

**EXPERIMENTAL, QUANTUM CHEMICAL, MONTE CARLO
SIMULATIONS AND QSAR STUDIES OF SOME HYDANTOIN
DERIVATIVES AS CORROSION INHIBITORS FOR MILD STEEL
IN 0.5 M HCl SOLUTION**

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B.Sc (UL), B.Sc (Hons) (UL)

Dissertation submitted in fulfilment of the requirements for the
degree Master of Science in Chemistry at the Mafikeng Campus
of the North-West University

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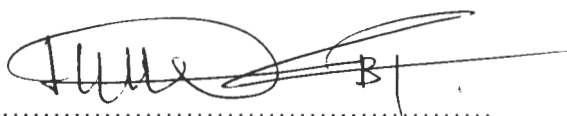
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DECLARATION

I hereby declare that this project which is submitted in fulfilment of the requirements for the degree of Master of Science in Chemistry (MSc.) at the North-West University, Mafikeng Campus has not been previously submitted at this university or any other university. The following research study was compiled and written by me under the supervision of Prof. Eno E. Ebenso. All sources of my information are acknowledged in the reference pages and quotations are indicated by appropriate punctuation marks.

A handwritten signature in black ink, consisting of a series of loops and a long horizontal stroke ending in a vertical line.

Bryan Phuti Moloto

DEDICATION

This research work is solely dedicated to my mother, Mapitsi Julie Moloto and my late father, Moloko Sophonia Moloto (MAY YOUR UNIFYING SPIRIT REST IN PEACE). I am who I am today, because of you.

ACKNOWLEDGEMENT

First and foremost, I am grateful to GOD ALMIGHTY for without His grace and blessings, this study would not have been possible.

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GOD ALMIGHTY MAY CONTINUE BLESSING YOU ALL.

ABSTRACT

Effects of some hydantoin derivatives namely, 1-methylhydantoin (MHYD), 5,5-dimethylhydantoin (DMHYD), hydantoin-5-acetic acid (HYDAC), 1,3-dibromo-5,5-dimethylhydantoin (DBDMHYD), 5-methyl-5-phenylhydantoin (MPHYD), and the parent hydantoin (HYD) on mild steel corrosion in 0.5 M HCl solution were investigated using experimental and theoretical methods. The hydantoin and its derivatives act as good inhibitors towards mild steel corrosion in acidic solution of 0.5M HCl and their inhibition efficiencies at the optimum concentration of 50 mM follows the order: DBDMHYD (89.79%) > HYD (88.06%) > DMHYD (86.40%) > HYDAC (78.38%) > MPHYD (74.49%). The difference in their inhibition efficiencies is attributed to presence of different substituents/ groups in their molecular structures those affect their adsorption tendency due to steric hindrance as well as their solubility in the test solution. Tafel polarization measurements showed that the hydantoin derivatives are mixed type inhibitors. In addition, MHYD, DMHYD and HYD showed predominantly anodic inhibitive actions. Impedance studies revealed that the compounds inhibit mild steel corrosion in the acid by adsorbing on the steel surface to form protective film. The inhibitive actions of the compounds did not change the mechanism of corrosion reaction. The adsorption of inhibitor molecules obeyed the Langmuir adsorption isotherm model. The values of change in Gibbs free energy for the adsorption process suggest physisorption mechanism. Inhibition efficiency increased with increasing concentration of hydantoin derivatives. Quantum chemical calculations and molecular dynamic simulations were carried out to corroborate experimental results. Both the experimental and theoretical studies revealed that DBDMHYD showed the best inhibition performance. Quantitative structure activity relationship (QSAR) studies showed that the inhibitive performances of the studied compounds are well correlated with their molecular weights, frontier molecular orbitals energy gap, fraction of electron transferred and binding energy.

LIST OF ABBREVIATIONS

CR	Corrosion rate
EIS	Electrochemical impendence spectroscopy
PDP	Potentiodynamic polarization
MCS	Monte Carlo simulation
DFT	Density functional theory
EA	Electron affinity
EIS	Electrochemical impedance spectroscopy
HF	Hatree-Fock
HOMO	Highest occupied molecular orbital
IE	Inhibition efficiency
IP	Ionization potential
LUMO	Lowest unoccupied molecular orbital
MD	Molecular dynamics
OCP	Open circuit potential
PCM	Polarizable continuum model
SiC	Silicon carbide
SEM-EDX	Scanning electron microscopy-energy dispersive X-ray
FTIR	Fourier-transformed infrared
HCl	Hydrochloric acid
M	Metal
US	United States
MINTEK	National Minerals Research Organization
CorrISA	Corrosion Institute of South Africa
QSAR	Quantitative structure activity relationship
SCC	Stress corrosion cracking
ΔG	Free energy gap

ΔG°	Standard free energy change
VPI	Vapor-phase inhibitors
SEM-EDX	Scanning Electron Microscopy with Energy-dispersive X-ray
MHD	Dimethylol-5-methyl hydantoin
HYD	Hydantoin
MHYD	1-Methylhydantoin
DMHYD	5,5-Dimethylhydantoin
DBDMHYD	1,3-Dibromo-5,5-dimethylhydantoin
MPHYD	5-Methyl-5-phenylhydantoin
HYDAC	Hydantoin-5-acetic acid
FMOs	Frontier molecular orbitals
ΔN	Fraction of electrons transferred from the inhibitor to the metal
η	Global hardness
χ	Global electronegativity

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CHAPTER 1

INTRODUCTION TO CORROSION

1.1. BACKGROUND OF CORROSION

The word corrosion is as old as the earth itself, commonly known as rust, an undesirable phenomena which destroys the luster and the beauty of the objects and shortens their life. An essay titled “Ferrum Corrumpitar” explains in detail the destruction of iron, which was written by Roman Philosopher, Pliny (AD 23-79). Corrosion had affected and is still affecting the technical progress as well as the quality of daily lives of people. The AHMAD:Business Research Projects further explained that there’s a historical record of corrosion observations by several scientists and philosophers, but a little regarding the causes and the mechanism of corrosion until the article titled “Mechanical Origin of Corrosiveness” was written by Robert Boyle.¹

Acid attack was regarded as electrochemical process in 1801 by Wollaston and anonymous French scientist also suggested that rusting of iron was due to a similar cause.^{2,3}

The effect of impurities in the metal on non-oxidizing acid attack was first reported in 1830 by de la Rive, who noticed that impure zinc was more rapidly affected than that the pure form. Impurities are, however, only one possible cause of this type of attack. Structural properties of the metal such as orientation and variation in size of grains may have some effect on corrosion in certain circumstances and frequently attack takes place at the grain boundaries³.

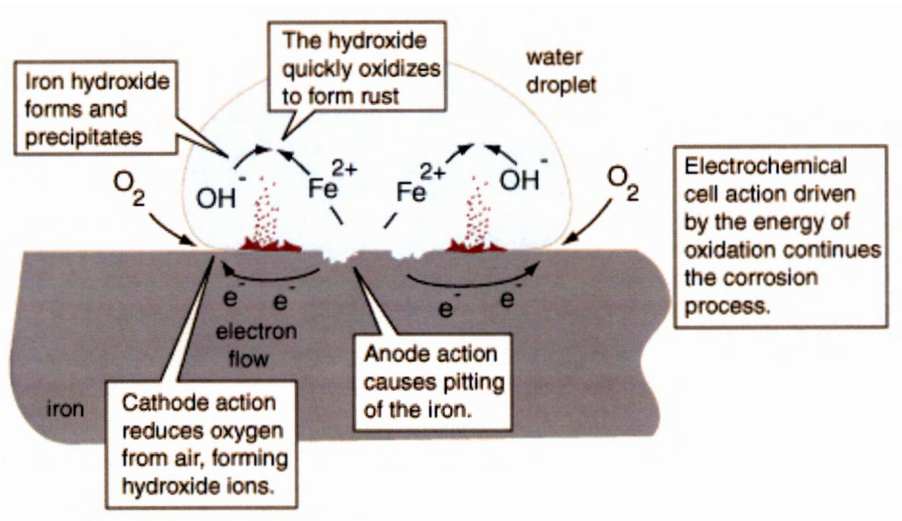
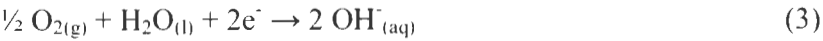
Uhlig suggested that the phenomenon of metallic corrosion was recognized in ancient times and although a considerable amount of work has now been done in this field especially during the last few decades, the complete mechanism is by no means understood².

1.1.1. DEFINITION OF CORROSION

Corrosion is defined as the deterioration or degradation of a metal’s properties as a consequence of chemical reactions with the surrounding environment. Metals generally corrode when exposed to natural environments. Mild steel is a widely used material for various industrial purposes and structural constructions. However, it is highly susceptible to corrosion in various environments, including acidic media.⁴⁻⁷ Corrosion has, in various aggressive media, earned a considerable amount of interest in the past few years.⁴⁻⁶ Corrosion takes place according to the anodic reaction (Eq. 1):



For the corrosion process to occur, the electrons from anodic dissolution of the metal are consumed by adjacent cathodic reaction. There are two possible reactions at the cathodic site, namely: reduction of hydrogen ion to produce hydrogen gas (Eq. 2), which will predominate in acidic solutions; or reduction of dissolved oxygen to form hydroxide ion (Eq. 3), which is often the leading cathodic reaction in neutral to near neutral environments. On the scheme below Metal (M) used to demonstrate this phenomenon is Iron (Fe).



Scheme 1. Corrosion of Iron (Fe).

1.1.2. CORROSIVE ENVIRONMENT

Corrosion is an electrochemical process that involves oxidation (anodic) and reduction (cathodic) reactions on metal surfaces. For metals in soil or water, corrosion is typically a result of contact with soluble salts found in these environments. This process requires moisture to form solutions of soluble salts⁸.

Factors that influence the rate and amount of corrosion include the amount of moisture. A corrosive environment is defined in terms of resistivity, pH and soluble salt content of the soil or water.^{1,8}

Description of an environment is clarified by the following factors:

- Physical state – gas, liquid or solid
- Chemical composition – constituents and concentrations
- Temperature

Examples of these factors are the relative velocity of a solution because of flow or agitation.⁹

1.2. SIGNIFICANCE OF THE STUDY

1.2.1. COST OF CORROSION

Corrosion plays a highly negative role on the world's GDP in general, causing companies to lose more and it is because of this reason why corrosion control studies have been given attention. The economic loss of corrosion globally is estimated to be greater than US1.8-trillion,¹⁰ while in South Africa, according to MINTEK(National Minerals Research Organization) and CorrISA(Corrosion Institute) , the direct cost of corrosion is estimated to be around R130-billion annually. The figure below summarizes the concept of corrosion cost in manufacturing industries.

