Adsorption, thermodynamic and quantum chemical studies of some ionic liquids as corrosion inhibitors for mild steel in HCl

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in the

Department of Chemistry

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DECLARATION

I declare that this project which is submitted in fulfillment of the requirements for the degree of Master of Science in Chemistry (M.Sc) at North West University, Mafikeng Campus has not been previously submitted for a degree at this university or any other university. The following research was compiled, collated and written by me. All the quotations are indicated by appropriate punctuation marks. Sources of my information are acknowledged in the reference pages.

........................................
Motsie Elija Mashuga
This work is dedicated to Deeper Life Ministries International and Transformation Miracle Centre under the leadership of Pastor Regina Naryho.
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Bless the Lord all my soul and all that is within me bless His holy name, to the Lord Jesus Christ, I am highly grateful. I acknowledge Him for the strength and grace given to push this project, it is truly not by my power and might but by His Spirit.

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To the Chemistry Department of North-West University (Mafikeng campus), I would like to say thank you.
The corrosion inhibition of mild steel in 1.0 M HCl solution by some ionic liquids namely 1-hexyl-3-methylimidazolium trifluoromethanesulfonate [HMIM][TfO], 1-hexyl-3-methylimidazolium tetrafluoroborate [HMIM][BF₄], 1-hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF₆], and 1-hexyl-3-methylimidazolium iodide [HMIM][I] was investigated using electrochemical measurements (potentiodynamic polarization and electrochemical impedance spectroscopy) and quantum chemical calculations. All the ionic liquids showed appreciably high inhibition efficiency. The results of the electrochemical technique agreed with the quantum chemical calculation for some of the ionic liquids. At 303K, the polarization measurements indicated that all the ionic liquids studied are mixed-type inhibitors. The adsorption studies showed that [HMIM][TfO], [HMIM][BF₄] and [HMIM][I] obeyed the Langmuir adsorption isotherm whereas [HMIM][PF₆] obeyed the Temkin adsorption isotherm. Infra-red (IR) and Ultraviolet visible (UV-vis) spectroscopic studies were carried out to support the results obtained. Thermodynamic parameter such as change in free energy ($\Delta G^\circ$) has been calculated.
LIST OF ABBREVIATIONS

MS
IlS
PPM
DS
GS
HCl
MIC
IE
SCC
MIC
RTIL
HMIM][I]
HMIM][TfO]
HMIM][PF₆]
HMIM][BF₄]
CorriSA
NACE
HIC
VPI
VCI
RTIL
BMIM][Br

Mild Steel
Ionic Liquids
Parts Per Million
Designer Solvents
Green Solvents
Hydrochloric Acid
Microbial Corrosion
Inhibition Efficiency
Stress Corrosion Cracking
Microbial corrosion
Room Temperature Ionic Liquids
1-Hexyl-3-methylimidazolium iodide
1-Hexyl-3-methylimidazolium trifluoromethanesulfonate
1-Hexyl-3-methylimidazolium hexafluorophosphate
1-Hexyl-2-methylimidazolium tetrafluoroborate
Corrosion Institute of Southern Africa
National Association of Corrosion Engineers
Hydrogen-induced cracking
Vapour Phase Inhibitors
Volatile Corrosion Inhibitors
Room Temperature Ionic Liquids
1-butyl-3-methylimidazolium bromide
ZCP  Zero Charge Potential
BMIC  1-butyl-3-methylimidazolium chloride
[BM1]HSO₄  1-butyl-3-methylimidazolium hydrogen sulphate
SEM  Scanning Electron Microscopy
EDX  Energy-dispersive X-ray
XRD  X-ray Diffraction
UV  Ultraviolet Spectrometry
PCE  Platinum Counter Electrode
SCE  Saturated Calomel Electrode
WE  Working Electrode
PDP  Potentiodynamic Polarization
EIS  Electrochemical Impedance Spectroscopy
HOMO  Highest Occupied Molecular Orbital
LUMO  Lowest Unoccupied Molecular Orbital
EA  Electron Affinity
IP  Ionization Potential
ΔE  Energy Gap
DFT  Density Functional Theory
B3LYP  The Becke's Three Parameter Hybrid Functional using the Lee-Yang-Parr Correlation Functional Theory
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CHAPTER 1

INTRODUCTION

1.1 HISTORICAL BACKGROUND

Corrosion has been around for very long time as recorded in ancient books such as the bible, and its 2000 years ago since corrosion was mentioned in scripture [Matthew 6v19]. Interestingly, in that particular scripture, the negative effects of corrosion are stated using the term “corrupting” or in other translations “destroying”, which goes to show that corrosion has being a problem ever so long not starting now. Corrosion is not particularly a phenomenon that only takes place in metals such as steel and zinc, but it also takes place on ceramics, plastics and other non-metal materials, but in such cases it is often referred to as degradation than corrosion. Several papers published in 1800s had alluded to the fact that corrosion was electrochemical in nature, it was the classic 1903 paper by Whitney that persuaded others that corrosion was indeed an electrochemical process [1]. During the first two decades of the twentieth century, significant work was done on electrolytic corrosion and reported at the Transactions of The American Electrochemical Society which awarded $100 to A.T Lincoln for his research on the electrolytic corrosion of brass [1]. In 1788 way before the Transactions of The American Electrochemical Society, Austin observed that when neutral water acts on iron it becomes alkaline, in which in 1829, Hall established that iron does not rust in the absence of oxygen [2].

During the 1960s, significant advances were made in understanding the growth, properties and breakdown of passive films, this era also saw the emergence of new electrochemical and non-electrochemical techniques for the study of corrosion reactions and corrosion products, a trend that greatly accelerated during the 1970s and has continued to the present day [1]. Corrosion goes without saying of how much a problem it has been and still is in impacting negatively humans and the economy.
1.1.1 DEFINITION OF CORROSION

Corrosion is the deterioration of materials as a result of reaction with its environment [3] or the interaction between a metal (generally) and its environment (and it is generally detrimental). Therefore corrosion concerns metals (generally), the environment (always) and it is detrimental (generally) to the metal. The process of corrosion of metal (e.g. iron) starts first by the iron being oxidized to ferrous (Fe\(^{2+}\)), followed by the oxidation of ferrous ions to form ferric ions (Fe\(^{3+}\)), then the reduction of oxygen, then lastly the reaction between ferrous (Fe\(^{2+}\)) and oxygen (O\(_2\)) resulting in the production of ferric oxide (rust) (2Fe\(_2\)O\(_3\)XH\(_2\)O\(_6\)). This metal oxide (rust) is the damage that is of serious concern to most industries all over the world. Corrosion is not only limited to metals, it can also take place on other materials such as polymers and ceramics. Nevertheless, in polymers it is more often than none explained as degradation than corrosion although the process is similar. Amongst many metals, corrosion is experienced strongly in iron and steel. This is because the oxide that is formed during the process of oxidation does not hold firmly to the surface of the metal, as a result it moves off the metal easily. In the case of aluminum metal, an oxide coating that aluminum forms assist in bringing the oxide to bond strongly to the surface of the metal thereby slowing down the corrosion (or stop further exposure to oxygen) [4]. Below is a diagram of the process of iron corrosion courtesy of Total Materia Corrosion protection of Steel.

\[
\begin{align*}
Fe &\rightarrow Fe^{2+} + 2e^- \\
O_2 + 4e^- + 2H_2O &\rightarrow 4OH \\
Fe^{2+} + 2OH^- &\rightarrow Fe(OH)_2 \\
4Fe(OH)_2 + O_2 &\rightarrow 2Fe_2O_3 + 4H_2O \\
Fe_2O_3 \cdot nH_2O (rust) &
\end{align*}
\]

\[
\begin{align*}
Fe (iron metal) &
\end{align*}
\]

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\end{align*}
\]

\[
\begin{align*}
Fe (iron metal) &
\end{align*}
\]

**Figure 1.1:** Process of iron corrosion

1.1.2 COST OF CORROSION

The cost of corrosion can either be directly or indirectly. Direct costs involve the replacements of the affected parts and the upkeep of the operations. While in the indirect costs, problems such as the downtime (the whole plant down), loss of product due to leak, contamination of product, loss
of efficiency can be encountered [5]. In South Africa, the direct cost of corrosion to the economy is R154 billion per annum according to the reports by Corrosion Institute of Southern Africa (CorriSA). Seeing how much of a problem and cost-full corrosion is, immediate action must be taken as to reduce this problem. In funerals and other events, there is a constant use of what is called cast iron three legged pots (3 foot cooking pots); these pots are used for cooking for many people as they are large enough to cook for many people and do not require electricity to do so but open fire, thus they cut costs, mostly in South Africa. These pots are used in high temperatures (open fire) resulting in high vapor, since they are made of mostly iron among other metals, the film painted (seasoning) on the walls of the pot in and out, including the cover as an anti-rust agent comes off in the long run resulting in rusting(corrosion) of the iron. These pots are too expensive to be disposed when rusted, thus they are still used, when trying to get rid of the rust, cooking oil is applied on the rusted portion, then placed in direct fire for some time, then immediately scraped using steel wool while hot, this is a very cumbersome process which puts one at risk of a serious burn. One can immediately see the cost and danger of corrosion in these two instances among many others. Corrosion knows no nationality or personality, it affects us all. So it is clear that the corrosion problem is not an individual problem but rather a collective problem.

The effect of corrosion is experienced by all countries in the world and this effect comes in the form of one or more of the ways given below;

- The economy of the world or individual country has its part in corrosion control. Industries such as oil, petrol and chemical industries make use of metallic pipes and containers in which if corroded will cause a lot of money to repair or replace in turn affecting the economy because it can go as far as loss of jobs.

- Health and safety of the population because metal objects are commonly used by humans for making life much easy, objects such as cups and plates for eating, to machinery such as washing machines and dish washers, to housing as there are a lot of people living in shacks. Corroded cups and plates may contaminate its contents, which may cause health related problems [6], also getting a cut from corroded zinc, steel or iron may pose a serious health related problems.

- Toxicity of the resources.

- Polluted environment due to corroded materials.

- Loss of mechanical properties by substances due to corrosion.

- A technological effect, e.g. metal plays a very huge rule in devices like electrical power stations, network poles and street light poles. In which if attacked by corrosion and damage will lead to negative technological effects.
1.1.3 TYPES OF CORROSION

There are many different types of corrosion that are known today [6]. Some of which are briefly described below:

**Uniform corrosion:** which is also known as general corrosion since the corrosion is caused by direct chemical attacks on the substance.

**Galvanic corrosion:** when two different metals are placed in contact under electrochemical action.

**Concentration cell corrosion:** when two metals or more are allowed to come into contact with different concentration of the same solution.

**Pitting corrosion:** this type of corrosion takes place as microscopic defects on a metal surface.

**Crevice corrosion:** also known as contact corrosion. It takes place right at the point of contact of the metal with the other metal or a metal with a non-metal.

**Filiform corrosion:** this type of corrosion takes place on substances that are painted. When moisture finds its way in the coating of the surface that is painted, the result is likely to be a filiform corrosion.

**Intergranular corrosion:** the grain boundaries of a substance are attacked perhaps by a strong acid.

**Stress corrosion cracking:** this type of corrosion is also commonly abbreviated as SCC. The simultaneous effects of stress and the environment cause SCC.

**Corrosion fatigue:** when the effects of cyclic stress and corrosion are combined the likely product is corrosion fatigue.

**Erosion corrosion:** the harsh chemical environment combined with high fluid surface speeds lead to a corrosion known as erosion corrosion.

**Dealloying:** although this type of corrosion is not commonly encountered, it remains problematic. This process occurs when the alloy losses its atomic component of the metal and retains its corrosion resistance component on the metal surface.

