OTf].

The value of $[n(\alpha n_a)^{1/2}D^{1/2}]$ can also be obtained by plotting $I_p$ against the concentration of s-psc$_4$ at a given scan rate. The voltammograms at different concentration are shown in Figure 4.6 (a) and (b). However in this work, the value of $[n(\alpha n_a)^{1/2}D^{1/2}]$ were only calculated from scan rates studies. The voltammograms show that peak current increases with the increasing of concentration. Combining the two parameters of $\alpha n_a$ and $[n(\alpha n_a)^{1/2}D^{1/2}]$, the value of $nD^{1/2}$ can be evaluated as $9.07 \times 10^5$ cm$^{-1}$ s$^{-1/2}$ and $6.46 \times 10^{-5}$ cm$^{-1}$ s$^{-1/2}$ in [BMIM][BF$_4$]/water and [BMIM][OTf]/water respectively.
Figure 4.5 Plot of \( I_p \) versus \( \nu^{1/2} \) for (a) s-psc\(_4\) in [BMIM][BF\(_4\)]/water mixture, (b) s-psc\(_4\) in [BMIM][OTf]/water mixture.
Figure 4.6 Cyclic voltamogram of s-psc\textsubscript{4} in (a) [BMIM][BF\textsubscript{4}]/water mixture (b) [BMIM]OTf/water mixture (0.012 M, 0.12 M and 1.2 M) at 25°C, 100 mV/s, GC versus SCE.
<table>
<thead>
<tr>
<th>$n(\alpha n_a)^{1/2}D^{1/2}$ / cms$^{-1/2}$</th>
<th>$\alpha n_a$</th>
<th>$nD^{1/2}$ / cms$^{-1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x$10^{-5}$)</td>
<td></td>
<td>(x $10^{-5}$)</td>
</tr>
<tr>
<td>s-psc$_4$ in [BMIM][BF$_4$]/water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.03</td>
<td>0.99</td>
<td>9.07</td>
</tr>
<tr>
<td>s-psc$_4$ in [BMIM][OTf]/water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.99</td>
<td>1.17</td>
<td>6.46</td>
</tr>
</tbody>
</table>

**Table 4.2.** Data from the plot of $I/A$ versus $\nu^{1/2} / V^{-1/2}$
To get the value of $n$ and $D$, a steady voltammetry of 0.1 M of $s$-$p$sc$_4$ in [BMIM][BF$_4$]/water and [BMIM][OTf]/water on the same electrode was determined and shown in Figure 4.7 (a) and (b). The limitation diffusion current, $I_l$ is $8.38 \times 10^{-11}$ A and $5.80 \times 10^{-11}$ A respectively. Therefore the value of $nD$ can be calculated as $1.20 \times 10^{-8}$ cm$^2$s$^{-1}$ in [BMIM][BF$_4$]/water mixture and $8.35 \times 10^{-9}$ cm$^2$s$^{-1}$ in [BMIM][OTf]/water mixture by using the following formula;

$$I_1 = 4nFDC^*_r r$$  \hspace{1cm} \text{Equation 4.3}

Combining with the value of $nD^{1/2}$ as described previously, the value of $D$ is calculated as $1.15 \times 10^{-8}$ cm$^2$s$^{-1}$ and $1.67 \times 10^{-8}$ cm$^2$s$^{-1}$ and the value of $n$ is calculated as 0.83 and 0.71 respectively. Taking account the error of calculation, it was assuming that the number of electron transfer for $s$-$p$sc$_4$ in both IL/water mixture is 1. Table 4.3 summarised the data that was evaluated and calculated above. Assuming $n_a$=$n$, therefore the value of $\alpha$ is 0.99 (in [BMIM][BF$_4$]/water) and 1.17 (in [BMIM][OTf]/water).
Figure 4.7 The steady state voltammogram of s-psc₄ in (a) [BMIM][BF₄]/water mixture and (b) [BMIM][OTf]/water on a GC electrode  \( \nu = 5 \text{ mV} \text{s}^{-1} \).
<table>
<thead>
<tr>
<th>$I / A$</th>
<th>$nD / \text{cm}^2\text{s}^{-1}$</th>
<th>$D / \text{cm}^2\text{s}^{-1}$</th>
<th>$n$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x10$^{-11}$)</td>
<td>(x 10$^{-8}$)</td>
<td>(x 10$^{-8}$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**s-psc$_4$ in [BMIM][BF$_4$/water**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8.38</td>
<td>1.20</td>
<td>1.15</td>
<td>0.83 $\approx$ 1</td>
<td>0.99</td>
</tr>
</tbody>
</table>