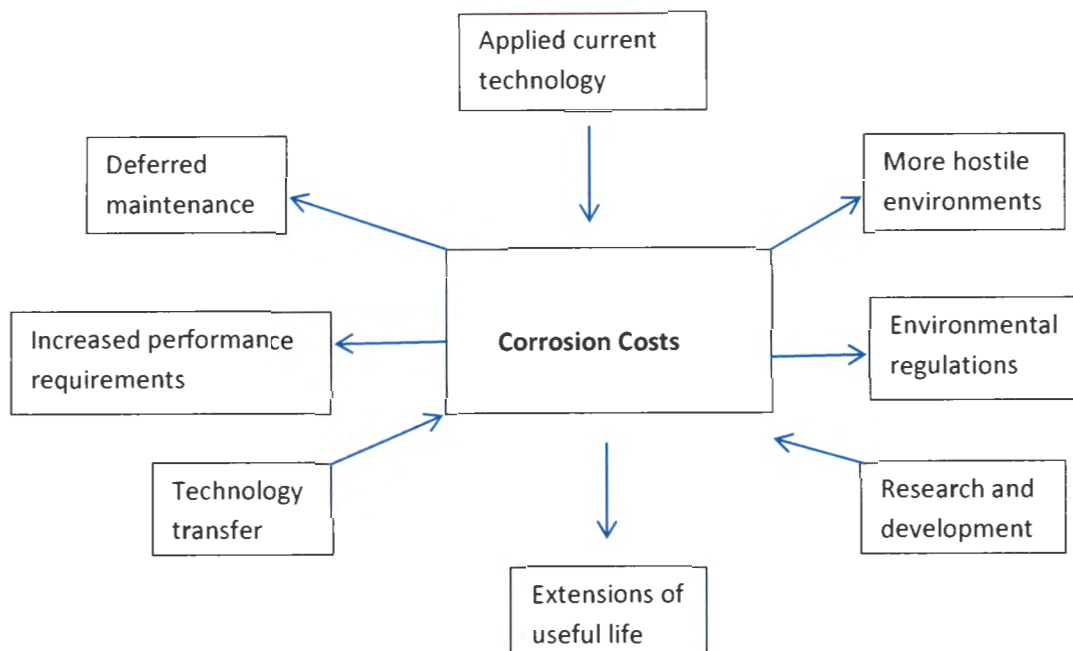


Fig. 1: Factors that increase or reduce costs of corrosion.¹¹

1.3. PROBLEM STATEMENT

1.3.1. THE EFFECTS OF CORROSION

It has been proven that the effects of corrosion affect us directly (it affects the useful lives of our possessions) and indirectly (in that producers and suppliers of goods and services incur corrosion costs, which they pass on to consumers¹⁰).

The impacts of corrosion are often described in economic terms. Financial losses have been assessed in several studies which concluded that premature materials degradation costs industrialized nations approximately three percent of their gross domestic product (GDP). In the United States it is estimated that between \$2- 4 trillion are lost to corrosion each decade²².

In South Africa, according to MINTEK and CorriSA, the direct cost of corrosion is estimated to be around R130-billion

1.4. AIMS AND OBJECTIVES OF THE STUDY

The aim of this study is to investigate the corrosion inhibition properties of six derivatives of hydantoin, namely: Hydantoin, 5,5-dimethylhydantoin, 1,3-Dibromo-5,5-dimethylhydantoin, 1-Methylhydantoin, Hydantoin-5-acetic acid and 5-Methyl-5-phenylhydantoin. The set of compounds selected for the present study has not been considered as corrosion inhibitors or reported anywhere in literature. The work upon completion will make an original contribution to knowledge in the area of corrosion science, electrochemical, quantum chemical and Monte-Carlo simulation and QSAR studies.

The main research aim and objectives of this study are to:

- Study the inhibition efficiency of the hydantoin and its derivatives for mild steel corrosion in 0.5M HCl using electrochemical techniques in order to assess the effect of different substituents attached to the common hydantoin nucleus.
- Study the interaction between the mild steel surface and the inhibitor molecules using UV-Vis spectroscopic method.
- Correlate the experimental order of inhibition efficiency with its molecular structure by computing some computational parameters derived from DFT based quantum chemical calculation, Monte-Carlo simulations and QSAR studies.
- Study the mechanism of adsorption of this new set of compounds on to mild steel surface in acidic medium using several computational studies.
- Study the adsorption of the tested molecules on mild steel surface using Langmuir adsorption isotherm.

CHAPTER 2

LITERATURE REVIEW ON CORROSION INHIBITION AND HYDANTOINS

2.1. CORROSION INHIBITION

2.1.1. TYPES OF CORROSION

The basic types of corrosion can be broken down into eight visually identifiable forms, which are different from one another. This difference enables one to examine a specimen and make a reasonable assumption on the general cause of corrosion and possible measures that can be taken¹².

Different types of corrosion are briefly described below.

General Corrosion: This is also known as uniform attack, it occurs uniformly over the entire surface that is exposed. The metal gets thinner over the entire surface leading to the largest tonnage of metal loss. This form of corrosion is the cheapest to deal with in the industry.¹²

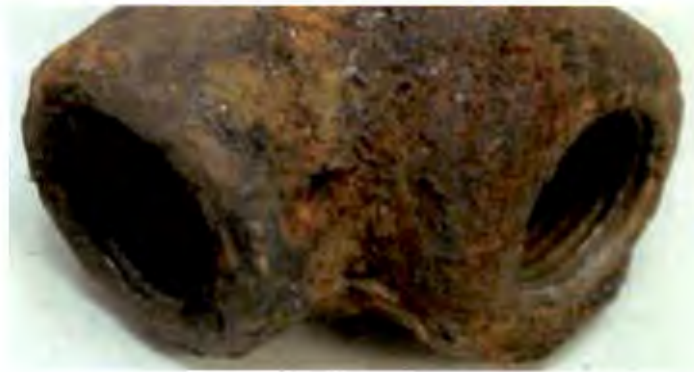


Fig. 2: General corrosion on steel fitting

Galvanic Corrosion: This is also known as two-metal corrosion, it occurs because of the potential difference that exists between two dissimilar metals.¹²

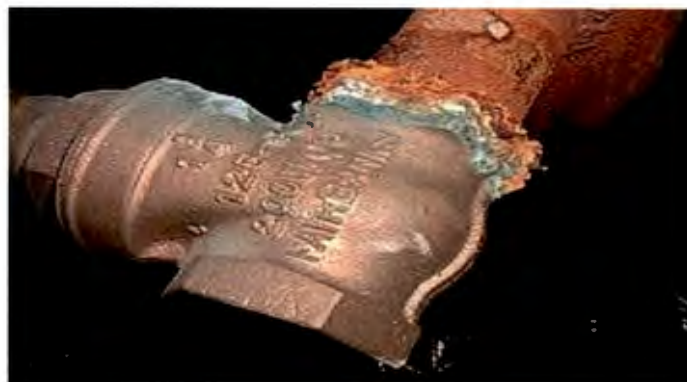


Fig. 3: Galvanic corrosion on pipes.

Crevice Corrosion: This is also known as localized form of corrosion, it generally occurs in cracks, holes, crevices, lap joints and anywhere else that small amounts of solution can lay stagnate.

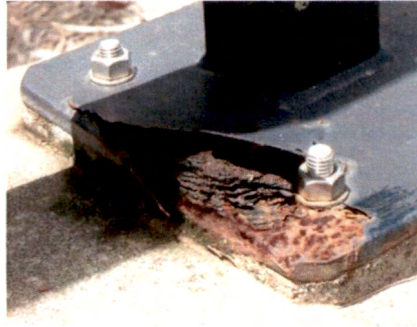


Fig. 4: Crevice corrosion on a handrail post base.

Pitting: It is an extremely localized form of attack that often causes rapid penetration of the wall thickness. The holes that pitting causes can be very small or quite large in diameter.



Fig. 5: Pitting on an oily water line.

Intergranular Corrosion: is the corrosion of the edges of the individual grains that make up the metal.

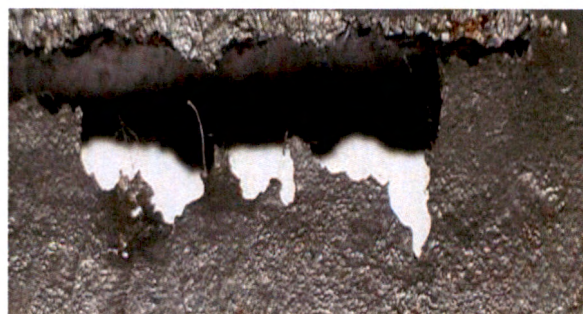


Fig. 6(a): Intergranular corrosion on the heat-affected zone.



Fig. 6(b): Intergranular corrosion on the heat-affected zone of a circumferential weld.

Selective Leaching: This is also known as dealloying, it is the removal of one element from an alloy through a corrosion process. An excellent example of selective leaching is the removal of zinc from brass alloys.¹³



Fig. 7: Selective leaching or dealloying corrosion

Erosion Corrosion: is the accelerated increase in deterioration of a metal due to the velocity of the fluid.



Fig. 8: Erosion corrosion of the shell side fluid in the tube and shell exchanger.

Stress Corrosion Cracking (SCC): is the cracking from a combined presence of tensile stresses and a corrosive medium.



Fig. 9: Stress corrosion cracking

2.1.2. RATE OF CORROSION

The loss of metal per unit of surface and time defines the metallic corrosion rate. This parameter may be measured by weight differences before and after having submitted the metal to the corrosive environment. The speed or rate of deterioration depends on the environmental conditions and the type and condition of the metal under reference. Corrosion rate is best expressed in terms of thickness or weight loss where the surface of the metal corrodes uniformly across the area that has been exposed¹⁴.

For the rate of corrosion to be calculated the following data must be collected:

- (a) Weight lost (the decreased in weight of the metal during the period of reference)
- (b) Density of the metal
- (c) Total surface area initially present
- (d) Length of time taken.

2.1.3. FACTORS THAT AFFECT THE RATE OF CORROSION

The rate of corrosion may be affected in two distinctive ways and they are:

- (a) Nature of the metal
- (b) Nature of the corroding environment

Nature of the Metal¹⁵:

- **Physical state:** the physical state of a metal (such as its grain size) may affect the rate of corrosion. The smaller the grain size of the metal, the greater will be its solubility and therefore experience corrosion.
- **Purity of the metal:** impurities in metal cause heterogeneity and form electrochemical cells, and the anodic parts get corroded.
- **Over voltage:** the over voltage of a metal in a corrosive environment is inversely proportional to corrosion rate.
- **Nature of surface film:** in an aerated atmosphere, practically all metals get covered with a thin surface film of a metal oxide. The ratio of the volumes of the metal oxide to the metal is known as a specific volume ratio. The greater the specific volume ratio, the lesser is the oxidation corrosion rate.
- **Relative areas of the anodic and cathodic parts:** when two dissimilar metals are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part.