**Hydrogen damage:** this type of corrosion is mostly experienced in high-strength steels.

**Corrosion in concrete:** self-explanatory type of corrosion. In the concrete material, there is a carbon steel among the components therein. While the steel is a very crucial component of the
concrete for the strength purposes of the building, it is also important to note that steel is capable of undergoing corrosion.

**Refinery corrosion:** this is the type of corrosion that results from the equipment surface that has been attacked by the strong acid.

**Microbial corrosion,** also abbreviated as MIC is caused by the activities of microbes.

All these types of corrosion can be prevented in one way or the other using techniques such as coating, cathodic protection, anodic protection and corrosion inhibitors among other preventive techniques [7]. These are some pictures showing some of the types of corrosions already mentioned above courtesy of Corrosion Technology Laboratory (http://www.nstcenter.biz/writeup)

![Figure 1.2: Concentration corrosion](image1)

![Figure 1.3: Microbial corrosion](image2)

![Figure 1.4: Uniform corrosion](image3)
1.1.4 RATE OF CORROSION

Corrosion rate is the speed at which it takes for corrosion to occur. On metals, a passive film must provide a protective barrier that keeps the effects of corrosion on a metal low enough value so that the extent of corrosion damage is minimized. An effective film is one that resists the breaching (called the breakdown) of the passive film. Breakdown processes lead to the forms of localized corrosion that are some of the major sources of corrosion failures, pitting, crevice, intergranular and stress corrosion are some of the examples of this localized corrosion. They cause the disruption of the passive film and thus expose discrete bare sites on the metal surface increasing the rate of corrosion on the metal surface to an environment where the tendency for attack is very high [8].

1.1.5 FACTORS THAT AFFECT THE RATE OF CORROSION

There are several factors that affect the rate of corrosion and can be divided into two parts, namely factors affecting on the metal and factors affecting on corrosive environment [8].

(a) Nature of the metal: The tendency of the metal to undergo corrosion is mainly dependent on the nature of the metal. Generally the metals with lower electrode potential have more reactive and more susceptible for corrosion, example, metals like K, Na, Mg, Zn have low electrode potential and undergo corrosion very easily, in comparison with noble metals like Ag, Au, Pt which have higher electrode potential and thus have negligible corrosion rate.

(b) Surface state of the metal: The corrosion product is usually the oxide of the metal; the nature of the product determines the rate further corrosion process. Metals like Al, Cr, Ti have an oxide layer on the surface which is stoichiometric, highly insoluble and non-porous in nature with low ionic and electronic conductivity, thus that type of products layer effectively prevents further corrosion. The opposite goes for metals such as Zn, Fe, Mg which the oxide layer formed on the metal surface is non-stoichiometric, soluble, unstable and porous in nature, thus they cannot control corrosion on the metal surface.

(c) Anodic and Cathodic area: Rate of corrosion is greatly influenced by the relative sizes of cathodic and anodic areas. If the metal has smaller anodic area and larger cathodic area exposed to corrosive atmosphere, more intense and faster is the corrosion occurring at anodic area because at anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed. If the cathode is smaller than the reverse process takes place, a decrease of the rate of corrosion.

(d) Hydrogen over voltage: A metal with low hydrogen over voltage on its surface is more susceptible for corrosion. When the cathodic reaction is hydrogen evolution type with low hydrogen over voltage, liberation of H₂ gas is easier so that cathodic reaction is very fast, that
makes anodic reaction faster hence overall corrosion process is very fast. If the $H_2$ over voltage is high so cathodic reaction is slow hence corrosion reaction also slower.

Now factors that affect the rate of corrosion

For corrosion to occur, four main elements must be present, and these collectively are referred to as the corrosion cell: an anode (+), a cathode (-), a metallic conductor and an electrolyte. Five factors that do play a highly important role in determining corrosion rates are as follows; [8]

**Oxygen:** Like water, oxygen increases the rate of corrosion, yes corrosion can take place in an oxygen deficient environment but not as rapid and quick as in an oxygen sufficient environment.

**Temperature:** It has been proven beyond doubt that the higher the temperature the faster the corrosion, thus corrosion occurs rapidly in warmer environments than in cooler ones.

**Chemical Salts:** Chemical salts increase the rate of corrosion by increasing the efficiency (conductivity) of the electrolyte. The most common chemical salt is sodium chloride, a major element of seawater, one must note that sodium chloride is a hygroscopic material, that is, it extracts moisture from the air which then increases the rate of corrosion in non-immersed areas.

**Humidity:** Humidity and time of wetness play a large role in promoting and accelerating the rate of corrosion. Time of wetness refers to the length of time an atmospherically exposed substrate has sufficient moisture to support the corrosion process, thus the wetter the environment, the more corrosion is likely to occur.

### 1.1.6 MECHANISM OF CORROSION

The corrosion phenomenon is an electrochemical process. When metal atoms are exposed to water molecules, they become positively charged ions through loss of electrons (provided the electrical current is complete [9]. Corrosion is the disintegration of any material including metals into its constituent atoms due to chemical reaction with its surrounding. Rusting of a metal is a commonly known type of electrochemical corrosion, and takes place in the following stages;

1. The oxidation process in which the metal losses its electrons:

   \[ M \rightarrow M^{2+} + n\, e^- \quad (1) \]

2. The hydrogen-evolution, when the metal is subjected to acidic media:

   \[ 2\, H^+ + 2\, e^- \rightarrow H_2 \uparrow \quad (2) \]

3. The reaction for the reduction of oxygen in acidic media:
4. The reaction for the reduction of oxygen in basic media

\[ \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 3 \text{H}_2\text{O} \]  

4. The reaction for the reduction of oxygen in basic media

\[ \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \]  

The understanding of the mechanism of corrosion unlocks doors to combatting this serious problem of corrosion because one will know which “tools” to use to fight this problem.

**Figure 1.5:** Schematic of a corroding metal electrode. Formal breakdown into two half-cells of a galvanic element (oxidation reaction at the anode, reduction reaction at the cathode)

### 1.1.7 CLASSIFICATION OF CORROSION PROCESS

Corrosion phenomenon can be classified into three processes, namely; electrochemical, chemical and physical [10].

**Electrochemical corrosion:** Perhaps this is the most common and frequently encountered of all corrosion processes. The electrochemical reaction that is responsible for metal corrosion is composed of four factors, namely; anode, cathode, electrolyte and electronic circuit. The kinetics of electrochemical reactions is the most dominant factors behind electrochemical corrosion.

**Chemical corrosion:** The most dominant factor in chemical corrosion is the law of ordinary heterogeneous chemical reactions. Here the metal is destroyed at high temperatures by aggressive gases since these gases prevent the condensation of moisture on the surface of the metal.

**Physical corrosion:** This type of corrosion process is not caused by any chemical reactions but through physical dissolution of the material. These dissolutions are not to be confused with chemical reactions. The dissolution of a material in liquid metals such as mercury is a good example of this phenomenon.
1.1.8 KINETICS AND THERMODYNAMICS OF CORROSION

Kinetics of corrosion involves how fast the rate of corrosion takes at a given time and place. Equations like that of Arrhenius gives the relationship between rate constant and temperature and how the rate constant depends on the temperature [11].

The rate of corrosion can be measured using the gravimetric methods (i.e. weight loss). The Arrhenius equation shows that the rate of corrosion is directly proportional to temperature. When temperature is increased, the rate of corrosion increases while the activation energy and pre-exponential factor may vary with temperature. Below is the Arrhenius equation;

$$k = Ae^{-E_a/RT}$$  \hspace{1cm} (5)

where:
- $k$ = the rate constant
- $A$ = the pre-exponential factor or the pre-factor
- $R$ = the gas constant
- $E_a$ = the activation energy
- $T$ = the absolute temperature

The equation corrosion rate using the weight loss method is as follows;

$$\rho = \left( \frac{\Delta w}{St} \right)$$ \hspace{1cm} (6)

where:
- $\rho$ = the corrosion rate
- $\Delta w$ = the average weight loss of the material
- $S$ = the total area of the of the material
- $t$ = the immersion time

This equation can be used directly to determine the rate constant.

One of the advantages of thermodynamics is that it can be used to calculate the theoretical activity of a given metal. The concept of spontaneous and non-spontaneous reactions is also important in the study of corrosion process. Corrosion processes are known to be spontaneous processes and for a reaction to occur spontaneously, the free energy of that particular reaction should have a negative value [11]. It is important to note that corrosion involves both oxidation and reduction half reactions which the overall free energy for the redox reaction is negative, $\Delta G^0$ (The standard free energy of the cell reaction) under standard conditions can be calculated by the following equation;

$$\Delta G^0 = -nFE^0$$ \hspace{1cm} (7)

where $\Delta G^0$ = the standard free energy change

$n$ = the number of electrons exchanged
\[ F = \text{the Faraday constant and } \Delta E^0 \text{ is the standard energy change in the reaction} \]

From studies, it is indicated that the value of \( \Delta G^0 \) of around -20 k J mol\(^{-1}\) or lower imply physisorption (physical adsorption) and those around -40 k J mol\(^{-1}\) or higher imply chemisorption (chemical adsorption) for a particular corrosion process [11, 12].

### 1.1.9 THE EFFECTS OF CORROSION

The effect of corrosion is experienced in all countries in the world in one or more of the ways given below.

- Industries such as oil, petrol and chemical industries use metallic pipes and containers that if corroded will need finances to repair or replace. This will affect the economy as in South Africa, Corrosion Institution of Southern Africa (Corrisa) estimated the direct cost of corrosion to be about R154 billion per annum. The National Association of Corrosion Engineers (NACE) showed that the direct cost of corrosion in the U.S. was estimated to equal $276 Billion in 1998.

- Health, safety and comfort of the population will be affected. This is because metal objects are commonly used by humans for making life easy and comfortable. Corroded cups and plates may contaminate food, which may cause health related problems [7].

- Technological problems: metals form a part of devices in electrical power stations, network poles and street light poles. Corrosion enhances damage of these devices and this will lead to negative technological effect.

### 1.1.10 CORROSION OF MILD STEEL

Mild steel is made up of many components with the main component being (Fe). An example of a known composition of mild steel is as follows: 0.02% Phosphorous (P), 0.37% Manganese (Mn), 0.03% Sulphur (S), 0.01% Molybdenum (Mo), 0.039% Nickel (Ni), 0.21% Carbon (C) and the remaining part being iron (Fe) which constitutes about 99.321% [13]. Corrosion of mild steel involves mainly iron in a few steps as follows;

\[
\text{Fe(s)} \rightarrow \text{Fe}^{2+} \text{(aq)} + 2e^- \quad (8)
\]

Then ferrous (Fe\(^{2+}\)) ions are oxidized to ferric ions (Fe\(^{3+}\))

\[
\text{Fe}^{2+} \text{(aq)} \rightarrow \text{Fe}^{3+} \text{(aq)} + 1e^- \quad (9)
\]
Then the next step involves the reduction of oxygen by electrons from the two above equation (8 and 9)

\[ \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4e^- \rightarrow 4\text{OH}^- (\text{aq}) \]  

(10)

The last step involves the reaction between Fe\(^{2+}\) and O\(_2\) to produce ferric oxide [iron (iii) oxide].

\[ 4\text{Fe}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + \text{XH}_2\text{O}(\text{l}) \rightarrow 2\text{Fe}_2\text{O}_3\cdot\text{XH}_2\text{O}(\text{s}) + 8\text{H}^+ (\text{aq}) \]  

(11)

1.1.11 CORROSION CONTROL MEASURES

Corrosion can be minimized by using techniques such as coating, cathodic protection, anodic protection and corrosion inhibitors and other techniques [7]. Coating includes organic, inorganic and metallic substances. Cathodic protection uses external sources of electrons for the cathodic reactions. Anodic protection involves keeping the material surface at a positive potential that ensures the formation of a passive film that remains adherent and intact. Corrosion inhibitors include substances introduced to the environment in minute concentrations to inhibit corrosion [5].