**s-psc$_4$ in [BMIM][OTf]/water**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5.80</td>
<td>0.84</td>
<td>1.67</td>
<td>0.71 $\approx$ 1</td>
<td>1.17</td>
</tr>
</tbody>
</table>

**Table 4.3.** Steady state voltammogram data and the values of $n$ and $D$
4.4 Temperature dependence

As shown in Figure 4.8 (a) and (b), both peak current and peak potential for the electrochemical reaction of s-$\text{psc}_4$ were affected by temperature. The anodic peak current increased with temperature. The peak potential shifted in negative direction with the temperature increasing, which tells us that it is easier for the oxidation of s-$\text{psc}_4$ at high temperature. This behaviour is due to the viscosity of the ionic liquid. At higher temperature the viscosity of IL will slightly decrease in viscosity$^{42}$. Therefore, it was assumed that the movement of electroactive species of s-$\text{psc}_4$ in the solution easier at higher temperature. Taking account of $n_a$, $\alpha$ as independent of $T$, then according to Nicholson, the peak current, $I_p$ at different temperature should be described as follows;

$$I_p = -0.04985nFAG(\alpha n_a F/RT)^{1/2}C^*_0D^{1/2}v^{1/2}$$  \text{Equation 4.4}

From Equation 4.4, the diffusion coefficient, $D$ for different temperature can be calculated and the relationship between $D$ and temperature is

$$\log D = -E_d/(2.303 RT) + \log D_0$$  \text{Equation 4.5}
$E_d$ is the active energy of diffusion of s-psc$_4$. By plotting $\log D$ over $1/T$ (Figure 4.9) the active energy diffusion of s-psc$_4$ can be evaluated as 18.41 kJ mol$^{-1}$ in [BMIM][BF$_4$]/water and 17.97 kJ mol$^{-1}$ in [BMIM][OTf]/water.

By comparing the value of activation energy with reported in the literature$^{26,27,28}$, 29.00 kJ mol$^{-1}$ and 18.80 kJ mol$^{-1}$ which is in different solvent, it can be concluded that, in ionic liquid/water mixture, the activation energy of s-psc$_4$ are much lower then in other solvents. Guowang Diao reported that, the diffusion of calixarene in organic solvent is much easier then in aqueous solution$^{26}$, however, the study in ionic liquid/water mixture show that it is much difficult to diffuse in ionic liquid due to the viscosity of the ionic liquid although in the presence of water.
Figure 4.8 Cyclic voltammograms of s-psc$_4$ in (a) 0.12 M [BMIM][BF$_4$]/water mixture (b) 0.12 M [BMIM][OTf]/water mixture up to 60°C, 100 mV/s, GC versus SCE.
Figure 4.9. Plot log $D$ versus $1/T (K^{-1})$ (a) 0.12 M [BMIM][BF$_4$]/water mixture

(b) 0.12 M [BMIM][OTf]/water mixture
0.12 M s-$\text{psc}_4$ in [BMIM][OTf]/water mixture

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<th>T / K</th>
<th>1 / T</th>
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<th>$\nu^{1/2}$ / V$^{-1/2}$s</th>
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0.12 M s-$\text{psc}_4$ in [BMIM][BF$_4$]/water mixture

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<th>T / K</th>
<th>1 / T</th>
<th>$\nu$ / Vs$^{-1}$</th>
<th>$\nu^{1/2}$ / V$^{-1/2}$s</th>
<th>$I / A$ (10$^{-5}$)</th>
<th>$D / \text{cm}^2\text{s}^{-1}$ (10$^{-7}$)</th>
<th>log D</th>
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**Table 4.4** Data for temperature dependence studies
CHAPTER IV