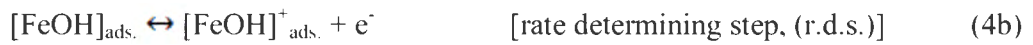
Nature of the Corroding Environment¹⁶:

- **Temperature:** the rate of corrosion is directly proportional to temperature, that is, rise in temperature increases the rate of corrosion because the rate of diffusion of ions increases with the rise in temperature.
- **Humidity of air:** the rate of corrosion will be more when the relative humidity of the environment is high. The moisture acts as solvent (for example, of oxygen) in the air to produce the electrolyte which is required for setting up a corrosion cell.
- **Presence of impurities in atmosphere:** atmosphere in industrial areas contains corrosive gases such as CO₂, H₂S and fumes of HCl, H₂SO₄ etc. In the presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases with the rate of corrosion increasing.
- **Influence of pH:** generally acidic media are more corrosive than alkaline and neutral media.

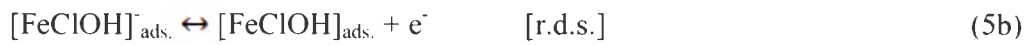
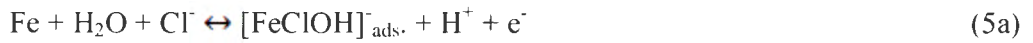
2.1.4. MECHANISM OF CORROSION

A mechanism of corrosion is the actual atomic, molecular, or ionic transport process that takes place at the interface of a material. These processes usually involve more than one definable step, and the major interest is directed towards the slowest (rate determining) step that essentially controls the rate of the overall reaction. The mechanisms for the dissolution of iron are given by¹⁷:

(i) Aqueous solutions:



(ii) Aqueous solutions containing Cl^- ions:



Where $[\text{FeOH}]_{\text{ads.}}$ and $[\text{FeClOH}]_{\text{ads.}}^-$ are the adsorbed intermediates which each of them is involved in the rate determining step (Eq. 4b and 5b respectively) of iron dissolution according to mechanism (i) and (ii), respectively. The presence of the Cl^- ions does not exclude dissolution through the $[\text{FeOH}]_{\text{ads.}}$ Intermediate in chloride free acid media, as the two mechanisms can proceed simultaneously.

2.1.5. CLASSIFICATION OF CORROSION PROCESS

The electrochemical cell, which brings this phenomenon to occur, has three fundamental constituents, namely anode, cathode and the electrolyte. Electrons flow through a metallic path from sites where the anodic reactions are occurring to sites where they allow cathodic reactions to occur.

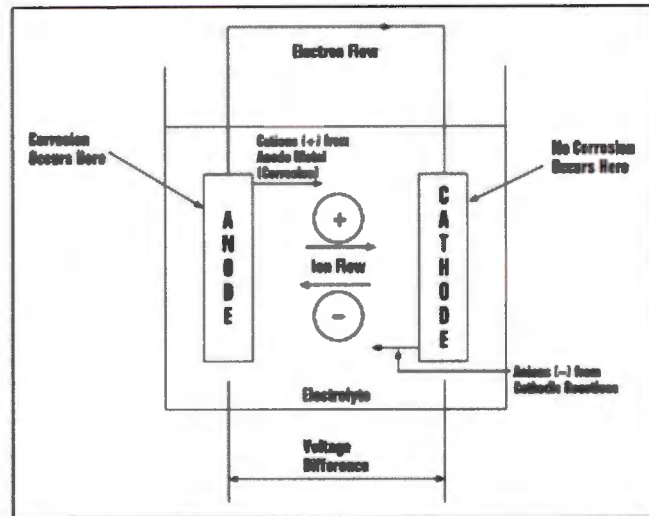


Fig. 10: Electrochemical cell

- An anode: the site where the metal gets corroded.
- A cathode: cathode (part of the same metal surface or of another metal surface in contact with it) forms the other electrode in the cell and is not consumed in the corrosion process.
- An electrolyte: it is the corrosive medium which is electrically conducting.

At the anode the corroding metal passes into the electrolyte as positively charged ions, releasing electrons, which participate in the cathodic reaction. Hence the corrosion current between anode and the cathode consists of electrons flowing with the metal and flowing within the electrolyte¹⁸.

2.1.6. KINETICS AND THERMODYNAMICS OF CORROSION

Chemical kinetics, also known as kinetics, is the study of rates of chemical processes. There are three kinetic laws that have been utilized to characterize the oxidation of pure metals namely¹⁹:

- The parabolic rate law
- Logarithmic rate law
- Linear rate law

The parabolic rate law (Eq. 6): it assumes that the diffusion of metal cations or oxygen anions is the rate-determining step and is derived from Fick's first law of diffusion. The concentrations of diffusing species are assumed to be constant both at the metal and gas-oxides interfaces. It is further assumed that the diffusivity of the oxide layer be invariant and the layer has to be uniform, continuous and of the phase type. The diffusion rate constant (k_p) is related to the temperature according to the following relationship (Arrhenius type):

$$x^2 = k_p t - x_0 \tag{6}$$

Where x is oxide film thickness

t is time

k_p is diffusion rate constant

x_0 is the constant

The equation above shows that the diffusion rate constant changes with temperature.

The logarithmic rate law (Eq. 7): is an empirical relationship that has no fundamental underlying mechanism. It is mainly applicable to thin oxide layers formed at relatively low temperatures.

$$x = k_p \log(ct + b) \tag{7}$$

Where k_p rate constant, and c and b are constants.

The linear rate law (Eq. 8): is also an empirical relationship that is applicable to the formation and build-up of a non-protective oxide layer.

$$x = k_L t \tag{8}$$

Where k_L is a constant.

Thermodynamic principles play a major role in determining the corrosion behavior of materials. It indicates the spontaneous direction of a chemical reaction. Thermodynamics is used to determine whether or not corrosion is theoretically possible.

It is concerned with energy states²⁰. Thermodynamics can predict whether a corrosion reaction will take place, but it does not provide an indication of the rate of corrosion. A reaction to take place spontaneously there must be a free energy change (ΔG) and since the energy, in the case of spontaneous reaction, is given out, the sign is therefore negative. The magnitude of ΔG and its sign are of great importance, since it denotes whether or not the corrosion reaction will occur. The free energy change is given by the following equation (Eq. 9):

$$\Delta G = -nFE \quad (9)$$

Where : ΔG is the free energy change

N is the number of electrons transferred in the half-cell reaction.

F is the charge transported by one mole of electrons

E is the measured potential in Volts.

Similarly,

$$\Delta G^\circ = -nFE^\circ \quad (10)$$

Where: ΔG° is the standard free energy change.²¹

2.1.7. CORROSION OF MILD STEEL

Mild steel comprises of a composition (wt. %) of Carbon = 0.18, Manganese = 0.71, Silicon = 0.37, Sulphur = 0.03, Phosphorus = 0.03, Nickel = 0.01, Chromium = 0.07 and the balance being Iron²⁶. It is the most common form of steel and because of its low cost it is a vital material of construction. It has a good strength, hard and can be bent, worked or can be welded into endless variety of shapes for uses from vehicles to building materials²³. Mild steel is used extensively in chemical and allied industries for handling alkalis, acids and salts solutions^{24,25}. Corrosion of mild steel involves the following electrochemical reactions:

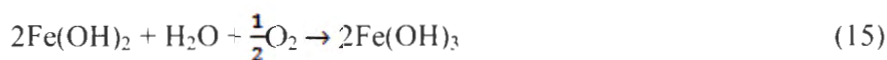


It is commonly referred to as the anodic reaction (Eq. 11), whereby the electrons from the metal dissolution are consumed by the adjacent cathodic reaction (Eq. 12). Cathodic reaction

is chiefly common in acids and in the pH range of 6.5 – 8.5 and the essential reaction is the oxygen reduction reaction (Eq. 13). The reaction between both the anodic and the cathodic reactions results with the formation of iron (II) hydroxide (Eq. 14).



Due to partial oxidation of air the material produced in equation 12 turns from white to greenish (hydrated iron (III) oxide is formed, Eq. 15).



2.1.8. CORROSION CONTROL MEASURES

Although corrosion affects us adversely, there are methods in which metals can be prevented from this malady. These include application of protective coatings, polarize or shift the potential of the metal, cathodic protection, material selection and corrosion inhibitors²⁷.

Application of Protective Coatings:

- The coatings form an impervious barrier between the metal and the oxidant but are only effective when the coating completely covers the structure.

Polarize or Shift the Potential of the Metal:

- This involves polarizing or shifting the potential of the metal enabling it to act as a cathode rather than an anode.

Cathodic Protection:

- The metal is forced to be the cathode in an electrochemical cell.

Material Selection:

- This involves the use of corrosion-resistant materials including plastics and non-metallics in severe environments.

Corrosion Inhibitors:

- Inhibitors retard the corrosion when added in to an environment in small concentration without significantly changing the concentration of any other corrosive agent²⁸.

2.2. INHIBITORS AND INHIBITION

2.2.1. DEFINITION OF CORROSION INHIBITORS

A corrosion inhibitor is a chemical substance which, when added in small concentrations to an environment, minimizes or prevents corrosion²³⁻²⁹. Corrosion inhibitors are used to protect metals from corrosion, including temporary protection during storage or transport as well as localized protection²⁹. The prerequisite that needs to be satisfied for a corrosion controlling chemical to be termed as the corrosion inhibitor is that the chemical should be adsorbed at corroding interface either in the form of molecule or as ions (anions or cations).

2.2.2. TYPES OF INHIBITORS

Inhibitors are classified mainly as interface inhibitors which retard corrosion by forming a film at the metal/environment interface. They are in turn divided/classified into two phases namely, liquid and vapor-phase inhibitors³⁰.

Liquid-Phase Inhibitors:

They are classified as anodic, cathodic, or mixed inhibitors, depending on whether they inhibit the anodic, cathodic, or both electrochemical reactions.

- **Anodic Inhibitors:** they are usually used in near-neutral solutions where soluble corrosion products, such as oxides, hydroxides or salts are formed. They form or facilitate the formation of passivating 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.

- **Cathodic Inhibitors:** they retard corrosion by either decreasing the reduction rate (referred to as 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 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.

- **Mixed Inhibitors:** about eight out of ten 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.
- They protect the metal in three ways namely, physical adsorption, chemisorption and film formation.

Physical 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 anions in a solution adsorb on the positively charged metal surface and organic cations subsequently adsorb on the dipole.

In the previous studies Frignani et al, also investigated that corrosion of iron in sulphuric acid containing chloride ions is inhibited by quaternary ammonium cations through this synergistic effect³¹.

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 occurs more slowly than physical adsorption. As temperature increases, adsorption and inhibition also increases. Sastri in his previous writing emphasized that chemisorption is specific and not completely reversible³².