1.2 INHIBITORS AND INHIBITION

1.2.1 DEFINITION OF CORROSION INHIBITORS

Corrosion inhibitors can be defined as chemical substances that when added in small amounts to the environment in which a metal would corrode, will reduce, slow down, or prevent corrosion to the metal. Acid solutions are widely used in industry, such as acid packing, industrial acid cleaning, acid descaling and oil well acidizing [6]. Because of the general aggression of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. There are various organic inhibitors which tend to decrease the corrosion rate of steel and iron in acidic solutions [6]. Most of the effective organic inhibitors used contain heteroatom such as O, N, S and multiple bonds in their molecules through which they are adsorbed on the metal surface [6]. It has been observed that adsorption depends mainly on certain physico-chemical properties of the inhibitor group, such as electronic density at the donor atom, \(\pi\)-orbital character, and the electronic structure of the molecule [14].
1.2.2 TYPES OF INHIBITORS

The chemical functionality of an inhibitor determines their classification, e.g., interface inhibitors. Interface inhibitors control corrosion by forming a film at the metal/environment interface. Interface inhibitors can be classified into liquid- and vapor-phase inhibitors.

1.2.2.1 Liquid-Phase Inhibitors. Liquid-phase inhibitors are classified as anodic, cathodic, or mixed inhibitors, depending on whether they inhibit the anodic, cathodic, or both electrochemical reactions [15].

Anodic inhibitors: Anodic inhibitors are usually used in near-neutral solutions where sparingly soluble corrosion products, such as oxides, hydroxides, or salts, are formed. They form, or facilitate the formation of, passivating (being less affected by environmental factors such as air and water) films that inhibit the anodic metal dissolution reaction. Anodic inhibitors are often called passivating inhibitors. When the concentration of an anodic inhibitor is not sufficient, corrosion may be accelerated, rather than inhibited. The critical concentration above which inhibitors are effective depends on the nature and concentration of the aggressive ions [16]. When it comes to its mechanistic aspects of corrosion inhibition, the mechanism of anodic inhibition can be explained using the polarization diagram of an active-passive metal [3]. In the absence of inhibitors, the metal corrodes in the active state at a certain rate. As the concentration of inhibitor is increased, the corrosion rate also increases until a critical concentration and a critical corrosion rate are reached. At the critical concentration, there is a rapid transition of the metal to the passive state, and the corrosion rate is decreased.

Cathodic inhibitors: Cathodic inhibitors control corrosion by either decreasing the reduction rate (cathodic poisons) or by precipitating selectively on the cathodic areas (cathodic precipitators). Cathodic poisons, such as sulfides and selenides, are adsorbed on the metal surface; whereas compounds of arsenic, bismuth, and antimony are reduced at the cathode and form a metallic layer. In near-neutral and alkaline solutions, inorganic anions, such as phosphates, silicates, and borates, form protective films that decrease the cathodic reaction rate by limiting the diffusion of oxygen to the metal surface. Cathodic poisons can cause hydrogen blisters and hydrogen embrittlement (a loss of ductility of a material, making it brittle) due to the absorption of hydrogen into steel. This problem may occur in acid solutions, where the reduction reaction is hydrogen evolution, and when the inhibitor poisons, or minimizes, the recombination of hydrogen atoms to gaseous hydrogen molecules. In this situation, the hydrogen, instead of leaving the surface as hydrogen gas, diffuses into steel causing hydrogen damage, such as hydrogen-induced cracking (HIC), hydrogen embrittlement or sulfide stress cracking [15]. Cathodic precipitators increase the alkalinity at cathodic sites and precipitate insoluble compounds on the metal surface. The most widely used cathodic precipitators are the carbonates of calcium and magnesium [17]. In the case of mechanistic aspects of corrosion inhibition, in
acid solution, the cathodic reaction is typically the reduction of hydrogen ions to hydrogen, which combine forming hydrogen molecules [19]:

\[ \text{H}^+ + e^- \rightarrow \text{H} \quad (11) \]
\[ 2\text{H} \rightarrow \text{H}_2 \quad (12) \]

In alkaline solution, the cathodic reaction is typically oxygen reduction [eq. (10)]. Cathodic inhibitors impede reduction reactions. Substance with high over potential for hydrogen and those that form precipitates at the cathode are effective in acid and alkaline solution, respectively. In this case, the slope of the anodic polarization curve is unaffected, but the slope of the cathodic polarization curve is changed [19].

Mixed inhibitors: About 80% of inhibitors are organic compounds that cannot be designated specifically as anodic or cathodic and are known as mixed inhibitors. The effectiveness of organic inhibitors is related to the extent to which they adsorb and cover the metal surface. Adsorption depends on the structure of the inhibitor, on the surface charge of the metal, and on the type of electrolyte. Mixed inhibitors protect the metal in three possible ways: physical adsorption, chemisorption and film formation. Physical (or electrostatic) adsorption is a result of electrostatic attraction between the inhibitor and the metal surface. When the metal surface is positively charged, adsorption of negatively charged (anionic) inhibitors is facilitated. Positively charged molecules acting in combination with a negatively charged intermediate can inhibit a positively charged metal. Anions, such as halide ions, in solution adsorb on the positively charged metal surface, and organic cations subsequently adsorb on the dipole [15]. Corrosion of iron in sulphuric acid containing chloride ions is inhibited by quaternary ammonium cations through this synergistic effect [20]. Physically adsorbed inhibitors interact rapidly, but they are also easily removed from the surface. Increase in temperature generally facilitates desorption of physically adsorbed inhibitor molecules. The most effective inhibitors are those that chemically adsorb (chemisorb), a process that involves charge sharing or charge transfer between the inhibitor molecules and the metal surface. Chemisorption takes place more slowly than physical adsorption. As temperature increases, adsorption and inhibition also increase. Chemisorption is specific and is not completely reversible [21]. Adsorbed inhibitor molecules may undergo surface reactions, producing polymeric films. Corrosion protection increases markedly as the films grow from nearly two-dimensional adsorbed layers to three-dimension films up to several hundred angstroms thick. Inhibition is effective only when the films are adherent, are not soluble, and prevent access of the solution to the metal. Protective films may be non-conducting (sometimes called ohmic inhibitors because they increase the resistance of the circuit, thereby inhibiting the corrosion process) or conducting (self-healing films) [15]. Water molecules adsorb on the metal surface immersed in an aqueous phase. Organic molecules adsorb by replacing the water molecules:
\[ [\text{Inhibitor}]_{\text{soln}} + [n\text{H}_2\text{O}]_{\text{adsorbed}} \leftrightarrow [\text{Inhibitor}]_{\text{adsorbed}} + [n\text{H}_2\text{O}]_{\text{soln}} \] (13)

where \( n \) is the number of water molecules displaced by one inhibitor molecule. The ability of the inhibitor to replace water molecules depends on the electrostatic interaction between the metal and the inhibitor. On the other hand, the number of water molecules displaced depends on the size and orientation of the inhibitor molecule. Thus, the first interaction between inhibitor and metal surface is nonspecific and involves low activation energy. This process, called “Physical adsorption”, is rapid and in many cases, reversible [19].

1.2.2 Vapour phase inhibitors
Temporary protection against atmospheric corrosion, particularly in close environments can be achieved using vapour phase inhibitors (VPI). Substances having low but significant pressure of vapour with inhibitive properties are effective [18]. The VPIs are used by impregnating wrapping paper or by placing them loosely inside a closed container. The slow vaporization of the inhibitor protects against air and moisture. In general, VPIs are more effective for ferrous than non-ferrous metals [18].

1.2.3 MECHANISM OF CORROSION INHIBITION
Corrosion can either be cathodic or anionic, hence the work of the inhibitor is to bind either at the cathodic part or the anionic part to reduce if not to prevent the electrons or protons from the metal from reacting with the environment like water. Inhibitors normally adhere to the surface of the metal to prevent or reduce corrosion either by chemical adsorption (chemisorption) or physical adsorption (physisorption). The ability of an inhibitor to adsorb on the surface of the metal determines its efficiency to inhibit corrosion. Equation (13) shows the interaction between the inhibitor and the solution as the mechanism of corrosion inhibition.

1.2.4 TECHNIQUES OF APPLICATION OF CORROSION INHIBITORS
Corrosion inhibitors are used to reduce corrosion; thus in industries like paint, petrol and oil industries they come as a useful tool. In paint industries, corrosion inhibitors are added into paints as primers to protect the metal especially when the second layer of the paint is peeled off. Petrol and oil industries too use corrosion inhibitors mostly in their pipes that transport them. Oil leakage has been of a problem to factors including the corroding of pipes, thus corrosion inhibitors come into play to minimise such leakage that is detrimental to the surrounding environment. Corrosion inhibitors such as Volatile Corrosion Inhibitors (VCI) also called Vapour Phase Inhibitors (VPI) are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in the condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH towards less acidic and
corrosive values. In closed vapour spaces, such as shipping containers, volatile solids such as salts of dicyclo-hexylamine, cyclohexylamine and hexamethyleneamine are used. When these inhibitors come in contact with the metal surface, the vapour of these salts condenses and is hydrolysed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods [22].

1.2.5 AIMS AND OBJECTIVES OF THE PRESENT STUDY
This research aims to study the effect of the following ionic liquids namely; 1-Hexyl-3-methylimidazolium tetrafluorobutane, 1-Hexyl-3-methylimidazolium iodide, 1-Hexyl-3-methylimidazolium hexafluorophosphate and 1-Hexyl-3-methylimidazolium trifluoromethanesulfonate as corrosion inhibitors. It has been found that corrosion inhibition ability of imidazolium and pyridinium compounds depends on the specific interaction between the functional groups and the metal surface due to the presence of the –C=N- group and electronegative nitrogen (N) in the molecule. Organic compounds containing electronegative functional groups and π-electrons in triple or conjugated double bonds are usually good corrosion inhibitors [23-26]. The study will use electrochemical techniques namely electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques.

The main objectives of the research are:

a) to apply thermodynamics, kinetics and adsorption principles to study the inhibition potentials of the ionic liquids.

b) to study the effect of concentration of ionic liquids and temperature on the corrosion rate;

c) to propose possible mechanisms, (e.g. type of adsorption and adsorption isotherm) for the corrosion inhibition;

d) to calculate quantum chemical parameters of the selected inhibitors and correlate them with the experimentally obtained inhibition efficiency

e) to determine nucleophilicity, electrophilicity, Fukui and global software’s indices for the ionic liquids used.
CHAPTER 2

LITERATURE SURVEY ON IONIC LIQUIDS

2.1 BACKGROUND OF IONIC LIQUIDS

The investigation into ionic liquids began in 1914 with an observation by Paul Walden [27], who reported the physical properties of ethyl ammonium nitrate \([\text{EtNH}_3][\text{NO}_3]\) with melting point of 13-14 °C, which was formed by the neutralisation of ethylamine with concentrated nitric acid [27]. However, despite Walden’s clear exposition, and his discovery of a new class of liquids, this paper did not prompt any significant interest at the time. After two decades of silence, ionic liquids appear in a patent in 1934, which claimed that when halide salts of nitrogen-containing bases were mixed with cellulose at the temperature above 100 °C, the cellulose dissolved and solutions of a different viscosity were formed [28]. After yet another silent phase in the history of ionic liquids, they re-emerged in the period just after World War II. In the patent literature in 1948 [29], and later in the open literature [30], the application of mixtures of aluminium (III) chloride and 1-ethyopyridinium bromide to the electrodeposition of aluminium was described. This was an important discovery, but the selected system based on mixed bromide and chloride salts meant that the solvent was chemically complicated and hence difficult to investigate. After another 25 years, this problem was dealt with when the Osteryoung group in 1975 [31], aided by Bernard Gilbert [32], studied in detail the chemical and physical properties of ionic liquids made from 1-butylpyridinium chloride and aluminium (III) chloride. Though Osteryoung’s group work was a true breakthrough, their system which they came up with \([\text{C}_4\text{py}]\text{Cl}\cdot\text{AlCl}_3\), had serious limitations because it was liquid at room temperature, but only a very narrow compositional range, and the cation was very easily reduced [32].