RESULTS AND DISCUSSION

Part 2: Characterization and electrochemical study of \((\text{N}_{1444})\text{SO}_3\text{calix}[4]\text{arene}\) in pure ILs
4.5 Characterization of (N$_{1444}$)SO$_3$calix[4]arene

Chapter 4 (Part 1) discussed the electrochemical behaviour of s-psc$_4$ in [BMIM][BF$_4$]/water and [BMIM][OTf]/water. The studies showed that s-psc$_4$ cannot be dissolved directly in neither [BMIM][BF$_4$] nor [BMIM][OTf], therefore water has to be used as a solvent or co-solvent to dissolve it for electrochemical studies. In order to dissolve s-psc$_4$ in pure ionic liquids, new calixarene had been synthesised by modification of s-psc$_4$. Initially, the synthesis of s-psc$_4$ ionic liquid was attempted by metathesis reaction between [BMIM][Br] and s-psc$_4$ to replace Na$^+$ with [BMIM]$^+$. However, the NaBr didn’t precipitate from the reaction mixture. Therefore the modification of calixarene had been done by replacing Na$^+$ with N$_{1444}^+$. In the first instance, the acid derivative was prepared (see Scheme 3.2 Chapter 3).

The HSO$_3$-calix[4]arene was prepared from the sodium salt using a hydrogen-exchange resin and the product characterised by $^1$H-NMR spectroscopy (Figure 4.10) which was consistent with that previously published $^2$. The spectrum in D$_2$O contained one singlet at 4.12 ppm corresponding to the methylene group and one singlet at 7.68 ppm for the aromatic protons.

When the HSO$_3$-calix[4]arene was reacted with 4 equivalents of N$_{1444}$OH in water, the pH of the resulting solution was tested and remained acidic. It is believed that this may be due to excess acid incorporated into the product from the exchange resin. To fully neutralised the HSO$_3$-calix[4]arene solution, N$_{1444}$OH was added drop wise. Upon addition of total 18 equivalents of N$_{1444}$OH the pH was neutral. However, the $^1$H-NMR spectrum of (N$_{1444}$)SO$_3$calix[4]arene showed that the integration between N$_{1444}^+$ and [SO$_3$calix[4]arene]$^-$ was 17:1. This might be due to the purity of
ammonium hydroxide used and the concentration of the sample. Besides, the amount of water in HSO₃-calix[4]arene could also influence the (N₁₄₄₄)SO₃-calix[4]arene preparation. Generally, s-psc₄ crystallizes with water. Although it was difficult to determine the exact amount in our case, but it was estimated to be 22.4 molecules of water from the ¹H-NMR of two solutions with different concentration.

![Figure 4.10](image)

**Figure 4.10** ¹H-NMR spectrum of HSO₃-calix[4]arene. ¹H NMR (D₂O, 300 MHz) δ:

- 4.12 (s, 2H, Ar-CH₂), 7.68 (s, 2H, Ar-SO₃H).

Other preparations of (N₁₄₄₄)SO₃-calix[4]arene were tried following similar procedures, but samples with different ¹H-NMR spectra were obtained in each case. In addition to various N₁₄₄₄⁺:[SO₃-calix[4]arene]⁻ ratios, the spectra also showed general shifting of the signals and/or splitting of the methylene singlet. Also, not all new samples dissolved in ILs. Only with the excess of N₁₄₄₄OH added to HSO₃⁻
calix[4]arene (N\textsubscript{1444}:SO\textsubscript{3}calix[4]arene\textsuperscript{-}) is 8:1, showed in Figure 4.11, the (N\textsubscript{1444})SO\textsubscript{3}calix[4]arene can be dissolved in ILs. Therefore this (N\textsubscript{1444})SO\textsubscript{3}calix[4]arene was used for electrochemical study in pure [BMIM][BF\textsubscript{4}]. The methylene protons appeared as two broad doublets, indicating that a “cone” conformation is favoured in solution.