Vapor-Phase Inhibitors:

Temporary protection against atmospheric corrosion particularly in closed environments can be achieved using vapor-phase inhibitors (VPI). Substances having low but significant pressure of vapor with inhibiting properties are effective. In their previous investigation, Levin et al concluded that VPIs are used by impregnating wrapping paper or by placing them loosely inside a closed container³³. VPIs are generally more effective for ferrous than non-ferrous metals.

2.2.3. THE MECHANISM OF CORROSION INHIBITION

Mechanism of corrosion inhibitors takes place through the ways, which are³⁴:

- Forming a thin film that is adsorbed onto the metal surface, also known as adsorption.
- Inducing the formation of corrosion products, which are passivating species.
- Changing the media characteristics, producing precipitates that can be protective and eliminating or inactivating an aggressive constituent.

Several heterocyclic organic compounds have been reported as corrosion inhibitors³⁵⁻³⁷. The inhibit corrosion by adsorption, forming a barrier between the metal and the environment. The polar group of the molecule is directly attached to metal and the nonpolar end is directed in a vertical direction to the metal surface which repels corrosive species, thus establishing a barrier against chemical and electrochemical attack by fluids on the metallic surface³⁴.

2.2.4. TECHNIQUES OF APPLICATION OF CORROSION INHIBITORS

Several types of techniques have been developed to understand the mechanism of action of inhibitors for corroding interface. These includes, amongst others, electrochemical techniques, surface analysis and analysis of corrosion products³⁸. Electrochemical Techniques: this includes cathodic and anodic polarization, impedance studies, polarization resistance, potential-time plots, order of reaction rates, etc.

Surface Analysis: techniques such Scanning-electron microscopy with energy dispersive X-ray (SEM-EDX), which provides clarity about the film formed on the surface of metal.

Analysis of Corrosion Products: Techniques such as Infrared spectroscopy (to investigate the functional group moieties of the adsorbed molecules), Raman, Ultraviolet-visible spectroscopies, etc. may also be employed to characterize the interaction between the metal surface and the inhibitor molecules.

2.3. BACKGROUND OF HYDANTOINS

The history of hydantoin and its class of compounds can be dated back to the year 1861 when Adolph von Bayer, a former Munich professor of organic chemistry and noble prize winner in 1905, discovered hydantoin. He found that 2,4-imidazolidinedion is a product of hydrogenation of allantoin³⁹. It is a saturated heterocyclic imidazole derivative compound. Hydantoin class of compounds has not been used clinically for a variety of reasons, primarily toxicity and relative ineffectiveness. One of its classes, Phenytoin, also known as anti-epileptic drug, was first synthesized by Blitz in 1908 and it was examined first for hypnotic activity⁴⁰. Its anti-convulsant activity was recognized by Merrit and Puttman in 1938, and was mainly used to treat all variety of epilepsy, except absence and myoclonic seizures. Its introduction was of value for several reasons unrelated to its immediate therapeutic application. It provided the first evidence of the selective nature of antiepileptic therapy. Phenytoin is not a sedative and for this reason it was responsible for the recognition that sedation is not a requisite for anti-convulsant action⁴¹. Hydantoins are thus representing the second chemical class of organic compounds to find applicability in the treatment of epilepsy. It has been succinctly reported that a review of literature through 1958 showed that there were 504 hydantoin derivatives synthesized and tested in various experimental models of epilepsy, compared with only 131 barbituric acid derivatives, 163 succinimides and 80 substituted oxazolidinediones⁴². Hydantoins have been found to have broad spectrum of activities in the field of medicine⁴³, industry and agriculture. Until now several research groups have documented the androgenic, antischistosomal and hypotensive actions of hydantoins^{44,45}.

Hydantoins such as 2-(2,3,6-Trichlorophenylimino) and 2-(2,3-dichloro-6-methylphenylimino) imidazolidine have been reported to have hypertensive activity in pithed

normotensive rats⁴⁶. Astropisomeric imidazolidines were found effective in controlling heart rate by producing either agonistic or antagonistic effect on histamine chronotropic effect⁴⁷. Some class of imidazolidines have been utilized as effective drugs against parasitic disease such as schistosomiasis caused by *schistosomamansonii*⁴⁸. Derivatives such as sodium benzyl hydantoin have been reported to act as transporter for moving molecules across cell membrane by coupling this process with energetically favorable downhill movement of ions and protons⁴⁹. In agricultural field they have been reported as effective pesticides and research is still ongoing to improve their fungicidal action⁵⁰. For nearly thirty years after the last review on the chemistry of hydantoins published by Lopez and Trigo in 1985, the rapid development of organic medicinal and pharmaceutical chemistry has led to an enhanced interest in hydantoins once more⁵¹. In 1912 hydantoin was reported by Lewis to pets to not readily getting broken in their bodies⁵². Some years later Gaebler and Keltch showed that some hydantoin was excreted as hydantoic acid after injection into dogs⁵³. Claims were further made by Wada that urea was produced from hydantoin after incubation with milk or certain tissue suspensions⁵⁴. Kozelka and Hine ultimately gave diphenyl-hydantoin to men and dogs and discovered that one to five percent was excreted as the corresponding hydantoic acid and ten to twenty seven percent as alpha-aminodiphenyl-acetic acid. About thirty percent of the drug was not accounted for, it was therefore of great interest to investigate the metabolism of hydantoin and diphenyl derivative in detail by in vitro methods and more research is currently underway till today⁵⁵.

2.4. THE DEFINITION OF HYDANTOINS

Hydantoin is a heterocyclic organic compound with molecular formula, $C_3H_4N_2O_2$, having a molecular weight of $100.08 \text{ g.mol}^{-1}$ and exists as a colorless solid. It is also known as glycolylurea because is a cyclic double-condensation reaction product of glycolic acid and urea⁵⁶. It is an oxidized derivative of imidazolidine. Its chemical structure (fig. 11) is similar to that of imidazolidine except that the molecule of hydantoin has carbonyl groups in the number two and four positions in the ring. Imidazolidine is the hydrogen-saturated analogue of imidazole. Generally we can refer to a group and a class of compounds with the same ring structure as the parent.. Phenytoin has two phenyl groups substituted onto the number 5 carbon in a hydantoin molecule⁵⁷, which makes it one of the derivatives of hydantoin.

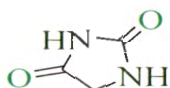


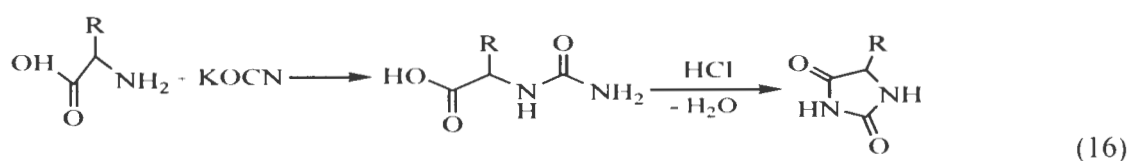
Figure 11: Structure of hydantoin

2.5. SYNTHESIS OF HYDANTOINS

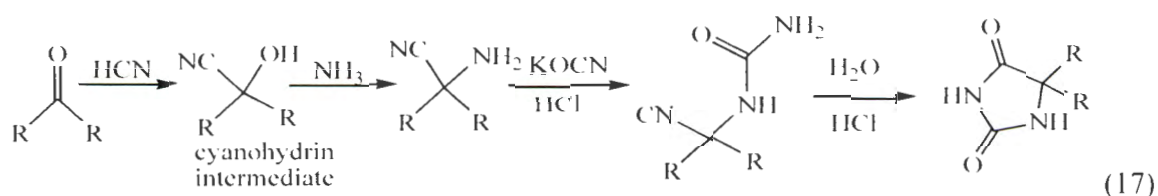
Hydantoins have long been the focus of attention as a ubiquitous moiety incorporated into compounds with numerous biological and therapeutic applications⁵¹. They were first obtained in a clean synthesis from bromoacetyl-urea, although in poor yield, by Bayer. Its derivatives are synthetically valuable, for example, as precursors to alpha-amino acid and pyruvic acid derivatives⁵⁸. They were originally observed as undesired by-products in the synthesis of peptides⁵⁹. There are many different methods of synthesising hydantoins, depending on the choice of starting materials, however, there are a few classical methods that are still commonly employed. Some of these methods are listed and briefly discussed below:

i. Urech hydantoin synthesis

This is the first classical synthetic route to hydantoins discovered in 1873 by Friedrich Urech, when he published his work on the formation of 5-monosubstituted hydantoins from amino acids and potassium cyanate followed by cyclization of the intermediate hydantoic acid with hydrochloric acid⁵⁶ (Eq. 16).

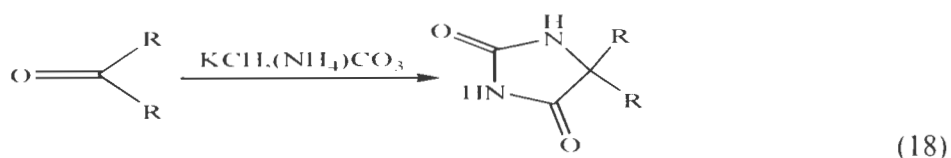


This methodology was improved further by Read, in 1922, for the synthesis of 5,5-disubstituted hydantoins from alpha-aminonitriles. The intermediate alpha-ureido nitrile cycles under acidic conditions to provide the corresponding hydantoin⁴⁰ (Eq. 17).



ii. Bucherer-Bergs synthesis

Bucherer and Berg have reported the multi-component reaction between a ketone, potassium cyanide and ammonium carbonate, which leads to the formation of hydantoins⁶⁰. This method is also regarded as another general synthetic route to 5-mono and 5,5-disubstituted hydantoins. According to the Bucherer-Bergs method, N-1 and N-3 unsubstituted hydantoins can be generated by reaction of a carbonyl compound with inorganic cyanide and introducing a second nitrogen and a carbonyl unit by ammonium carbonate⁶⁴ (Eq. 18).



2.6. PROPERTIES OF HYDANTOINS

Hydantoin, like any other existing compounds, have unique properties such as excellent melting point [220 °C (428 °F: 493 K)] and high solubility in water [39.7 g/L (100 °C)]⁵⁷. Hydantoin and its derivatives were prepared having the same chemical properties similar to the corresponding carbonyl compounds. They exhibit interesting biological activities such as being antimicrobial, anticonvulsant and schistosomicidal. Most compounds containing hydantoin moieties have antifungal and antibacterial properties, such as Iprodione, which has the most important hydantoin fungicide inhibiting the same long spore germination and mycelial growth of fungi⁶¹. 2-thiohydantoin obtained by condensation of aromatic aldehydes with hydantoins have bacterial and fungicidal activities. Hydantoin and thiohydantoin were reported to have good chemical reactivity with electrophilic and nucleophilic reagents⁵¹. 2,4-imidazolidinedione was suggested by Edward and Liu in 1969 that is primarily in protonated sulphur atom at 2- position⁶². Spectroscopically, hydantoin shows two bands in the carbonyl region at approximately 1720 and 1780 cm⁻¹. Infrared and Raman spectra studies have also linked to these bands symmetric and asymmetric coupling between the vibrations of carbonyls⁶³.