Seven years later in 1982, Wilkes and Hussey [33] tried to look for less reducible cation by MNDO calculations comparing several known heterocyclic cations with the outcome that imidazolium presented itself as the most stable cation. At this point the prominence of the imidazolium based ionic liquids commenced. At a later date Seddon, Hussey and others investigated metal complexes in ionic liquids trying to understand spectroscopic and complex chemical aspects of these metal compounds [34 - 36]. In 1985/86, the chemical properties of ionic liquids were rediscovered and successfully established in reaction like Friedels-Craft acetylation [37] or nucleophilic aromatic substitution [38]. Encouraged by these findings, in 1990, Chauvin et al, Wilkes et al and Carlin et al used metal catalysts in acidic ionic liquids to catalyse the dimerisation of propene and the polymerisation of ethene [39 - 41]. On the grounds of these successful reactions, Wilkes and Zaworotko [41] polished homogeneous reactions in ionic liquids by applying more stable species in 1992. The tetrafluoroborate-based ionic liquids...
showed to be tolerant to multiple functional groups and more resistant in the presence of water compared to the chloroaluminate ones, this paved way for more combinations of cations and anions ionic liquid [42]. Howarth et al synthesised a chiral imidazolium-based ionic liquid and described its use in a Diels-Alder reaction in 1997 [43]. Seddon et al [44] used a readily available substance from the chiral pool for the synthesis of an ionic liquid carrying the chiral information in the anion, a lactate. In 2001, Wasserscheid et al [45] used the chiral pool as a source for chiral ionic liquids by synthesising them from amino acids. From 2005, a number of award ceremonies and conferences were held, namely the 1st International Congress on ionic liquids held in Salzburg in Austria, the Presidential Green Chemistry Challenge Awards by the Environmental Protection Agency in the USA [46]. Between 2008 and 2010, a lot of interest increased in the area of ionic liquids, 2500 papers being published in 2008 alone [46].

2.2 THE DEFINITION OF IONIC LIQUIDS

Generally, the term “ionic liquids” stands for liquids composed of ions [47]. Ionic liquids are organic salts that melt below 100 °C, unlike traditional solvents, ionic liquids comprise entirely of ions [6]. These are usually molten salts or molten oxides and it has been noted that the properties of molten salts as a solvent for chemical processes differ from those of aqueous and organic solvents. Some processes, for instance, the electrochemical reduction of aluminum from alumina, can be conducted only in molten salts and are impossible in aqueous solutions. However, until recently the use of molten salts were considered to be confined to high-temperature applications [47].

2.3 SYNTHESIS OF IONIC LIQUIDS

A proper choice of cation and anions is required to achieve ionic salts that are liquids at room temperature and are appropriately termed room temperature ionic liquids (RTIL). Ionic liquids containing highly electronegative anions such as ones that consists of imidazolium or pyridinium cation and anion such as BF₄⁻, PF₆⁻, CF₃SO₃⁻ or halides [48]. Common room temperature ionic liquids consist of N,N-dialkylimidazolium, alkylammonium, alkylphosphonium as cations [49].

An efficient method for the preparation of ionic liquids involve neat reactants in open glass containers to microwaves using household microwave oven. In contrast to several hours needed under conventional heating conditions which uses an excess of reactants, this solvent-free approach requires only few minutes of reaction time [48]. A representation for the preparation for of the mono (1) and dicationic (2) 1,3-dialkyl-imidazolium halide is shown below.
The $\text{X}^-$ represents the anion such as BF$_4$, PF$_6$, CF$_3$SO$_3$ or halides, R represents the alkyl chain and MW microwave. There are other ways of synthesising ionic liquids including:

**Halide-free synthesis**

\[
\text{H}_3\text{C}-\text{N} + (\text{C}_2\text{H}_5)_2\text{SO}_4 \rightarrow \text{H}_3\text{C}-\text{N}^+ + \text{C}_2\text{H}_5\text{SO}_4^- \quad (14)
\]

**Anion Exchange**

\[[\text{HMIM}]\text{Cl} + [\text{NH}_4][\text{BF}_4] \rightarrow [\text{HMIM}][\text{BF}_4] + \text{NH}_4\text{Cl} \quad (15)\]

**Alkylation**

\[
\text{H}_3\text{C}-\text{N} + \text{C}_2\text{H}_5\text{Cl} \rightarrow \text{H}_3\text{C}-\text{N}^+ + \text{C}_2\text{H}_5^- + \text{Cl}^- \quad (16)
\]

**2.4 PROPERTIES OF IONIC LIQUIDS**

Ionic liquids have unique properties such as wide liquid range, stability at high temperatures, no flammability and negligible vapour pressure [50]. Ionic liquids are intrinsically excellent candidates for industrial applications compared to volatile organic solvents. Organic solvents have been used for several centuries, and obviously occupy most of the solvent market in industry. However, if the properties of ionic liquids and organic solvents are compared, ionic liquids may often work better than organic solvents in industrial processes [51]. It is crucial to note that the common solvents such as water and organic solvents (e.g., benzene) are made up of
molecules while ionic liquids are made up of cations and anions. One can relate the structure of an ionic liquid to that of salts such as lithium chloride, potassium chloride and sodium chloride because these salts are also made up of charged cations and anions. The only difference between these salts and ionic salts/liquids is that these salts possess high melting points whereas ionic liquids possess low melting points. The ions in ionic liquids do not form a packed system and as a result they remain liquid at room temperature [52]. Obviously, the chemical composition of ionic liquids determines their melting point.

The ionic liquids have attracted the attention of environmental scientists because of the following properties:

- Many organometallic, organic and inorganic materials are soluble in ionic liquids.
- Ionic liquids do not evaporate since they are non-volatile.
- Ionic liquids are thermally stable and simultaneously polar.
- They are designer solvents—which mean they can be prepared for a specific designation objective or purpose by simply varying the anion-cation combination.
- They have low melting points [52].

Molecular structures of ionic liquids show they can form micelles and lower interfacial tension of aggressive media. This should lead to an improvement in surface wetting and adsorption, and hence have a beneficial effect on corrosion of exposed surfaces [53].

### 2.5 IONIC LIQUIDS AS CORROSION INHIBITORS

As already stated, ionic liquids have attracted a lot of attention all over the world because of their remarkable properties such as thermal stability, low melting and boiling points and their eco-friendly nature because they can be recycled [52]. Not much work has been done, however on ionic liquids being used as corrosion inhibitors. But a few have ventured into using ionic liquids as corrosion inhibitors as the following.

Ashassi-Sorkhabi and Es’haghi [54] investigated the corrosion inhibition of mild steel in 1.0 M HCl by 1-butyl-3-methylimidazolium bromide [BMIM]Br ionic liquid. The obtained results showed that [BMIM]Br acts essentially as a mixed type inhibitor. The effect of inhibitor concentration on zero charge potential (ZCP) of the mild steel in 1.0 M HCl was studied and its comparison with OCP has been made for evaluation of the mechanism of adsorption of [BMIM]$^+$ cation. The effect of temperature on the corrosion behavior of mild steel in 1.0 M HCl with addition of [BMIM]Br was studied in temperature range 25-45 °C. The inhibition efficiency decreases with increase in temperature.

Zhang and Hua [55] investigated the corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. In their research, the acid corrosion inhibition process of mild
steel in 1.0 M HCl by 1-butyl-3-methylimidazolium chloride (BMIC) and 1-butyl-3-methylimidazolium hydrogen sulphate ([BMI]HSO₄) was investigated using electrochemical impedance, potentiodynamic polarization and weight loss methods. The inhibition efficiency increased with increase in concentration of inhibitor for both inhibitors and the effectiveness of the two inhibitors are in the order [BMI]HSO₄ > BMIC. Langmuir’s adsorption isotherm was obeyed for the adsorption of the inhibitors on mild steel. The effect of temperature on the corrosion behavior in the presence of 5 ×10⁻³ M of the inhibitor was studied in the temperature range of 30 °C – 60 °C. The mechanism of corrosion inhibition was elaborated by using the calculated values of thermodynamics parameters such as enthalpy of activation (ΔH), entropy of activation (ΔS), adsorption equilibrium constant (Kₘₐₜ) and the standard free energy of adsorption (ΔG).

Likhanova et al [53] studied the effect of ionic liquids with imidazolium cation (namely, 1,3-dioctadecylimidazolium bromide) and pyridinium cation (namely, N-octadecylpyridinium) on the corrosion inhibition of mild steel in acidic environment. In their work, ILs tested as corrosion inhibitors displayed corrosion protection efficiency within 82- 88% at 100 ppm for mild steel in a 1.0 M aqueous solution of sulphuric acid. Chemical adsorption process was proposed from the calculated values of the standard free energy of adsorption (ΔG). The presence of carbon species pertaining to the inhibitor and corrosion products was indicated by surface analysis (SEM, EDX) completed by XRD and Mossbauer spectroscopy. This was also rationalized in their inhibition mechanism.

Murulana [10] investigated the corrosion inhibition of ionic liquids with imidazolium on mild steel in 1.0 M of HCl using four ionic liquids namely 1-Propyl-1-3-methylimidazolium bis(trifluoromethylsulfonyl), 1-Butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) amide, 1-Hexyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) amide, 1-Propyl-2,3-Dimethylimidazolium bis(trifluoromethyl-sulfonyl) amide. The result from the weight loss, electrochemical analysis and quantum chemical studies showed that the ionic liquids were effective in inhibiting corrosion following the order: [PDMIM][NTf₂] > [HMIM][NTf₂] > [BMIM][NTf₂] > [PMIM][NTf₂], from 100 ppm to 500 ppm corrosion inhibition increased.

Ionic liquids have molecular structures that are capable of forming micelles and lowering interfacial tension of aggressive media, which leads to an improvement in surface wetting and adsorption. These properties have a beneficial effect on corrosion inhibition of exposed surfaces and may be responsible of the corrosion inhibition of metals [53]. All this makes ionic liquids an interesting study as corrosion inhibitors.
CHAPTER 3

EXPERIMENTAL DETAILS

3.1 MATERIALS

The mild steel sheet was of the composition 0.02 % Phosphorus (P), 0.37 % Manganese (Mn), 0.03 % Sulphur (S), 0.01 % Molybdenum (Mo), 0.039 % Nickel (Ni), 0.21 % Carbon (C) and the remaining part being iron (Fe).

3.2 REAGENTS

The hydrochloric acid used for this study was obtained from MERCK CHEMICALS.

3.3 INHIBITORS

SIGMA-ALDRICH CHEMICALS was the source of the ionic liquids that were used in this investigation. The ionic liquids investigated were:

- 1-Hexyl-3-methylimidazolium trifluoromethanesulfonate [HMIM][TfO]
- 1-Hexyl-3-methylimidazolium tetrafluoroburate [HMIM][BF₄]
- 1-Hexyl-3-methylimidazolium iodide [HMIM][I]
- 1-Hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF₆]

The ionic liquids used were of the imidazolium base ring, their structures, names, and their formulas are given below.
Ionic Liquids with the same cation but different anions

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Structural Formula</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Hexyl-3-methylimidazolium PF₆</td>
<td><img src="image1.png" alt="Image" /></td>
<td>C₁₀H₁₉F₆N₂P, MW=312.24</td>
</tr>
<tr>
<td>Hexyl-3-methylimidazolium TFO</td>
<td><img src="image2.png" alt="Image" /></td>
<td>C₁₂H₂₁F₃N₂O₃S, MW=330.37</td>
</tr>
<tr>
<td>1-Hexyl-3-methylimidazolium I</td>
<td><img src="image3.png" alt="Image" /></td>
<td>C₁₀H₁₉IN₂, MW=294.18</td>
</tr>
<tr>
<td>1-Hexyl-3-methylimidazolium BF₄</td>
<td><img src="image4.png" alt="Image" /></td>
<td>C₁₀H₁₉F₄N₂B, MW=254.08</td>
</tr>
</tbody>
</table>

Figure 3.1: Molecular structures of the imidazolium based ionic liquids utilized in this study.