In order to monitor the reaction progress, the step-wise addition of N\textsubscript{1444}OH to HSO\textsubscript{3}-calix[4]arene was done. The samples were prepared and send for \textsuperscript{1}H-NMR analysis. 0.36 mol/dm\textsuperscript{3} of HSO\textsubscript{3}-calix[4]arene in D\textsubscript{2}O and N\textsubscript{1444}OH was added (50 µL

**Figure 4.11** \textsuperscript{1}H-NMR spectrum of (N\textsubscript{1444})SO\textsubscript{3}calix[4]arene with excess of N\textsubscript{1444}OH.

\textsuperscript{1}H-NMR (D\textsubscript{2}O, 300 MHz) \(\delta\): 7.39 (s, 2H, Ar-N), 3.5 (d, 1H, Ar-CH\textsubscript{2}-Ar), 4.3 (d, 1H, Ar-CH\textsubscript{2}-Ar), 3.05 (m, 2H, \(^{3}\text{J}_{\text{HH}} = 8.4\) Hz, NCH\textsubscript{2}), 2.79 (s, 3H, CH\textsubscript{3}), 1.53 (m, 2H, CH\textsubscript{2}), 1.21 (m, 2H, CH\textsubscript{2}), 0.75 (t, 3H, \(^{3}\text{J}_{\text{HH}} = 7.2\) Hz, CH\textsubscript{3}).
each time until a total of 300 µL. The $^1$H-NMR of the product after addition of the first 50 µL (Figure 4.12 (a)) showed the signals corresponding to the N$_{1444}$ cation between -0.5 to 3.5 ppm, together with those for the [SO$_3$calix[4]arene]$^-$ fragment (two singlets) at 7.68 ppm and 4.12 ppm for the aromatic and methylene protons, respectively. The integration showed the ratio of 0.3:1 for the N$_{1444}^+:$[SO$_3$calix[4]arene]. This integration ratio indicated that the reaction between HSO$_3$-calix[4]arene and N$_{1444}$OH was not yet completed.

Therefore excess amount of N$_{1444}$OH (300 µL) was added to the same solution and characterised by $^1$H-NMR until the integration ratio between N$_{1444}$ cation and SO$_3$-calix[4]arene show the 1:1 ratio (Figure 4.12 (c)).

However, the peak that was assigned for the methylene hydrogen started to split into 2 different peaks when the ratio between N$_{1444}$ cation and SO$_3$-calix[4]arene was 0.62:1 (Figure 4.12 (b)). When the correct integration of (N$_{1444}$)SO$_3$calix[4]arene was recorded, the peak at 3.4 ppm was observed to split into a pair of doublets which were at 3.4 and 3.8 ppm respectively. This splitting is due to the changing conformation of the SO$_3$-calix[4]arene ring $^{2,3}$.

The methylene hydrogen observed as single broad peak in the $^1$H-NMR (Figure 4.12 (a)) is due to the mobility of SO$_3$-calix[4]arene ions in solution. There is a single peak observed for the methylene hydrogens because the protons are in the same environment. Therefore, the (N$_{1444}$)SO$_3$calix[4]arene can be assigned as 1,3-alternate conformation. However after adding excess amount of N$_{1444}$OH to the acidic calix[4]arene, the N$_{1444}^+$ might go into the cavity of calixarene and fix the conformation as cone type. The protons at the methylene bridge will be in the
different environments and therefore observed as a pair of doublets in the $^1$H-NMR spectrum (Figure 4.12 (c)).

Figure 4.12 $^1$H-NMR spectra of (N$_{1444}$)SO$_3$calix[4]arene. (a) 50 µL of N$_{1444}$OH added, (b) 200 µL of N$_{1444}$OH added, (c) 300 µL of N$_{1444}$OH added.
4.6 Characterization of Ph₄P(OTf)

Tetraphenylphosphonium trifluoromethanesulfonate was characterized by \(^1\)H-NMR and \(^{19}\)F-NMR spectroscopy (Figure 4.13). In the \(^1\)H-NMR, the aromatic protons of Ph₄P⁺ appear at 7.5-8.0 ppm, as in the precursor, Ph₄PBr. The presence of fluorine in the sample is shown by a singlet at -79 ppm in its \(^{19}\)F-NMR spectrum, corresponding to fluorine in trifluoromethanesulfonate. The absence of halide was confirmed by addition of AgNO₃ to a solution of the compound (i.e no precipitate of AgBr formed).