2.7. HYDANTOIN AS CORROSION INHIBITORS

The use of organic compounds containing oxygen, nitrogen and/ or sulphur heteroatoms, as well as functional groups with π -bonds to reduce corrosion attack on steel has been well documented^{4-7,65}. Most organic inhibitors adsorb on the metal surface by displacing water molecules on the surface and forming a compact barrier film⁶⁶. Hydantoin and its derivatives having heteroatoms, oxygen and nitrogen, and unique properties such as excellent melting point, high solubility in water and biological and therapeutical activities, are having qualities and efficiencies of being good corrosion inhibitors. Less work has been reported in literature about some of hydantoin derivatives as corrosion inhibitors in both acidic and basic media.

Al-Sawaad et al⁶⁷ have reported the inhibition effects of dimethylol-5-methyl hydantoin (MHD) and its derivatives on carbon steel alloy. The inhibition efficiencies of the tested compounds followed the order: MHD (97.81%) > A (72.78%) > B (40.93%) C (35.09% at 20mg/L) > D (52.06%) at their optimum concentration of 50 mgL⁻¹. The study exhibited that MHD has higher efficiency (97.81%) than its derivatives due to the steric effect, but the efficiency of MHD inhibitor was decreased as temperature increased due to destroying of the protective film of this inhibitor at 40°C, also the efficiency decreased for all the inhibitors in acidic media due to protonation of some hetero atoms that lower the basicity for other non-protonated hetero atoms thereby reducing the efficiency. It is also true for basic media, because in basic media caustic corrosion is an important factor that reduces the efficiency due to solubility of some of protective film.

Al-Sawaad⁶⁸ has reported the thermodynamic and quantum chemistry study for dimethylol-5-methyl hydantoin (MHD) and its derivatives as corrosion inhibitors for carbon steel N-80 in raw water (cooling water system). Their inhibition efficiency obeyed the order: MHD (60%) > DAM (20%) > DMM (12%) > DTM (4%) > DOM (1%) at the maximum concentration of 50 ppm. This decrease in inhibition efficiency of the hydantoin derivatives is attributed to the increased steric hindrance of the molecules on substitution which decreases the probability of meta-inhibitor interactions. The results obtained showed that MHD has higher inhibition efficiency than other inhibitors because the E_{HOMO} , $E_{\text{LUMO}}-E_{\text{HOMO}}$, has higher values in the presence of MHD than other inhibitors, and has a positive value of ΔG value, while in case of other inhibitors are negative values, and the partial charge on hetero atoms δ in case of inhibitor MHD is negative while in others are positive values.

As already mentioned above, less work has been done on hydantoin and its derivatives, that has basically triggered us to investigate into more details the corrosion inhibition of these compounds for mild steel in acidic media, the work upon completion will make an original contribution to knowledge in the area of corrosion science, electrochemical, quantum chemical, Monte Carlo simulation and QSAR studies.

Nowadays, corrosion has become a universal problem to be addressed by developed and developing countries. It has been estimated that recent annual global cost of corrosion is about US \$ 2.5 trillion that equates around 3.4% of total world GDP²². However, this cost of corrosion can be reduced from 15 (US \$ 375 billion) to 35% (US \$ 875 billion) by applying the available methods of corrosion protection. Previously, several methods of corrosion protection have been employed among which use of organic compounds as inhibitors is one of the most common, popular, effective and economic methods. From the ongoing discussion it can be concluded that previously hydantoin and several its derivatives have been investigated as effective corrosion inhibitors for metals and alloys using various experimental and computational methods. The high inhibition efficiency of the hydantoin based corrosion inhibitors is based on the fact that these molecules contain two nitrogen and two oxygen atoms in the form of amide bond which can act as adsorption centers during metal-inhibitor interaction. In view of the high inhibition efficiency of hydantoin and its derivatives, present study deals with the corrosion inhibition efficiency of mild steel in 0.5M HCl using hydantoin and its five derivatives for the first time.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1. MATERIALS AND INSTRUMENTATION

3.1.1. MATERIALS

Mild steel (MS) with the composition (wt. %) C = 0.17, Mn = 0.46, Si = 0.26, S = 0.017, P = 0.019 and Fe being the balance was used for all the experiments. MS specimens utilized for both gravimetric and electrochemical measurements were cut into specific dimensions. For the electrochemical studies, the working electrode (mild steel) was cut into 1 cm x 1 cm dimension and mounted in Teflon holder such that a 1 cm² surface area was exposed to the electrolyte. Before any corrosion study, the specimens were abraded with SiC abrasive papers of increasing grits, rinsed with deionized water, degreased in absolute ethanol and acetone, dried at room temperature and finally stored in a desiccator for prompt usage in corrosion studies.

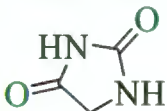
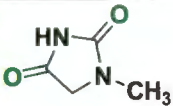
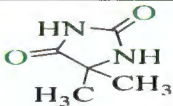
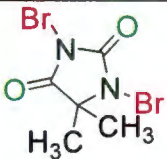
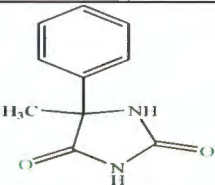
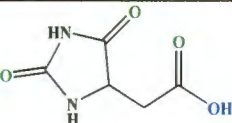
3.1.2. INSTRUMENTATION

- Autolab Galvanostat/Potentiostat (PGSTAT 302N) was employed to study the electrochemical measurements and obtained from Metrohm Eco-South Africa.
- UV/Vis Spectrometer was obtained from Agilent Technology-United State of America and of CARY series. It was utilized to characterize the interaction between the mild steel surface and the inhibitors.
- The STRUERS LaboPol-1-equipment was utilized mainly for the pre-washing of the mild steel coupons.
- RADWAG analytical balance, serial number AS220/C/2, was utilized for all weighing of chemicals with an accuracy of four decimals and was obtained from LABOTEC-South Africa.
- A three-cell electrode was utilized and obtained from Metrohm-South Africa

3.2. REAGENTS

The hydrochloric acid used for this study was obtained as 32% analytical grade reagent. The absolute ethanol and acetone were both analytical grade reagents and no further purification was done on them. All these reagents were obtained from Merck-South Africa. Distilled water was used for the dilution of hydrochloric acid and pre-washing of the mild steel coupons.

Table 1: The structures and molecular weights of the inhibitors:

S.No.	Structure of the Inhibitors	Name and Molar Masses of the Inhibitors
1		- Hydantoin $M_r = 100.08 \text{ g/mol}$ - Assigned Name: [HYD]
2		1-Methylhydantoin $M_r = 114.10 \text{ g/mol}$ - Assigned Name: [MHYD]
3		5,5-Dimethylhydantoin $M_r = 128.13 \text{ g/mol}$ - Assigned Name: [DMHYD]
4		1,3-Dibromo-5,5-dimethylhydantoin $M_r = 285.92 \text{ g/mol}$ - Assigned Name: [DBDMHYD]
5		5-methyl-5-phenylhydantoin $M_r = 190.20 \text{ g/mol}$ - Assigned Name: [MPHYD]
6		- Hydantoin-5-acetic acid $M_r = 158.11 \text{ g/mol}$ - Assigned Name: [HYDAC]

3.3. INHIBITORS

The inhibitors investigated were purchased from SIGMA-ALDRICH-South Africa and they are the following:

- Hydantoin [HYD]
- 1-Methylhydantoin [MHYD]
- 5,5-Dimethylhydantoin [DMHYD]
- 1,3-Dibromo-5,5-dimethylhydantoin [DBDMHYD]
- 5-Methyl-5-phenylhydantoin [MPHYD]
- Hydantoin-5-acetic acid [HYDAC]

3.4. ELECTROCHEMICAL MEASUREMENTS

A three-electrode glass cell with 50 mL capacity was used for all electrochemical measurements. 25 mL of 1.0 M HCl was used as an electrolyte with and without various concentrations of inhibitors. Mild steel was utilized as the working electrode, Ag/AgCl, in 3.0 M KCl as the reference electrode, and a high purity platinum foil as the counter electrode, respectively. All electrochemical measurements were conducted at 30 °C in thermostated water bath using AUTOLAB PGSTAT 302N electrochemical system.

The following electrochemical methods were employed:

3.4.1. Potentiodynamic polarization (PDP)

PDP was employed 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.

$$IE_{PDP}(\%) = \frac{(I'_{corr} - I_{corr})}{I'_{corr}} \times 100 \quad (19)$$

where I'_{corr} and I_{corr} represent the corrosion current densities in the absence and presence of the inhibitors, respectively.

3.4.2. Electrochemical Impedance Spectroscopy (EIS)

EIS 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;

$$IE_{EIS} (\%) = \frac{(R_{ct} - R'_{ct})}{(R_{ct})} \times 100 \quad (20)$$

where R_{ct} and R'_{ct} are the charge transfer resistances in the presence and absence of inhibitors.

3.5. SPECTROSCOPIC TECHNIQUES

The interaction between the mild steel surface and the inhibitor molecules was analyzed using UV-Vis spectroscopies. All these investigations were characterized in 0.5 M HCl solution with and without inhibitors.

3.6. QUANTUM CHEMICAL CALCULATIONS

Quantum chemical calculations were carried out on the hydantoin derivatives in water phase by using the density functional theory (DFT) method. The model chemistry, B3LYP/6-31G+(d,p), which comprises the Becke's three parameter hybrid functional together with the Lee-Yang-Parr correlation functional (B3LYP) and the Pople-type basis set, 6-31+g(d,p) was employed for all the calculations⁸⁷⁻⁸⁹. The B3LYP/Pople-basis set models have been proven to give satisfactory balance between speed and accuracy⁹⁰⁻⁹³. The optimized structures were confirmed to correspond to true energy minima with the absence of imaginary frequency in the force constant calculations. Relevant quantum chemical parameters were derived based on the ground state electronic properties of the optimized structures.

Frontier molecular orbitals (FMOs) energies, that is the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), and the energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) were calculated for all the inhibitors. Reactivity parameters such as global hardness (η), global electronegativity (χ), and the fraction of electrons transferred from the inhibitor to the metal (denoted as ΔN) were derived from the FMO energy parameters by using appropriate relations^{78,94}:

$$\eta = -\frac{1}{2}(E_{HOMO} - E_{LUMO}) \quad (21)$$

$$\chi = -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \quad (22)$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (23)$$

where approximate values of 7 eV/mol and 0 eV/mol were used for χ_{Fe} and η_{Fe} respectively⁹⁵. All calculations were carried out using the Gaussian 09 suite software⁹⁶, while the initial and optimized graphical structures were visualized using the GaussView software.