3.4 ELECTROCHEMICAL MEASUREMENTS

The electrochemical measurements were performed at room temperature (30 °C) using the Autolab electrochemical work station from Metrohm. A stabilization time of 30 minutes was allowed before the electrochemical measurements were performed and this time was deemed to be sufficient to attain a stable value of OCP (open circuit potential). A three-electrode cell composed of a platinum counter electrode (CE), a silver-silver chloride electrode in saturated KCl as a reference electrode and a carbon steel as a working electrode (WE), was used for electrochemical measurements. A potential range of -0.8 to -0.2 V with scan rate 100 mV s⁻¹ was utilized to generate the potentiodynamic polarization curves. All potentials were measured against Ag/AgCl in sat’d KCl. A frequency range, starting from 10000.0 kHz to 1.0 kHz was utilized to carry out the EIS measurements using the amplitude of 5 mV peak-to-peak, using AC signal at Ecorr. This was performed under potentiodynamic conditions.
3.4.1 Potentiodynamic Polarization (PDP)

Potentiodynamic polarization was used to get the values of corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), anodic and cathodic Tafel slopes ($b_a$ and $b_c$), Polar Resistance ($R_P$) and Corrosion Rate. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities ($i_{corr}$). The inhibition efficiency was evaluated from the measured $i_{corr}$ value using the relationship:

$$E_{PDP} \% = \frac{i_{corr}^0 - i_{corr}^i}{i_{corr}^0}$$

(17)

where $i_{corr}^0$ and $i_{corr}^i$ are values of corrosion current density in absence and in presence of inhibitor, respectively.

3.4.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy was used to obtain parameters such as the resistance of charge transfer ($R_{ct}$), and the capacity of double layer ($C_{dl}$), and from this obtained parameters, the inhibition efficiency was calculated using the equation below:

$$E_{EIS} \% = \left(1 - \frac{R_{ct}^0}{R_{ct}^i}\right) \times 100$$

(18)

where, $R_{ct}^0$ is the charge transfer resistance in the absence of the inhibitor and $R_{ct}^i$ is the charge transfer resistance in the presence of the inhibitor.

3.5 FOURIER TRANSFORM INFRARED (FTIR) AND ULTRAVIOLET-VISIBLE (UV-vis) SPECTROSCOPY EXPERIMENT

The FTIR and UV-vis experiments were carried out for the ionic liquids alone, and ionic liquid in the presence of mild steel immersed in 1.0 M HCl solution using Fourier transformed infrared spectrophotometer (Agilent Technology, Cary 600 series FTIR spectrometer, USA) and UV-visible spectrophotometer (Agilent Technology, Cary series UV-vis spectrometer, USA). The FTIR and UV-vis spectra obtained are reported and discussed in Chapter 4.

3.6 QUANTUM CHEMICAL CALCULATIONS

A number of quantum chemical properties are often utilised to understand the behaviour of corrosion inhibitors. These quantum chemical properties include the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), dipole moment, Fukui functions, ionization potential, electron affinity, energy gap and the global hardness and softness. They can all be defined as follows:

The highest occupied molecular orbital (HOMO) is the orbital which is lastly occupied. It is therefore closest to the unoccupied molecular orbitals and it has the highest energy among the
occupied molecular orbitals. For this reason, if any electron has to be donated to the unoccupied molecular orbitals of an electron deficient species, they are likely to come from this orbital. The lowest unoccupied molecular orbital (LUMO) is the first orbital without electrons among the list of unoccupied (virtual) molecular orbitals. It therefore has the lowest energy among the orbitals without electrons and if any pair of electrons is to be accepted by the molecular system, it is likely to occupy the LUMO.

Dipole moments (μ) is the measure of net molecular polarity, which is the magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges [56].

\[ \mu = Q \times r \]  

Fukui function: The Fukui function, denoted by \( f(r) \), is defined as the differential change in electron density due to an infinitesimal change in the number of electrons [57]. The nucleophilic and electrophilic Fukui functions can also be calculated using the finite difference approximation as follows [58];

\[ f^+ = \rho_{(N+1)} - \rho_N \]  
\[ f^- = \rho_N - \rho_{(N-1)} \]

Ionization potential (I) is the amount of energy required to remove an electron from a molecule; it is related to the energy of the \( E_{\text{HOMO}} \) through the equation:

\[ I \equiv -E_{\text{HOMO}} \]  

Electron affinity (EA) is the energy released when an electron is added to a neutral molecule; it is related to \( E_{\text{LUMO}} \) through the equation:

\[ \Delta E \equiv -E_{\text{LUMO}} \]  

Energy Gap (\( \Delta E \)): The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) within a given inhibitor molecule is referred to as energy gap and denoted with a letter \( \Delta E \).

\[ \Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \]  

Global Hardness and Softness: Global hardness (\( \eta \)) and softness (\( \sigma \)) are molecular properties that also facilitate the analysis of the molecular reactivity [56]. Soft molecules are more reactive than hard molecules if electron transfer or rearrangement is necessary for the reaction. Hard molecules resist changes in their electron number and distribution [59].

\[ \eta \equiv -\frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}}) \]
\[ \sigma = \frac{1}{\eta} = -2/(E_{\text{HOMO}} - E_{\text{LUMO}}) \]  

All Geometry optimizations and quantum chemical calculations were performed using density functional theory (DFT) using the 6-31G(d) basis set. The Becke’s Three Parameter Hybrid Functional using the Lee-Yang-Parr correlation functional theory (B3LYP, [60]) was selected for the calculations. The DFT method is widely utilized in the analysis of the characteristics of the inhibitor/metal surface mechanisms and in the description of the nature of the inhibitor on the corrosion process [61]. Moreover, DFT/B3LYP is highly recommended for the understanding of chemical reactivity and selectivity in terms of frontier molecular orbitals (the HOMO and the LUMO) and related properties such as polarizability, hardness (\( \eta \)) and electronegativity [62], electron affinity (EA) and ionization potential (IP). In terms of the Koopman’s theorem [63-65], schematic structures were drawn using the ChemOffice package in the UltraChem 2010 version while optimized structures were drawn using the Spartan 10 V1.01 program.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 ELECTROCHEMICAL MEASUREMENTS

4.1.1 Potentiodynamic Polarization (PDP)

Potentiodynamic polarization curves for mild steel in 1 M HCl in the absence and presence of different concentrations (100 – 500 ppm) of the studied ionic liquid inhibitors are presented in Figures 4.1 – 4.4. The values of corrosion potential ($E_{\text{corr}}$), corrosion current density ($i_{\text{corr}}$), anodic and cathodic tafel slopes ($b_a$ and $b_c$), polarization resistance ($R_p$) and corrosion rate obtained from the fitting of the polarization curves are presented in Table 4.1. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities ($i_{\text{corr}}$). The inhibition efficiency was evaluated from the measured $i_{\text{corr}}$ value using Equation 17 (Chapter 3).
**Figure 4.1:** Potentiodynamic polarization curve for mild steel in 1 M HCl in the absence and presence of different concentrations of [HMIM][BF₄].

**Figure 4.2:** Potentiodynamic polarization curve for mild steel in 1 M HCl in the absence and presence of different concentrations of [HMIM][TfO].
Figure 4.3: Potentiodynamic polarization curve for mild steel in 1 M HCl in the absence and presence of different concentrations of [HMIM][PF$_6$].

Figure 4.4: Potentiodynamic polarization curve for mild steel in 1 M HCl in the absence and presence of different concentrations of [HMIM][I].
From the results, it is shown that in the presence of the inhibitor, the curves are shifted to the lower current regions. This trend confirms the inhibition ability of the ionic liquid corrosion inhibitors utilized in this study. The $E_{corr}$ values in the presence of all the four ionic liquids exhibit a little significant change in trend. It can be observed that both [HMIM][PF₆] and [HMIM][I] shift slightly toward the anodic region while [HMIM][BF₄] and [HMIM][TfO] shift slightly to the cathodic region as shown in Figures 4.1 to 44. The shift in $E_{corr}$ values falls within the range of 30 - 40 mV. Literature studies indicate that the values within this range confirm a mixed type mechanism by the inhibitors [66, 67].

The results from the Table 4.1 show that the anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$) changed on increasing the concentration of the tested inhibitors. This indicates that there is no change in the mechanism of inhibition in presence and absence of inhibitors [68]. The fact that the values of $\beta_c$ are slightly higher than the values of $\beta_a$ suggests a cathodic action of the inhibitor as shown in Table 4.1. It can be observed that both current density ($i_{corr}$) and corrosion rate (CR) decreases as concentration increases, while the polarization resistance ($R_p$) increases as the concentration increase showing the corrosion inhibition ability of the studied ionic liquids.

Similarly from the Table, it can be observed that the inhibition efficiency increases as concentration increases for all the studied ionic liquids with maximum inhibition efficiency (86.96%) obtained for [HMIM][TfO] thus confirming the ability of the inhibitors to inhibit corrosion efficiently. At 500 ppm concentration of the inhibitors, the %IE follows the order, [HMIM][TfO](86.96%) > [HMIM][PF₆](77.63%) ≥ [HMIM][I](77.34%) > [HMIM][BF₄](66.22%). This order is clearly summarised pictorally for all concentrations on the plot of %IE versus inhibitors concentrations graphs (Fig. 4.5). Values obtained in this study agreed favourably with other studies reported in literature where high % inhibition efficiency (%IE) has been reported [69-71]. The high % IE obtained for [HMIM][TfO] ionic liquid in this study compared with others can be attributed to presence of more than one heteroatoms with high electronegativity (S, O) in its anions which enhances its adsorption on the surface of the mild steel thus improving its inhibition efficiency compared to others [71].

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4.1.2 Electrochemical Impedance Spectroscopy (EIS)

The impedance method provides information about the kinetics of the electrode processes and simultaneously about the surface properties of the investigated systems. The shape of the impedance gives mechanistic information. The method is widely used for investigation of corrosion inhibition processes [72].

Electrochemical impedance spectroscopy was employed to study the corrosion behaviour of mild steel in 1M HCl at OCP (Open Circuit Potential) in the absence and presence of different concentrations (100 – 500 ppm) of [HMIM][BF₄], [HMIM][TfO], [HMIM][PF₆] and [HMIM][I] ionic liquids inhibitors after a total immersion time of 30 minutes at 30 °C. The Nyquist and Bode plots (Phase angle vs log f, and log Z vs log f) of mild steel in uninhibited and inhibited acid solutions containing various concentrations of studied ionic liquids are presented in Figures 4.6 – 4.9.
Figure 4.6: (a) Nyquist plot, (b) -Phase angle vs log f (c) log Z vs log f of mild steel in 1 M HCl in the absence and presence of different concentrations of [HMIM][BF₄].
The obtained Nyquist and Bode's plots for the studied compounds are shown in Figures 4.6 to 4.9. Each spectrum is characterized by a single full semicircle. It can be observed that the diameter of semicircle for the inhibited sample is much larger than that of the blank which suggest resistance to charge transfer by the inhibitors during mild steel oxidation process. The Figures also showed that each impedance diagram is made up of a large capacitive loop with low frequencies dispersion (inductive arc). Normally the anodic adsorbed intermediates that control the anodic reactions are the main factor behind the inductive arc [73, 74]. The increasing diameter of capacitive loop obtained in 1 M HCl with increasing concentration of the ionic liquids showed the inhibition of corrosion of mild steel.