\[
\text{Ph}_4\text{PBr} + \text{LiCF}_3\text{SO}_3 \rightarrow \text{Ph}_4\text{P(CF}_3\text{SO}_3) + \text{LiBr}
\]


Figure 4.13 \(^1\)H-NMR and \(^{19}\)F-NMR for Ph₄P(OTf). (a) \(^{19}\)F-NMR: (CDCl₃, 300 MHz) \(\delta\): -79 ppm (s, 3F, CF₃S). (b) \(^1\)H-NMR: (CDCl₃, 300 MHz) \(\delta\): 7.53-7.87 ppm (m, Ar-P). 1.50 ppm (H₂O), 0.05 ppm (vacuum grease impurities from the flask), 0.00 ppm (TMS from CDCl₃).
4.7 Electrochemical study of the \((N_{1444})SO_3calix[4]arene\) in ionic liquid

The voltammogram of \((N_{1444})SO_3calix[4]arene\) in \([BMIM][BF_4]\) at 100 mV/s (GC) is shown in Figure 4.14. Two peaks were observed at +0.50 V and +1.25 V when the potential was scanned from -0.5 V to +2.0 V versus ILRE. Both oxidation processes are irreversible as no cathodic peaks were detected at the reversed scan. This contrasts with that observed for the s-psc_4 in IL/water mixtures, for which only one irreversible peak at 0.88 V versus SCE was observed. It has been shown that phenol solutions in ILs can give rise to two irreversible oxidation peaks corresponding to the oxidation of phenolate and phenol\(^7\). Peaks I and II (Figure 4.14) are therefore assigned to the oxidation of phenolate and phenol groups of the \((N_{1444})SO_3calix[4]arene\), respectively. Factors that may influence the electrochemical behaviour of this sample are the parameters that were used such as the electrode and the electrolyte. In this work, glassy carbon was used as working electrode which is known as inert electrode. Furthermore, pure ionic liquid was used as electrolyte. The ionic liquid which contained anion and cation will behave differently from other solvents\(^7\). This behaviour also reported in the literature\(^7\) where in organic solvent only the oxidation of phenolate can be observed at +0.45 V for hindered phenol. However in ionic liquid the hindered phenol showed two oxidation processes which are assigned as the oxidation of phenol (+1.89 V) and phenolate (+0.45 V)\(^7\). The behaviour possibly due to the different diffusion coefficient and number of electron involve in the electrochemical reaction.
Figure 4.14 The cyclic voltammogram of (N\(_{1444}\))SO\(_3\)calix[4]arene (0.06 M) in [BMIM][BF\(_4\)] at 100 mV/s versus ILRE, GC.

Ionic liquid was the only source of protons in this system therefore given the equilibrium constant related to the reaction below.

\[
\text{OH} \quad \text{N}_{1444}\text{SO}_{3}^{-} \quad 4 \quad \text{IL} \quad \text{O}^{-} \quad \text{N}_{1444}\text{SO}_{3}^{-} \quad 4 \quad [\text{ILH}]^{+}
\]

Scheme 4.3. The reaction of (N\(_{1444}\))SO\(_3\)calix[4]arene with ionic liquid
IL = [BMIM][BF₄].

4.8 The electrochemistry of (N₁₄₄₄)SO₃calix[4]arene with phosphonium and lanthanide ions

Previous study⁹ showed that the combination of s-psc₄ with phosphonium and lanthanide ions produced single crystal structure. Therefore, this work was carried out to study the electrochemical behaviour of calixarene in the presence of phosphonium and lanthanide ions. As described in Chapter 4 (Part 1), s-psc₄ was insoluble in either [BMIM][BF₄] nor [BMIM][OTf], therefore, (N₁₄₄₄)SO₃calix[4]arene was used for this studies.

The electrochemical studies of Ph₄P(OTf) in [BMIM][BF₄] and lanthanide salts in [BMIM][BF₄] were studied first in the absence of calixarene. As expected, there was no electrochemical reaction for phosphonium in [BMIM][BF₄] (Figure 4.15).
Figure 4.15 Cyclic voltammogram of Ph₄P(OTf) in [BMIM][BF₄] (0.06 M) at GC versus ILRE, 100 mV/s.