Hong et al reported that the inhibition efficiency of inhibitors increased with the increase in energy of HOMO and decrease in energy gap of frontier molecular orbital⁶⁹. The areas containing heteroatoms are the most possible sites for bonding with the steel surface by donating electrons to the mild steel⁷⁰.

3.7. MONTE CARLO SIMULATIONS

Quench molecular dynamics simulation was carried out to simulate the interaction of the inhibitor molecules with iron surface. Fe (110) was used for the simulation because it is the most stable crystal surface of Fe⁹⁷. A crystal slab of 5 Å depth was built for the Fe (110) and the plane was enlarged to a (7 × 7) supercell to provide a large surface for the interaction of the inhibitors. A vacuum slab with 30 Å thickness was built above the plane and the Fe (110) surface was fixed before simulations.

Condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field was used to optimize the structures of all components of the respective systems. The simulations were performed in NVT canonical ensemble at 298K, a cut-off radius of 15.5 Å, a time step of 0.1 fs and a total simulation time of 100 ps using a Nose thermostat. A total of 1,000,000 number of simulation steps was carried out. Solvent and charge effects were ignored during the simulations, and calculations were performed at the metal/vacuum interface. Although this method oversimplifies the real situation, it has been successfully used to differentiate the adsorption behaviour of different organic molecules on metal surfaces, and yielded agreeable results with experimental findings⁹⁸⁻¹⁰⁰.

The quench molecular dynamics simulations were performed using Forcite module in the Material Studio Software 7.0 from BIOVIA-Accelrys, USA⁷¹. The interaction energy ($E_{interaction}$) of molecules with Fe surface was obtained using the equation⁹⁸⁻⁹⁹:

$$E_{\text{interaction}} = E_{\text{total}} - (E_{\text{Fe-surface}} + E_{\text{inhibitor}}) \quad (24)$$

where E_{total} is the total energy of the entire system, that is, inhibitor molecule and the Fe(110) surface system; $E_{\text{Fe-surface}}$ is the energy of Fe(110) alone, and $E_{\text{inhibitor}}$ is the energy of isolate inhibitor molecule. The binding energy ($E_{\text{binding}} = -E_{\text{interaction}}$) was also calculated for each Fe(110)/inhibitor system.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. ELECTROCHEMICAL MEASUREMENTS

4.1.1 Potentiodynamic Polarization (PDP)

Potentiodynamic polarization curves for mild steel in 0.5 M HCl in the absence and presence of different concentrations (5 mM – 50 mM) of the investigated inhibitors are presented in Figures 4.1 – 4.6 while their respective Nquist plots are presented in Figures 4.7 – 4.12. the values of corrosion potential (E_{corr}), corrosion density (I_{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 densitiers (I_{corr}).⁷³ The inhibition efficiency was evaluated from the measured I_{corr} value using the relationship.

$$IE_{pdp}(\%) = \frac{(I'_{corr} - I_{corr})}{I'_{corr}} \times 100 \quad (1)$$

where I'_{corr} and I_{corr} represent the corrosion current densities in the absence and presence of the inhibitors, respectively.⁷⁴

From table 4.1 it is evident that the inhibition efficiency has increased, while corrosion density decreased with increasing concentration of hydantoins. This could be explained on the basis of adsorption of hydantoins on the mild steel surface and adsorption process enhanced with increasing inhibitor concentration.⁷⁵ The potentiodynamic polarization study revealed that inhibitor efficiencies of these molecules followed the order: DBDMHYD (89.79%) > HYD (88.06%) > DMHYD (86.40%) > HYDAC (78.38%) > MPHYD (74.49%) at the optimum concentration of 50 mM. Literature study suggests that presence of substituents generally increases the probability of steric hindrance and thereby decreases the inhibition efficiency as compared to the hydantoin^{67,68}. For example, the inhibition performances of the hydantoin derivatives tested by Al-Sawaad et al⁶⁷ as corrosion inhibitors for mild steel in acidic solution showed the trend: MHD (97.81%) > A (72.78%) > B (40.93%) C (35.09% at 20mg/L) > D (52.06%) (at 50 mgL⁻¹). Similar observation was also reported by Al-Sawaad⁶⁸ where hydantoin derivatives showed inhibition efficiency order of MHD (60%) > DAM (20%) > DMM (12%) > DTM (4%) > DOM (1%) (at 50 ppm). Due to the presence of some active sites in the studied compounds, such as heteroatoms, aromatic rings for making adsorption, they may act as adsorption inhibitors.⁷⁶ The value of corrosion

potential of the inhibited solutions versus that of the blank plays a vital role in way that if $E_{corr} > 85$ mV is attributed to anodic or cathodic type inhibitors and similarly if it is less than 85 mV then the inhibitors are mixed types.⁷⁷⁻⁸⁰ It is further observed in table 4.1 that the studied compounds are mixed type inhibitors with $E_{corr} < 85$ mV. The studied compounds therefore tend to inhibit both anodic and cathodic reactions by forming a film on the steel surface thereby blocking anodic and cathodic reaction sites.

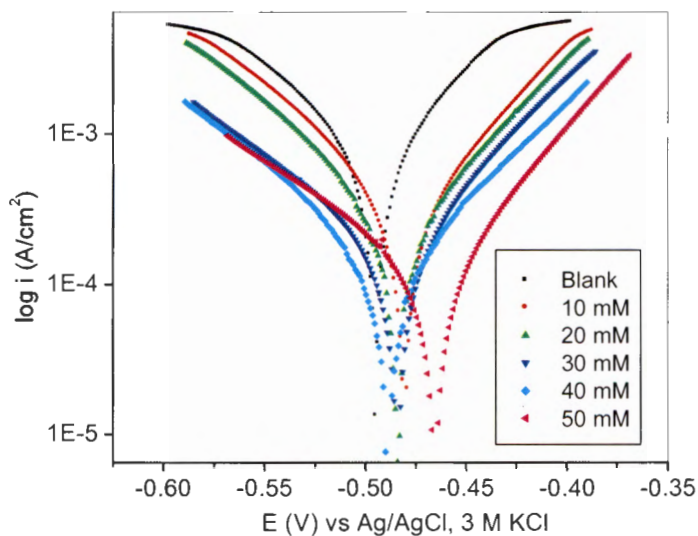


Figure 4.1: Potentiodynamic polarization curve for mild steel in 0.5 M HCl in the absence and presence of different concentrations of [HYD].

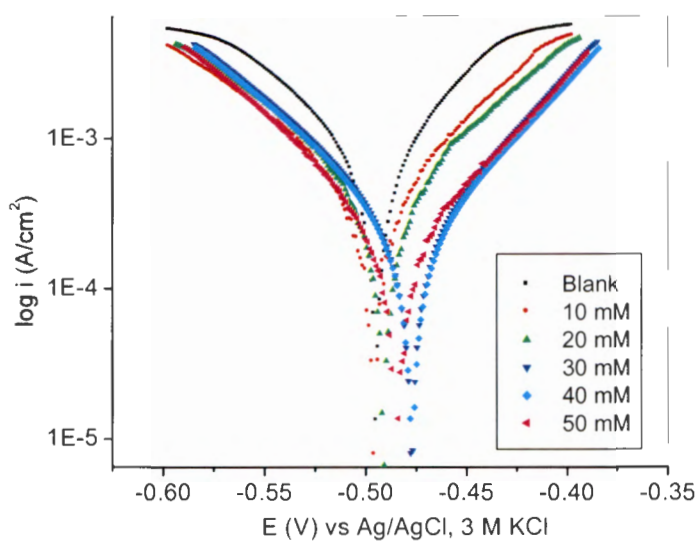


Figure 4.2: Potentiodynamic polarization curve for mild steel in 0.5 M HCl in the absence and presence of different concentrations of [MHYD].

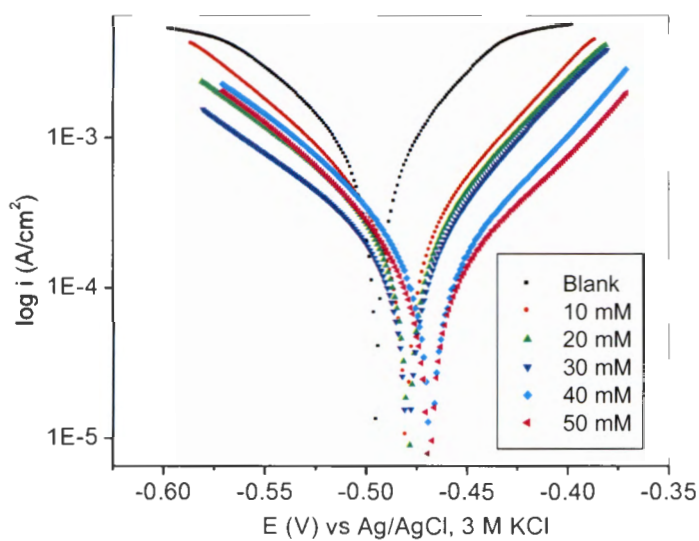


Figure 4.3: Potentiodynamic polarization curve for mild steel in 0.5 M HCl in the absence and presence of different concentrations of [DMHYD].

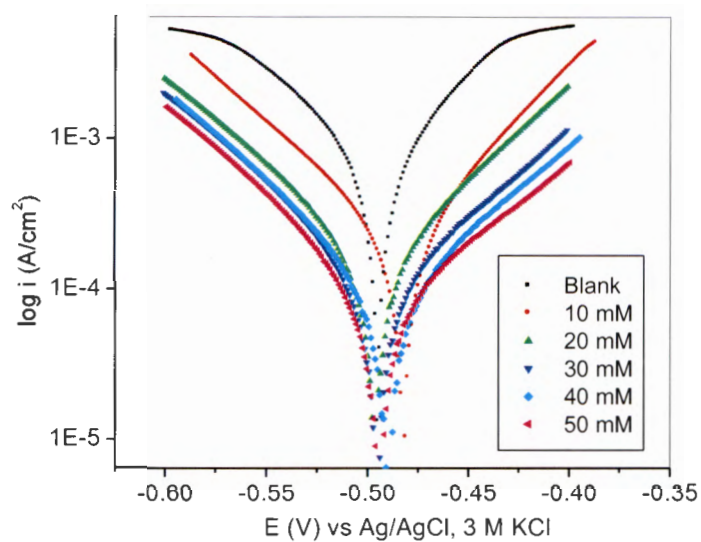


Figure 4.4: Potentiodynamic polarization curve for mild steel in 0.5 M HCl in the absence and presence of different concentration of [DBDMHYD].