The surface coverage (θ) and the inhibition efficiency (E_{EIS\%}) was calculated from the data obtained from the electrochemical impedance according to equations below.

$$
\theta = 1 - \frac{R_{ct}^0}{R_{ct}}
$$

(27)

where, $R_{ct}^0$ is the charge transfer resistance in the absence of the inhibitor and $R_{ct}$ is the charge transfer resistance in the presence of the inhibitor.

Corrosion kinetic parameters obtained from the fitting of the EIS measurements and the estimated % inhibition efficiencies are presented in Table 4.2. The EIS measurements are fitted using the equivalent circuit model represented in Figure 4.10.
Figure 4.7: (a) Nyquist plot, (b) Phase angle vs log f, (c) log Z vs log f of mild steel in 1 M HCl in the absence and presence of different concentrations of [HMIM][TfO].
Figure 4.8: (a) Nyquist plot, (b) Phase angle vs log f, (c) log Z vs log f of mild steel in 1 M HCl in the absence and presence of different concentrations of [HMIM][PF$_6$].
Figure 4.9: (a) Nyquist plot, (b) -Phase angle vs log f (c) log Z vs log f of mild steel in 1 M HCl in the absence and presence of different concentrations of [HMIM][I].
Figure 4.10: The equivalent circuit of the impedance spectra obtained for [HMIM][BF₄], [HMIM][TfO], [HMIM][PF₆] and [HMIM][I].

The depression in Nyquist semicircles is a feature for solid electrodes and often referred to as frequency dispersion and attributed to the roughness and other inhomogeneities of the solid electrode [75]. In this behavior of solid electrodes, the parallel network charge transfer resistance-double layer capacitance is established where an inhibitor is present. For the description of a frequency-independent phase shift between an applied ac potential and its current response, a constant phase element (CPE) is used.

The values of $C_{dl}$ (double-layer capacitance) were calculated using the equation below,

$$C_{dl} = (Y_0 R_{ct}^{1/n})^{1/n}$$  \hspace{1cm} (28)

where; $Y_0$ is the CPE (Constant Phase Capacitance) constant, $R_{ct}$ the resistance of charge transfer and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface [76].

Table 4.2 shows that the charge transfer resistance ($R_{ct}$) of the inhibited system increases with increasing inhibitors concentration. This result agreed favourable with other studies reported in literature for mild steel corrosion inhibition in 1 M HCl [69, 70]. The increase in the charge transfer resistance ($R_{ct}$) increases as the concentration of ionic liquids inhibitors and can be attributed to binding of the inhibitors to the mild steel surface therefore restricting direct or continuous contact with the corrosive acid medium which assist its oxidation process. On the other hand, the $C_{dl}$ values decreased accordingly except at 500 ppm concentration of [HMIM][BF₄] and [HMIM][I] where a small increase in the $C_{dl}$ value was noticed.
Table 4.2: Electrochemical impedance parameters such as the resistance of charge transfer (R\(_{ct}\)), capacity of double layer (C\(_{dl}\)), using R\(_1\) (R\(_2\)C\(_1\)) circuit by different inhibitors.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>R(_s) (Ω cm(^2))</th>
<th>C(_{dl}) (µF cm(^{-2}))</th>
<th>R(_{ct}) (Ω cm(^2))</th>
<th>E(_{EIS}) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.248(4.70)</td>
<td>42.1(4.406)</td>
<td>63.3(4.268)</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>1.759(8.695)</td>
<td>17.19(7.088)</td>
<td>125.2(7.008)</td>
<td>49.44</td>
</tr>
<tr>
<td>300</td>
<td>1.745(11.181)</td>
<td>10.24(7.523)</td>
<td>220.7(8.000)</td>
<td>71.32</td>
</tr>
<tr>
<td>400</td>
<td>2.150(11.434)</td>
<td>9.92(8.189)</td>
<td>254.4(8.762)</td>
<td>75.32</td>
</tr>
<tr>
<td>500</td>
<td>2.072(12.482)</td>
<td>7.01(7.776)</td>
<td>294.9(8.291)</td>
<td>78.54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>R(_s) (Ω cm(^2))</th>
<th>C(_{dl}) (µF cm(^{-2}))</th>
<th>R(_{ct}) (Ω cm(^2))</th>
<th>E(_{EIS}) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HMIM][TfO] 100</td>
<td>2.922(8.297)</td>
<td>30.2(7.584)</td>
<td>90.2(8.162)</td>
<td>29.82</td>
</tr>
<tr>
<td>200</td>
<td>1.871(7.783)</td>
<td>22.54(6.98)</td>
<td>129.9(7.107)</td>
<td>51.27</td>
</tr>
<tr>
<td>300</td>
<td>1.991(9.185)</td>
<td>20.16(7.970)</td>
<td>151.0(8.272)</td>
<td>58.08</td>
</tr>
<tr>
<td>400</td>
<td>1.768(10.594)</td>
<td>18.23(8.513)</td>
<td>170.0(9.164)</td>
<td>62.76</td>
</tr>
<tr>
<td>500</td>
<td>2.801(13.368)</td>
<td>11.30(10.549)</td>
<td>225.0(13.368)</td>
<td>71.87</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>R(_s) (Ω cm(^2))</th>
<th>C(_{dl}) (µF cm(^{-2}))</th>
<th>R(_{ct}) (Ω cm(^2))</th>
<th>E(_{EIS}) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HMIM][PF(_6)] 100</td>
<td>2.386(6.290)</td>
<td>30.02(6.738)</td>
<td>79.6(6.069)</td>
<td>20.48</td>
</tr>
<tr>
<td>200</td>
<td>1.796(6.958)</td>
<td>27.39(6.575)</td>
<td>99.6(6.435)</td>
<td>36.45</td>
</tr>
<tr>
<td>300</td>
<td>3.207(7.055)</td>
<td>16.93(6.883)</td>
<td>162.7(6.675)</td>
<td>61.09</td>
</tr>
<tr>
<td>400</td>
<td>2.487(8.392)</td>
<td>15.78(7.307)</td>
<td>192.7(7.572)</td>
<td>67.15</td>
</tr>
<tr>
<td>500</td>
<td>2.105(11.163)</td>
<td>14.29(8.944)</td>
<td>222.5(9.740)</td>
<td>71.55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>R(_s) (Ω cm(^2))</th>
<th>C(_{dl}) (µF cm(^{-2}))</th>
<th>R(_{ct}) (Ω cm(^2))</th>
<th>E(_{EIS}) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HMIM][I] 100</td>
<td>1.711(9.572)</td>
<td>14.73(7.289)</td>
<td>151.6(7.460)</td>
<td>58.25</td>
</tr>
<tr>
<td>200</td>
<td>1.706(11.029)</td>
<td>11.90(7.832)</td>
<td>173.1(8.030)</td>
<td>63.43</td>
</tr>
<tr>
<td>300</td>
<td>1.871(11.168)</td>
<td>8.35(7.251)</td>
<td>216.5(7.454)</td>
<td>70.76</td>
</tr>
<tr>
<td>400</td>
<td>7.95(14.705)</td>
<td>5.21(12.265)</td>
<td>313.5(11.029)</td>
<td>79.81</td>
</tr>
<tr>
<td>500</td>
<td>2.752(12.979)</td>
<td>11.91(10.451)</td>
<td>278.9(11.683)</td>
<td>77.30</td>
</tr>
</tbody>
</table>
The decrease of $C_{dl}$ at the metal/solution interface with increasing the inhibitor concentration can result from a decrease in local dielectric constant which indicates that the inhibitors were adsorbed on the surface at both anodic and cathodic sites [77]. Decrease in $C_{dl}$ could also mean an increase in the thickness of a protective layer at electrode surface, enhancing therefore the corrosion resistance of the studied mild steel. The thickness of the protective layer ($d$) is related to $C_{dl}$ according to the following equation.

$$C_{dl} = \frac{\varepsilon \varepsilon_0}{d}$$

(29)

where, $\varepsilon$ is the dielectric constant of the protective layer and $\varepsilon_0$ is the permittivity of free space.

It was also observed that the %IE increases as the concentration of the studied ionic liquids increases except at 500 ppm of [HMIM][BF₄] and [HMIM][I] inhibitors where a small and insignificant drop in the %IE value was observed and attributed to electrode surface saturation or the inhibitor achieving a maximum efficiency at critical inhibitor concentration thus decreasing their activities as reported by others in literature [78-80]. At 500 ppm concentration of the inhibitors, the %IE follows the order, [HMIM][BF₄] (77.39%) > [HMIM][I] (77.30%) > [HMIM][TIO] (71.87%) ≥ [HMIM][PF₆] (71.55%). This order is clearly summarized pictorially for all concentrations on the plot of %IE versus inhibitors concentrations graphs (Fig. 4.11). Therefore, within the limit of experimental errors employed in this study, it could be concluded that the %IE data obtained for the inhibitors from EIS study agreed favorably with values obtained using the potentiodynamic polarisation technique.

The corresponding Bode impedance plots are also shown in Figures 4.6 - 4.9. Bode plots are important because they give more insight information into the mechanism or reaction at the electrode/electrolyte interface, and provide clear pictures on the electrical properties of the system (i.e capacitive, resistive or inductive) based on the phase angles, or the logarithm function of the impedance. Similar to what was observed from the Nyquist plots, the Bode impedance plots for the mild steel in the presence of inhibitor showed increasing phase angles with increasing concentration of the inhibitors as compared with the blank test. This suggests that the corrosion rate is reduced in the presence of the corrosion inhibitor [81]. Similar phenomenon have been observed and reported for other corrosion inhibitors of mild steels in literature [69].

From the two methods used, EIS has been proven to be the most reliable and intensive method of interrogating what happens between the electrode and electrolyte interface as compared to PDP. From the results obtained in this work, [HMIM][BF₄] is the best inhibitor for mild steel corrosion in acidic medium. Below is the plot of inhibition efficiency vs concentration from the EIS technique.
Figure 4.11: Inhibition Efficiency versus Concentration from the Electrochemical Impedance Spectroscopy technique

4.2 ADSORPTION ISOTHERM AND THERMODYNAMIC PARAMETERS

Adsorption isotherms can be used to describe the metal inhibitor interactions. It helps in showing the mechanism followed during the adsorption process between the metal surface and the inhibitor [67, 82]. Example of adsorption isotherms includes Frumkin, Flory-Huggins, Freundlich, Temkin, Bockris-Swinkles and Langmuir adsorption isotherms. In this study, Temkin and Langmuir adsorption isotherms were used to determine the inhibitors adsorption equilibrium constant ($K_{ads}$) from the Tafel polarisation and the EIS data as they gave the best linear fit when applied to the studied inhibitors data. Langmuir adsorption isotherm which is the plot of concentration of the inhibitor/surface coverage against the concentration of the inhibitor (Eqn 30) gave the best linear relationship for [HMIM][BF₄], [HMIM][TfO], and [HMIM][I], while Temkin adsorption isotherm which is the plot of surface coverage ($\theta$) against logarithmic of concentration (Eqn 31) gave the best linear relationship for [HMIM][PF₆]. In Langmuir adsorption isotherm, surface coverage ($\theta$) of the inhibitor on the mild steel surface is related to the concentration of the inhibitor ($C_{inh}$) in the bulk solution according to the following equation: This equation can be rearranged to be like the equation of a straight line as follows;

$$\frac{C}{\theta} = mC + \frac{1}{K_{ads}}$$

where $C$ is the concentration of the inhibitors, $\theta$ the degree of surface coverage, $K_{ads}$ is the equilibrium constant of the adsorption/desorption process and $m$ is the slope. In Eqn 30, $C/\theta$
represents the y-axis, C the x-axis, m the slope and 1/K_{ads} the intercept on y-axis. For Temkin adsorption isotherm, the following equation was used:

\[-2a\theta = \ln K + \ln C\]  \hspace{1cm} (31)

where \(\theta\) is surface coverage, \(K_{ads}\) equilibrium constant of adsorption-desorption process, \(\text{"a"}\) is molecular interaction parameter, and C is the concentration of the inhibitor. The Temkin parameter was calculated using the following equation;

\[\text{Slope} = -\frac{1}{2a}\]  \hspace{1cm} (32)

Then \(K_{ads}\) was calculated using the following equation;

\[\text{Intercept} = -\frac{1}{2a} \ln K_{ads}\]  \hspace{1cm} (33)

Gibbs free energies of adsorption (\(\Delta G_0^{ads}\)) for the four ionic liquids studied were calculated from the \(K_{ads}\) value using the equation below;

\[\Delta G_0^{ads} = -RT\ln(55.5K_{ads})\]  \hspace{1cm} (34)

where \(\Delta G_0^{ads}\) is the Gibbs free energy of adsorption, the value 55.5 is the molar concentration of water in the solution, \(T\) is the absolute temperature in Kelvin and \(K_{ads}\) is the equilibrium constant for the adsorption process. Negative values of \(\Delta G_0^{ads}\) shows a spontaneous process while positive values indicate non-spontaneous.