According to the literature¹⁰, the lanthanide salts of Eu(NTf₂)₃, Sm(NTf₂)₃, and Yb(NTf₂)₃ show quasi-reversible reductions in [BMPyrr][NTf₂] and [EMIM][NTf₂]¹⁰. However, different behaviour was observed for Gd(NTf₂)₃ in [BMIM][BF₄], as shown in Figure 4.16. The cyclic voltammogram shows two irreversible cathodic peaks at -1.5 V and -2.25 V versus ILRE, which are ascribed to the successive reduction of Gd(III) to Gd(II) and Gd(I). This behaviour is due to the stabilization of different species in solution when a different ionic liquid is used.

Figure 4.16 Cyclic voltammogram of Gd(NTf₂)₃ in [BMIM][BF₄] (0.2 M) at GC versus ILRE, 100 mV/s.
Figure 4.17(a) shows the cyclic voltammogram of (N_{1444})SO_3calix[4]arene in [BMIM][BF_4] in the absence (red) and presence (blue) of Ph_4P(OTf). No significant changes are observed. In contrast, the cyclic voltammogram of s-psc_4 in ionic liquid/water mixture in the present of phosphonium shifted to the positive potential Figure 4.17(b). This behaviour indicated that the phosphonium does not interact with (N_{1444})SO_3calix[4]arene at all. The excess of N_{1444}^+ and/or the cation of ionic liquid might go into the cavity and the bulky molecule of ionic liquid protected the calixarene from interacting with the phosphonium. On the other hand, the electrochemical behaviour of (N_{1444})SO_3calix[4]arene in the presence of both phosphonium and lanthanide cations could not be studied because all of them could not be dissolved in the same IL even after heating at 50°C. This is probably due to the ionic liquid bulky ion is partially occupying the cavity of the calixarene. Therefore phosphonium and lanthanide cation cannot both interact with (N_{1444})SO_3calix[4]arene.

**Figure 4.17** Cyclic voltammogram of (N_{1444})SO_3calix[4]arene in [BMIM][BF_4] in the absence (red) and presence (blue) of Ph_4P(OTf) in [BMIM][BF_4] at 100 mV/s versus ILRE, GC.
CHAPTER V

CONCLUSIONS
The electrochemical behaviour of s-psc$_4$ in [BMIM][BF$_4$] and [BMIM][OTf] can be observed by adding minimum amount of water to the mixtures. This solubility behaviour were due to the viscosity of the ionic liquid and the s-psc$_4$ which containing the sodium ion.

In the presence of water in ionic liquid electrolyte, the s-psc$_4$ shows irreversible oxidation peak for [BMIM][BF$_4$]/water and [BMIM][OTf]/water systems. The pathway of oxidation of s-psc$_4$ have been discussed which proceed via a common one-electron intermediate of phenol. Temperature dependence study was carried out and the activation energy for different systems are 18.18 kJ mol$^{-1}$ and 18.78 kJ mol$^{-1}$ respectively.

In order to look at the electrochemical behaviour of calixarene in pure ionic liquid, the modification of calixarene had been done by replacing Na$^+$ with N$_{1444}^+$. The (N$_{1444}$)SO$_3$calix[4]arene obtained were dissolved completely in pure ionic liquids. The cyclic voltammogram shows two peaks that are assigned for two consecutives oxidation of phenol and phenolate. The proposed mechanism for (N$_{1444}$)SO$_3$calix[4]arene is shown in Scheme 5.1. The study of (N$_{1444}$)SO$_3$calix[4]arene in the presence of phosphonium and lanthanide could not be done since all of them did not dissolved in the same ionic liquid even after heating up to 50°C.

The following table summarises the electrochemical result that had been investigated throughout this study.
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<th>Sample</th>
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<th>No of electron, $n$</th>
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**Table 5.1** Results from Part 1.

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<td>phenolate</td>
</tr>
<tr>
<td></td>
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<td>phenol</td>
</tr>
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</table>

**Table 5.2** Result from Part 2.
Scheme 5.1 Proposed mechanism of the electrochemical study of $(N_{1444})SO_3$calix[4]arene with pure [BMIM][BF$_4$].
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