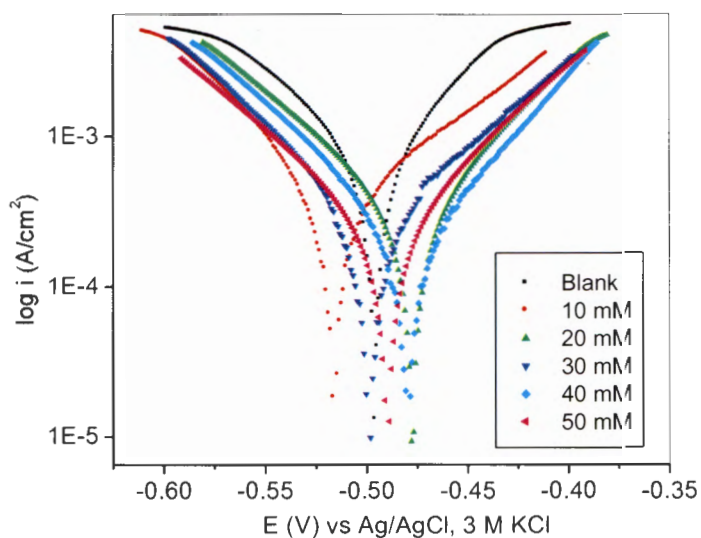


Figure 4.5: Potentiodynamic polarization curve for mild steel in 0.5 M HCl in the absence and presence of different concentrations of [MPHYD].

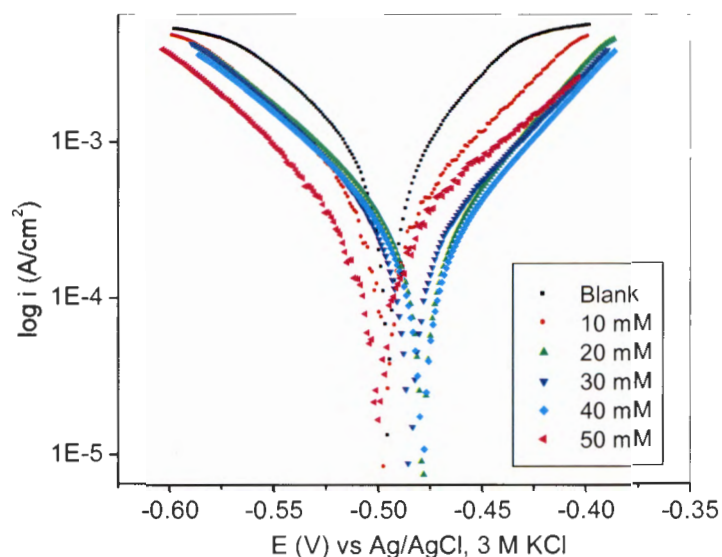


Figure 4.6 : Potentiodynamic polarization curve for mild steel in 0.5 M HCl in the absence and presence of different concentrations of [HYDAC].

Table 4.1: Potentiodynamic polazation parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) and anodic and cathodic Tafel slopes (β_a and β_c) using different inhibitors.

Inhibitors	Concentrati on of inhibitors (mM)	$-E_{corr}$ (mV)	I_{corr} (mA cm^{-2})	β_c (mV/dec)	β_a (mV/dec)	$EI_{PDP}(\%)$
[HYD]	Blank	490.76	1047.00	95.00	113.00	-
	5	475.55	473.17	74.66	88.07	62.77
	10	473.03	389.84	82.49	93.26	73.46
	20	479.45	277.85	80.50	84.88	81.27
	30	483.83	196.12	77.44	112.23	85.62
	40	487.54	150.53	87.98	93.86	85.62
	50	464.56	125.06	68.16	115.38	88.06

[MHYD]	5	477.01	563.18	77.17	95.69	46.15
	10	491.74	547.00	102.42	111.84	47.76
	20	489.82	518.59	100.78	106.55	50.47
	30	471.69	269.73	78.39	86.03	74.24
	40	472.36	253.90	81.46	85.78	75.75
	50	480.28	226.09	82.29	79.61	78.41
[DMHYD]	5	479.13	327.79	72.49	84.85	68.70
	10	475.73	284.56	79.42	86.82	72.82
	20	478.35	243.67	78.47	100.70	76.73
	30	477.86	187.56	73.54	110.67	82.09
	40	463.47	151.97	79.81	80.64	85.49
	50	462.97	142.37	92.68	84.48	86.40
[DBDMHYD]	5	475.50	539.43	77.58	77.58	48.48
	10	479.67	247.50	74.44	74.44	76.36
	20	491.35	194.54	93.34	93.34	81.42
	30	494.97	127.96	104.11	104.11	87.78
	40	486.07	116.28	104.37	104.37	88.89
	50	492.44	106.94	124.25	124.25	89.79
[MPHYD]	5	475.79	601.51	97.08	103.33	42.55
	10	539.23	539.23	146.17	86.47	48.50
	20	475.26	362.86	83.43	95.63	65.34
	30	500.21	297.18	98.31	76.78	71.62
	40	477.91	272.99	94.63	85.95	73.93
	50	488.85	267.14	84.82	93.25	74.49

	5	482.46	551.46	83.36	94.92	47.33
	10	491.00	423.16	92.30	85.96	59.58
[HYDAC]	20	473.49	276.93	74.81	88.18	73.55
	30	480.45	269.19	85.69	81.22	74.29
	40	474.59	242.05	78.89	87.39	76.88
	50	497.82	226.32	80.43	77.93	78.38

4.1.2. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy was employed to study the corrosion behaviour of mild steel in 0.5 M HCl in the absence and presence of different concentrations (5 mM – 50 mM) of [HYD], [MHYD], [DMHYD], [DBDMHYD], [MPHYD] and [HYDAC]. The Nyquist plots of mild steel in uninhibited and inhibited acid solutions of various concentrations of the investigated inhibitors are presented in Figures 4.7 – 4.12.

$$IE_{EIS} (\%) = \frac{(R_{ct} - R'_{ct})}{(R_{ct})} \times 100 \quad (2)$$

where R_{ct} and R'_{ct} are the charge transfer resistances in the presence and absence of inhibitors.

It is observed in table 4.2. that R_{ct} values increased in the presence of inhibitors while the C_{dl} values decreased. According to Ramagathan and Ebenso⁸¹ an increase in R_{ct} could be attributed to the molecular adsorption of the inhibitors at metal-acid interface, which retards the movement of the charges across the interface and thereby inhibiting corrosion. The Nyquist plots in figures 4.13 – 4.18 reveals a single depressed capacitive arc over the frequency range studied. The depressed semi-circle, according to ElBelghiti et al⁸², is generally related to the frequency dispersion as well as in homogeneities, roughness of the metal surface and mass transport process. This is an indication that the dissolution of mild steel is controlled by a single transfer process⁷⁸.

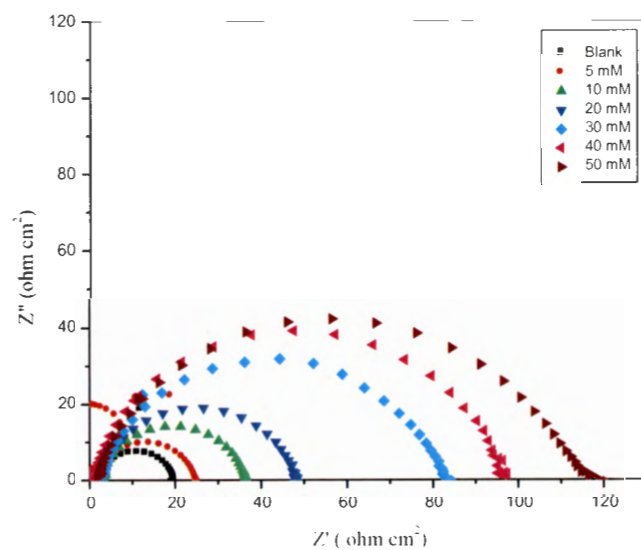


Figure 4.7: Nyquist plot for mild steel in 0.5 M HCl in the absence and presence of different concentrations of [HYD].

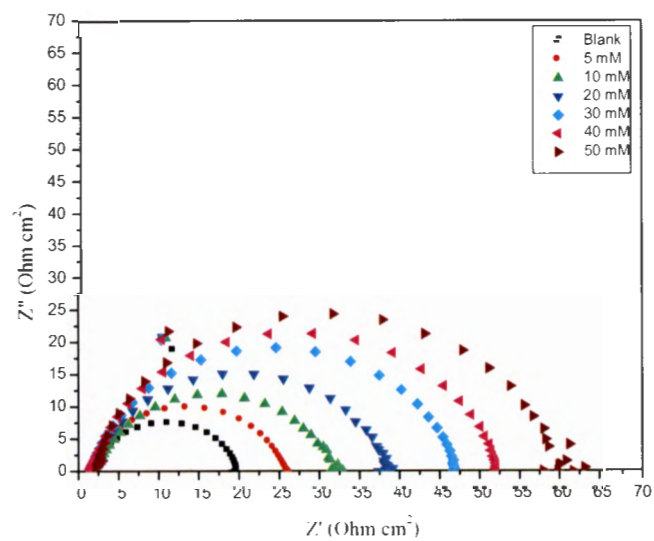


Figure 4.8: Nyquist plot for mild steel in 0.5 M HCl in the absence and presence of different concentrations of [MHYD].

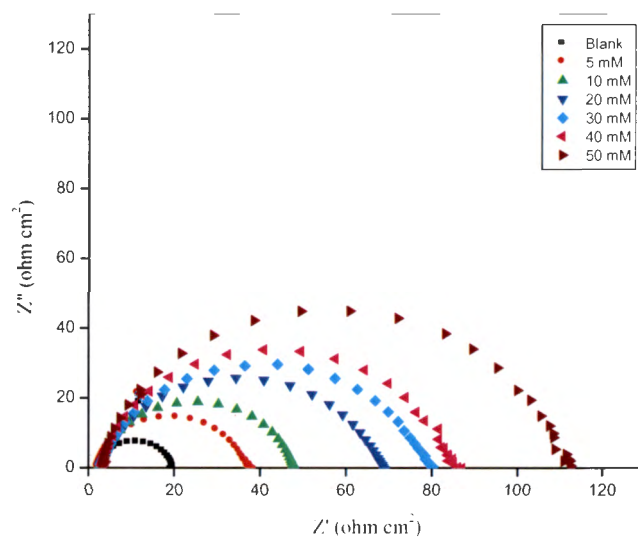


Figure 4.9: Nyquist plot for mild steel in 0.5 M HCl in the absence and presence of different concentrations of [DMHYD].