The Langmuir adsorption plots are presented in Figure 4.12 while the Temkin plot is presented in Figure 4.13. The estimated \(K_{ads}\) and Gibbs free energies of adsorption (\(\Delta G_0^{ads}\)) for the four inhibitors studied are presented in Table 4.3.
Figure 4.12: Langmuir adsorption isotherm plot for [HMIM][BF₄], [HMIM][TfO], and [HMIM][I] using the (a) Tafel and (b) EIS experimental data respectively.
Figure 4.13: Temkin adsorption isotherm plot for [HMIM][PF₆] using the (a) Tafel and (b) EIS experimental data respectively.
Table 4.3: Adsorption parameters derived from the Langmuir and Temkin adsorption isotherm plots for the inhibitors.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$K_{ads}$ $(10^3 \times \text{mol}^{-1})$</th>
<th>molecular interaction parameter (ppm)</th>
<th>$-\Delta G_{ads}^0$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TAFEL</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[HMIM][BF$_4$]</td>
<td>1.49</td>
<td></td>
<td>-28.53</td>
</tr>
<tr>
<td>[HMIM][TfO]</td>
<td>3.47</td>
<td></td>
<td>-30.66</td>
</tr>
<tr>
<td>[HMIM][I]</td>
<td>2.42</td>
<td>-1.475</td>
<td>-29.76</td>
</tr>
<tr>
<td>[HMIM][PF$_6$]</td>
<td>6.16</td>
<td></td>
<td>-32.10</td>
</tr>
<tr>
<td><strong>EIS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[HMIM][BF$_4$]</td>
<td>3.51</td>
<td></td>
<td>-30.69</td>
</tr>
<tr>
<td>[HMIM][TfO]</td>
<td>1.47</td>
<td></td>
<td>-23.76</td>
</tr>
<tr>
<td>[HMIM][I]</td>
<td>4.15</td>
<td>-1.475</td>
<td>-31.11</td>
</tr>
<tr>
<td>[HMIM][PF$_6$]</td>
<td>5.42</td>
<td></td>
<td>-31.80</td>
</tr>
</tbody>
</table>

$K_{ads}$ is an important parameter in corrosion inhibition studies as it helps in determining the efficiency in binding potential of the inhibitor onto the metal surface. Higher values of $K_{ads}$ suggests efficient binding potential of the inhibitor onto the metal surface [83]. The Temkin parameter ‘a’ values indicates the repulsive nature of the inhibitor on the metal surface. The negative values obtained for [HMIM][PF$_6$] in this study suggest that repulsion exists in the adsorption layer [84].

All values of $\Delta G_{ads}^0$ of the studied ionic liquids inhibitors are negative implying that the process is spontaneous. Similarly, adsorption mechanism such as physical and chemical adsorption can be evaluated using the calculated values of $\Delta G_{ads}^0$. Values around -20 kJ.mol$^{-1}$ and less are associated with physical adsorption mechanism (physisorption process) while values around -40 kJ.mol$^{-1}$ and more are associated with chemical adsorption mechanism (chemisorption process) [85, 86]. Values around -40 kJmol$^{-1}$ or less involve charge sharing or charge transfer between the metal and the organic molecules (chemisorption) [87]. From Table 4.3, it can be observed that the values of $\Delta G_{ads}^0$ range from -23.76 to -38.36 kJ.mol$^{-1}$ suggesting that the adsorption mechanism process by the studied ionic liquids inhibitors is chemical adsorption [87-91].
4.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fourier transform infrared spectroscopy was implored to study the ionic liquids. The FTIR spectra of pure ILs, and ILs with mild steel at an optimum concentration of inhibitor (500 ppm) at 303 K after 24 h immersion of mild steel specimens as shown in Figures 4.14-4.17.

The IR bands observed at 680, 776 and 858 cm\(^{-1}\) corresponds to (C-H) bending vibration. The intensity band observed at 1040 cm\(^{-1}\) corresponds to (C-H) stretching vibration. The band assigned at 1640 cm\(^{-1}\) corresponds to \(\delta\) (H-O-H) stretching vibration and the spectral band at 1100 cm\(^{-1}\) was due to \(\delta\) (C-H) stretching vibration which is mainly observed for pure Borate Ionic liquid. The intensity band at 637 cm\(^{-1}\) corresponds to C-C stretching and the spectral intensity bands observed at 1165 cm\(^{-1}\) corresponds to S=O stretching and the band at 1250 cm\(^{-1}\) corresponds to C-N stretching vibration and the spectral band assigned at 1648 cm\(^{-1}\) corresponds to C=C stretching vibration of alkene which is mainly observed for pure Sulphonate Ionic liquid. The spectral band at 630 cm\(^{-1}\) corresponds to C-I stretching vibration. A band at 1640 cm\(^{-1}\) was due to C=N stretching and 3320 cm\(^{-1}\) was due to N-H stretching vibration of secondary amine which is mainly observed for pure Phosphate Ionic liquid. The strong band 1040 cm\(^{-1}\) corresponds to (C-H) stretching vibration and the bands assigned at 1167 and 1237 cm\(^{-1}\) corresponds to terminal alkyl halides, the C–H wag of the –CH\(_2\)X group. The intensity band at 1465 cm\(^{-1}\) corresponds to C–H bending of alkane group. The spectral band at 1572 cm\(^{-1}\) was due to C=C stretching vibration of cyclic alkene. The spectral intensity bands at 2849, 2927 and 3070 cm\(^{-1}\) were assigned to C-H stretching vibration of alkene which is mainly observed for pure Iodide Ionic liquid. A band at 1640 cm\(^{-1}\) was due to C=N stretching and 3320 cm\(^{-1}\) was due to N-H stretching vibration of secondary amine which is mainly observed for the mild steel specimens at optimum concentration (500 ppm) and after 24 h of immersion for all Ionic liquids and all other peaks were disappeared.

Figure 4.14: IR Spectra of pure [HMIM][BF\(_4\)], 500 ppm [HMIM][BF\(_4\)] alone and 500 ppm [HMIM][BF\(_4\)] + Immersed MS.
Figure 4.15: IR Spectra of pure [HMIM][TfO], 500 ppm [HMIM][TfO] alone and 500 ppm [HMIM][TfO] + Immersed MS.

Figure 4.16: IR Spectra of pure [HMIM][I], 500 ppm [HMIM][I] alone and 500 ppm [HMIM][I] + Immersed MS.
Figure 4.17: IR Spectra of 500 ppm [HMIM][PF₆] alone, and 500 ppm [HMIM][PF₆] + Immersed MS.

4.4. ULTRAVIOLET-VISIBLE SPECTROPHOTOMETRY (UV)

UV-Visible spectroscopy provides a strong evidence for the interaction of the metal with the ILs as inhibitor. The UV-Visible absorption spectra of pure ILs, and ILs with mild steel at an optimum concentration of inhibitor (500 ppm) at 303 K after 24 h immersion of mild steel specimens as shown in Figures 4.18 – 4.21.

The electronic absorption spectrum of both the inhibitors before the mild steel immersion shows bands in the UV-Visible region due to π-π* and n-π* transitions with a considerable charge transfer character. After 24 h immersion of mild steel in the presence of inhibitors, the observed change in the position and absorbance of the absorption maximum indicate the interaction between the inhibitors and iron in solution. These experimental findings provide strong evidence for the complex formed between Fe²⁺ and inhibitors in a 1 M HCl solution. UV-Visible observation confirms the formation of a protective film of metal-inhibitor complex on the metal surface.
Figure 4.18: UV/Vis spectra of pure [HMIM][BF₄], 500 ppm [HMIM][BF₄] alone and 500 ppm [HMIM][BF₄] + Immersed MS.

Figure 4.19: UV/Vis spectra of pure [HMIM][TfO], 500 ppm [HMIM][TfO] alone and 500 ppm [HMIM][TfO] + Immersed MS.
**Figure 4.20:** UV/Vis spectra of pure [HMIM][I], 500 ppm [HMIM][I] alone and 500 ppm [HMIM][I] + Immersed MS.

**Figure 4.21:** UV/Vis Spectra of 500 ppm [HMIM][PF₆] alone, and 500 ppm [HMIM][PF₆] + Immersed MS.
4.5 QUANTUM CHEMICAL CALCULATIONS

Molecular modelling encompasses all theoretical methods and computational techniques used to obtain molecular properties. Studies have shown that the properties of molecules are related to the activity the molecule exhibit. Therefore studying the properties of molecules e.g., the structure of the molecule, the energy of the molecule, the dipole moment and electronic as well as magnetic properties influences the activity that the molecule would have. The main objectives of quantum chemical studies are therefore to find the properties that are related to a given activity of a molecule. The developed computational methodology belongs to either the molecular mechanics or quantum chemical mechanics. Quantum chemical mechanics methods are preferred because they provide information on the influence of electronic properties on the activity of the molecule.

In the study of corrosion inhibitors, the interest is in finding quantum chemical properties of a given molecule and to relate them to the corrosion inhibition ability of the given molecule. Computational parameters such as the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), dipole moment, energy gap (∆E), ionization potential (IP), electron affinity (EA), and the global hardness (η) and softness (σ). The following are the optimised structures of the studied ionic liquids (Fig. 4.22).

![Optimised geometries of the studied ionic liquids. The grey colour are the C atoms, the blue colour denote N atoms, white colour denote the H atoms, the purple colour denotes I, the yellow colour denotes the sulphate atom, the colour red colour denotes the oxygen atoms, the pink colour denotes the borate atom, the orange colour denotes the phosphate atom and the turquoise colour denotes the fluoride atoms.](image-url)

Figure 4.22: Optimised geometries of the studied ionic liquids. The grey colour are the C atoms, the blue colour denote N atoms, white colour denote the H atoms, the purple colour denotes I, the yellow colour denotes the sulphate atom, the colour red colour denotes the oxygen atoms, the pink colour denotes the borate atom, the orange colour denotes the phosphate atom and the turquoise colour denotes the fluoride atoms.
Figure 4.23: Highest occupied molecular orbital (HOMO) of the studied ionic liquids
Figure 4.24: Lowest unoccupied molecular orbital (LUMO) of the studied ionic liquids

From this optimised structures of the studied ionic liquids, it can clearly be seen that for both [HMIM][I] and [HMIM][TfO] the electron rich site is from the anion while for both [HMIM][BF₄] and [HMIM][PF₆] have their electron rich site on their cation. It is observed from the $E_{\text{HOMO}}$ calculated on Table 4.4 that both [HMIM][I] and [HMIM][TfO] have the highest $E_{\text{HOMO}}$ values than both [HMIM][BF₄] and [HMIM][PF₆] confirming the fact that they have high electron donating ability. This electron donating ability from both [HMIM][I] and [HMIM][TfO] is from the anion, since anions are generally negative. While [HMIM][BF₄] and [HMIM][PF₆] have their electron rich density on their cation have lower $E_{\text{HOMO}}$ as the cation is generally positive. From the $E_{\text{LUMO}}$, it can be seen that all of the lowest unoccupied molecular orbital are from the cation than from the anion since the cation is generally positive thus electron deficient than the anion.
Table 4.4: Quantum chemical parameters of the studied ionic liquids

<table>
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<tr>
<th>Calculated structures</th>
<th>Dipole Moment (Debye)</th>
<th>( E_{\text{HOMO}} ) eV</th>
<th>( E_{\text{LUMO}} ) eV</th>
<th>( \Delta E ) eV</th>
<th>IP eV</th>
<th>EA eV</th>
<th>Hardness ( \eta )</th>
<th>Softness ( \sigma )</th>
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<tr>
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<td>3.44</td>
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</table>

Dipole moments tell us about the charge separation in a molecule. The larger the difference in electronegativities of bonded atoms, the larger the dipole moment. The dipole moment gives information about the polarity and reactivity of the compounds and it is related to the hydrophobic character of the molecules [92]. Although literature is inconsistent on the use of dipole moment (\( \mu \)) as a predictor for the direction of a corrosion inhibition reaction, it is generally agreed that the adsorption of polar compounds possessing high dipole moments on the metal surface should lead to better inhibition efficiency. A comparison of the trend in the dipole moment of the studied ionic liquids show that there is no direct correlation.

The highest occupied molecular orbital (HOMO) is the orbital which is lastly occupied. It is therefore closest to the unoccupied molecular orbitals and it has the highest energy among the occupied molecular orbitals. For this reason, if any electron has to be donated to the unoccupied molecular orbitals of an electron deficient species, they are likely to come from this orbital. The lowest unoccupied molecular orbital (LUMO) is the first orbital without electrons among the list of unoccupied (virtual) molecular orbitals. It therefore has the lowest energy among the orbitals without electrons and if any pair of electrons is to be accepted by the molecular system, it is likely to occupy the LUMO. These energy values play very significant role in the understanding of the interaction between an inhibitor and a metal surface. \( E_{\text{HOMO}} \) is often associated with the electron donating ability of a molecule [93] and a higher \( E_{\text{HOMO}} \) value indicates higher tendency of the molecule to donate electron(s) to an electron deficient species, in this case the metal surface. The compound or molecule having the highest tendency to donate electrons to the surface of the metal will therefore have the highest tendency to be adsorbed onto the metal surface. \( E_{\text{LUMO}} \) indicates the ability of the molecule to accept electrons. The lower the value of \( E_{\text{LUMO}} \), the more probable the molecule would accept electrons [10]. So the order [HMIM][I] > [HMIM][TfO] > [HMIM][BF₄] > [HMIM][PF₆] is observed in order of decreasing \( E_{\text{HOMO}} \) values. The order [HMIM][I] > [HMIM][BF₄] > [HMIM][TfO] > [HMIM][PF₆] is observed for \( E_{\text{LUMO}} \) in decreasing order. The [HMIM][I] has the highest tendency of donating electrons to the metal and the also has the highest tendency of accepting electrons.

The energy gap is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As energy gap (\( \Delta E \)) decreases, the reactivity of
the molecule increases leading to increase in the %IE of the molecule, that is, when the values of the highest occupied molecular orbital energy (E_{HOMO}) increases, and the lowest unoccupied molecular orbital energy (E_{LUMO}) and energy gap decreases, the inhibition efficiency (%IE) will increases. Lower values of $\Delta E$ will render good inhibition efficiency because the energy to remove an electron from the last occupied orbital will be low because the orbitals will easily interact with each other [94]. So the order is [HMIM][PF_6] > [HMIM][BF_4] > [HMIM][TfO] > [HMIM][I]. [HMIM][I] has the smallest value of the $\Delta E$ thus it has higher tendency towards reaction with the metal surface.

Ionization Polarizability is the ratio of induced dipole moment to the intensity of the electric field. The induced dipole moment is proportional to polarizability [95]. Some attempts have been made to relate the polarizability of some corrosion inhibitors to their inhibition efficiency, as already mentioned, the induced dipole moment is proportional to polarizability, thus increasing with the increase in the molecular volume [96]. In general, polarizability correlates with the interaction between electrons and the nucleus. The amount of electrons in a molecule affects how tight the nuclear charge can control the overall charge distribution [97]. Polarizability is one of the main factors in electrostatic interaction between an inhibitor molecule and a metal. So the order is [HMIM][PF_6] > [HMIM][BF_4] > [HMIM][TfO] > [HMIM][I] in decreasing order. [HMIM][I] has the lowest ionization polarizability thus the electrons in the [HMIM][I] are not held tight as compared to the other ionic liquids and thus can react easily with the metal surface.

Electron affinity (A) is the energy released when an electron is added to a neutral molecule; it is related to $E_{LUMO}$ through the equation:

$$A \equiv -E_{LUMO} \quad (35)$$

Global hardness ($\eta$) and softness ($\sigma$) are molecular properties that also facilitate the analysis of the molecular reactivity [10]. Soft molecules are more reactive than hard molecules if electron transfer or rearrangement is necessary for the reaction. Hard molecules resist changes in their electron number and distribution [98]. Hard molecules have a large energy gap ($\Delta E$) value and the soft molecule has a small energy gap ($\Delta E$) value. So the order followed is [HMIM][PF_6] $\approx$ [HMIM][BF_4] > [HMIM][TfO] > [HMIM][I] in increasing hardness and [HMIM][I] > [HMIM][TfO] > [HMIM][PF_6] $\approx$ [HMIM][BF_4] in softness. [HMIM][I] has the lowest value of global hardness and the highest value of global softness denoting that it is more reactive in electron transfer and does not resist change in its electron number and distribution.

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Figure 4.25: Optimized structures of the studied ionic liquids with Mulliken atomic charges
Figure 4.26: Optimised structures of the studied ionic liquids and the atom numbering utilized in the Table 4.5. The atoms of the cation and the anion units are numbered.

4.5.1 Results From The Fukui Function Analysis

The Fukui function, denoted by \( f(r) \), is defined as the differential change in electron density due to an infinitesimal change in the number of electrons [99]. The preferred site for nucleophilic attack is the atom or region in the molecule where the value of \( f^+ \) is the highest while the site for electrophilic attack is the atom/region in the molecule where the value of \( f^- \) is the highest. The Fukui functions are utilised in the study of corrosion inhibitors in terms of characterising the inhibitors ability as electron donor or acceptor. The Fukui functions provide indication of the selectivity of the inhibitors. This means that it provides information on the preferred site on the molecule on which the inhibitor molecule is likely to interact with the metal surface.

They state "the regions of a molecule where the Fukui function is large are chemically softer than the regions where the Fukui function is small [100]. Fukui function provide information about the atoms in a molecule that have a tendency to either donate (nucleophilic character) or accept (electrophilic character) an electron or pair of electrons [101]. The local selectivity of a corrosion inhibitor is best analyses by means of condensed Fukui function. The calculated values of the Fukui functions for the non-hydrogen atoms in the ionic liquids are shown in Table 4.5. The preferred site for nucleophilic attack is the atom 7 which is a carbon. The preference for atom 7 for nucleophilic attack is due to the high positive charge at carbon arising from the electron deficiency in the N=C bond. The preferred site for electrophilic attack is the atom 8 of the cation and atom 13 of the anion.
Table 4.5: The condensed Fukui functions and their charges on the atoms of the studied ionic liquids

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<th>Charge on the Cation species</th>
<th>Charge on the Anion species</th>
<th>(f^-)</th>
<th>(f^+)</th>
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**[HMIM][PF_6]**

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CHAPTER 5

CONCLUSION

The following conclusions can be drawn from the results obtained from this study:

• The electrochemical measurements were performed and the inhibition efficiency of the ionic liquids studied was found to be increasing as the inhibitor concentration increased (from 100 ppm to 500 ppm).

• The thermodynamic parameter such as change in free energy ($\Delta G_{ads}^0$) was obtained from the calculations. Result showed that the reaction was spontaneous since $\Delta G_{ads}^0$ value was negative. The values of $\Delta G_{ads}^0$ range from -23.76 to -38.36 kJ.mol$^{-1}$ suggesting that the adsorption mechanism process by the studied ionic liquids inhibitors is by chemical adsorption.

• The mechanism of mixed-type inhibition adsorption has been proposed from the potentiodynamic polarization (PDP) studies.

• Three of the ionic liquids, 1-Hexyl-3-methylimidazolium iodide [HMIM][I], 1-Hexyl-3-methylimidazolium tetrafluoroborate [HMIM][BF$_4$] and 1-Hexyl-3-methylimidazolium trifluoromethanesulfonate [HMIM][TfO] obeyed the Langmuir adsorption isotherm while 1-Hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF$_6$] obeyed the Temkin adsorption isotherm.

• Fourier transform infrared (FTIR) and ultraviolet-visible (Uv-Vis) spectroscopy studies have been used to support the results obtained from the electrochemical technique.

• Trends in the quantum chemical parameters support some of the order of inhibition efficiency values obtained from the experimental data.
REFERENCES


10. L.C. Murulana. Experimental And Quantum Chemical Studies Of Some Imidazolium Based Ionic Liquids As Corrosion Inhibition For Mild Steel In Acidic Medium. MSc Thesis, North West University (Mafikeng Campus) 2012.


APPENDIX: FORMULAS USED

1. Electronegativity:

\[ \chi \equiv -\frac{1}{2} (E_{\text{HOMO}} + E_{\text{LUMO}}) \]

2. Global hardness:

\[ \eta \equiv -\frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}}) \]

3. Energy Gap

\[ \Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \]

4. Global softness:

\[ \sigma = \frac{1}{\eta} \equiv -\frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}}) \]

5. Electron affinity related to \( E_{\text{HOMO}} \):

\[ I \equiv -E_{\text{HOMO}} \]

6. Electron affinity related to \( E_{\text{LUMO}} \):

\[ \Delta \equiv -E_{\text{LUMO}} \]

7. Potentiodynamic polarization inhibition efficiency:

\[ \mu_{\text{PDP}} = \frac{i_{\text{cor}}^0 - i_{\text{cor}}^1}{i_{\text{cor}}^1} \times 100 \]

8. Electrochemical impedance spectroscopy inhibition efficiency:

\[ E_{\text{EIS}} \% = \left( 1 - \frac{R^0_{\text{ct}}}{R_{\text{ct}}} \right) \times 100 \]

9. Surface coverage (with thermodynamic parameters):
\[ \theta = \frac{K_{\text{ads}} C_{\text{inh}}}{1 + K_{\text{ads}} C_{\text{inh}}} \]

10. Surface coverage (with thermodynamic parameters) rearranged:

\[ \frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \]

11. Surface coverage (with thermodynamic parameters) for Temkin

\[ \theta = -\frac{1}{2a} (\ln K_{\text{ads}} + \ln C) \]

12. Current response, constant phase element:

\[ Z_{\text{CPE}} = Y_0^{-1} (i\omega)^{-n} \]

13. Double layer capacitance:

\[ C_{\phi} = (Y_0 R_{\text{cl}}^{1-a})^{1/n} \]

14. Thickness of the protective layer (d):

\[ C_{d1} = \frac{\varepsilon \varepsilon_0}{d} \]

15. Surface coverage (EIS):

\[ \theta = 1 - \frac{R_{\text{ct}}^0}{R_{\text{ct}}} \]

16. Nucleophilic Fukui function:

\[ f^+ = q_{(N+1)} - q_N \]
17. Electrophilic Fukui function:

\[ f^- = q_N - q_{(N-1)} \]

18. Gibbs free energy of adsorption:

\[ k = \frac{1}{55.5} \exp \left( -\frac{\Delta G_{ads}^o}{RT} \right) \]