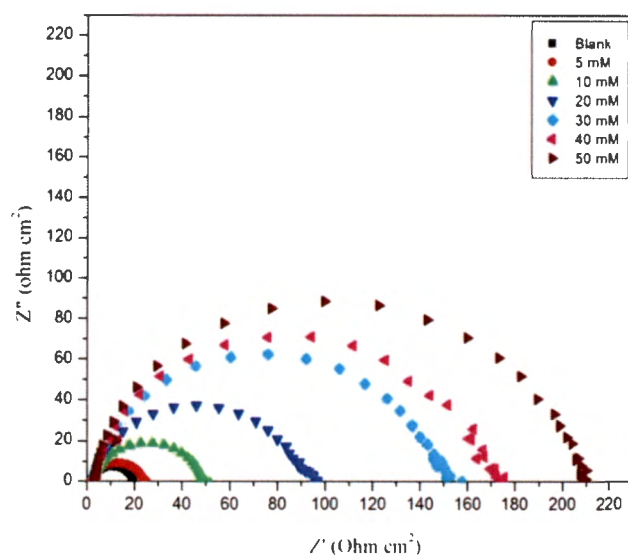


Figure 4.10: Nyquist plot for mild steel in 0.5 M HCl in the absence and presence of different concentrations of [DBDMHYD].

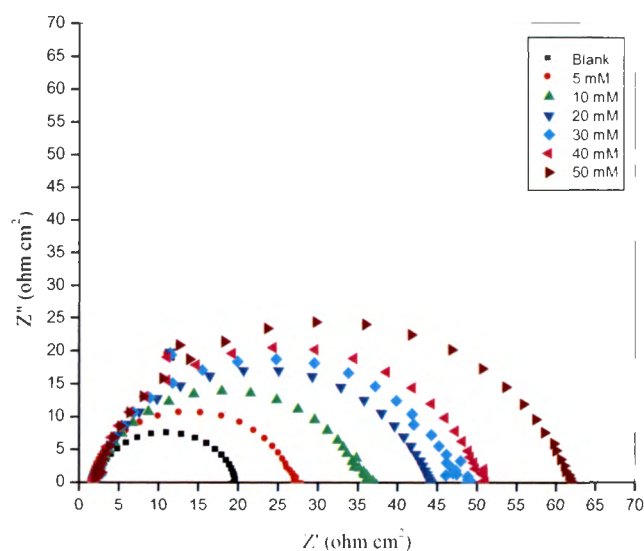


Figure 4.11: Nyquist plot for mild steel in the absence and presence of different concentrations of [MPHYD].

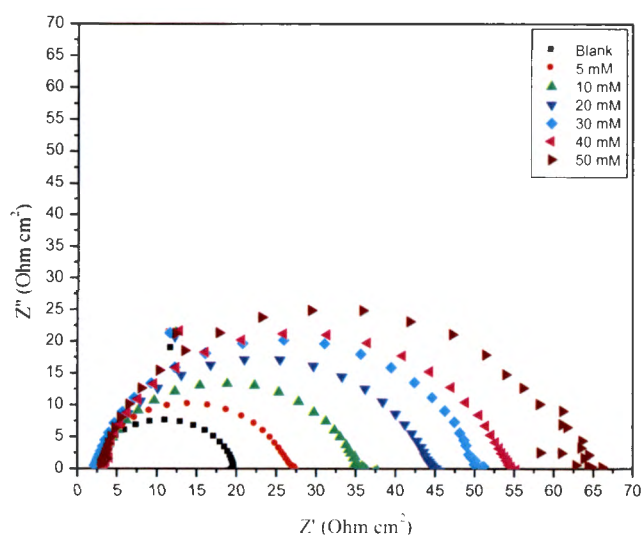


Figure 4.12: Nyquist plot for mild steel in the absence and presence of different concentrations of [HYDAC].

Table 4.2: Electrochemical impedance parameters such as the resistance of charge transfer (R_{ct}), capacity of double layer (C_{dl}) by different inhibitors.

Inhibitors	Concentrati on of inhibitors (mM)	R_s ($\Omega\text{ cm}^2$)	R_{ct} ($\Omega\text{ cm}^2$)	n	C_{dl} ($\mu\text{F cm}^{-2}$)	$IE_{EIS}(\%)$
[HYD]	Blank	2.28	17.51	0.99	102.96	-
	5	1.43	23.70	0.99	126.37	26.11
	10	2.79	33.92	0.99	111.09	48.38
	20	2.21	45.79	0.99	85.04	61.76
	30	2.80	80.45	0.99	38.15	78.23
	40	0.904	96.02	0.99	46.12	81.76
	50	1.56	113.35	0.99	52.09	84.55
[MHYD]	5	1.43	24.51	0.99	77.39	28.56
	10	2.05	29.44	0.99	55.69	40.52
	20	1.63	36.99	0.99	57.44	52.66
	30	1.42	45.25	0.99	91.13	54.67
	40	1.52	50.64	0.99	98.19	65.42
	50	2.20	58.09	0.99	95.01	69.86
[DMHYD]	5	1.93	35.39	0.99	85.65	50.52
	10	2.47	45.63	0.99	92.41	61.63
	20	2.64	65.88	0.99	51.34	73.42
	30	2.49	76.92	0.99	37.01	77.24
	40	2.94	83.10	0.99	76.10	78.93
	50	2.93	109.60	0.99	83.21	84.02
	5	1.74	22.18	0.99	85.98	21.06
	10	2.28	46.30	0.99	61.21	62.18

[DBDMHYD]	20	2.81	86.76	0.99	49.59	79.82
	30	2.62	143.99	0.99	50.78	87.84
	40	3.54	163.95	0.99	52.54	89.32
	50	2.97	202.54	0.99	51.46	91.35
[MPHYD]	5	1.54	26.00	0.99	85.06	32.65
	10	1.75	34.27	0.99	57.13	48.91
	20	1.79	42.04	0.99	65.81	58.35
	30	1.97	45.69	0.99	53.38	61.68
	40	1.92	48.39	0.99	96.03	63.81
	50	2.04	60.16	0.99	59.03	70.89
[HYDAC]	5	2.08	24.77	0.99	78.12	29.31
	10	2.76	32.52	0.99	75.95	46.16
	20	2.69	42.05	0.99	90.46	58.36
	30	2.13	47.59	0.99	90.13	63.21
	40	3.12	51.92	0.99	95.83	66.28
	50	3.08	60.64	0.99	62.56	71.12

4.2. ADSORPTION ISOTHERM AND THERMODYNAMIC PARAMETERS

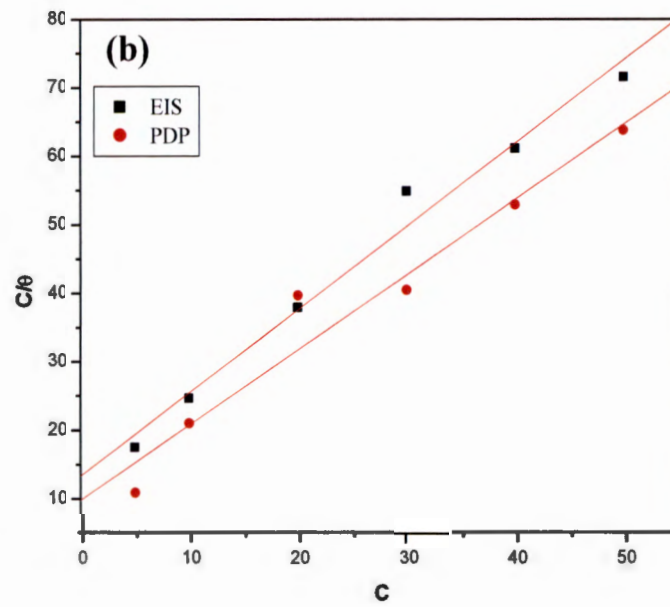
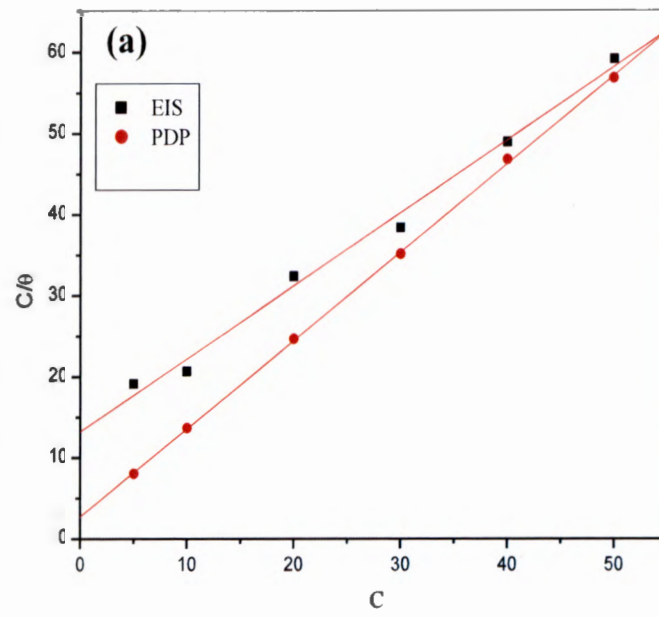
Adsorption isotherm provides information about the adsorption behaviour of the inhibitor molecule interactions on the metal surface. It facilitates the mechanism during the adsorption process between the metal surface and the inhibitor. Flory-Huggins, Temkin, Langmuir, Frumkin, Bockris-Swinkles and Freundlich adsorption isotherms are regarded as examples of adsorption isotherms⁸³. In this study, Langmuir adsorption isotherm was utilised to determine the inhibitors adsorption equilibrium constant (K_{ads}) from the Tafel polarisation and the EIS data, which resulted with the linear best fit, which is represented by the following equation:

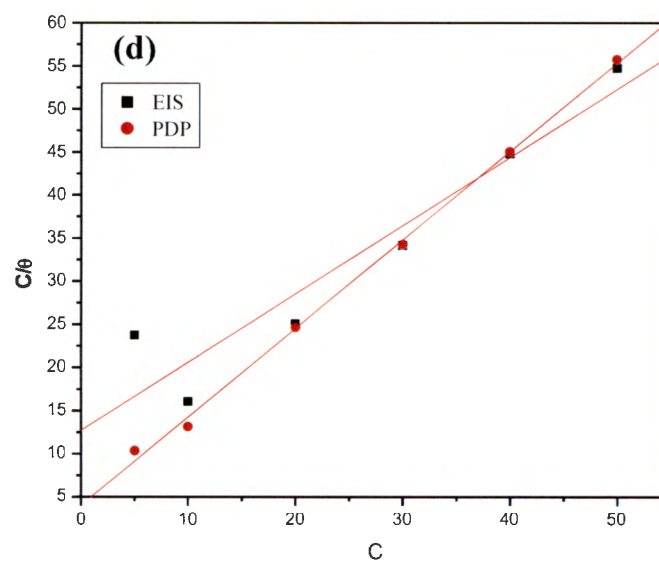
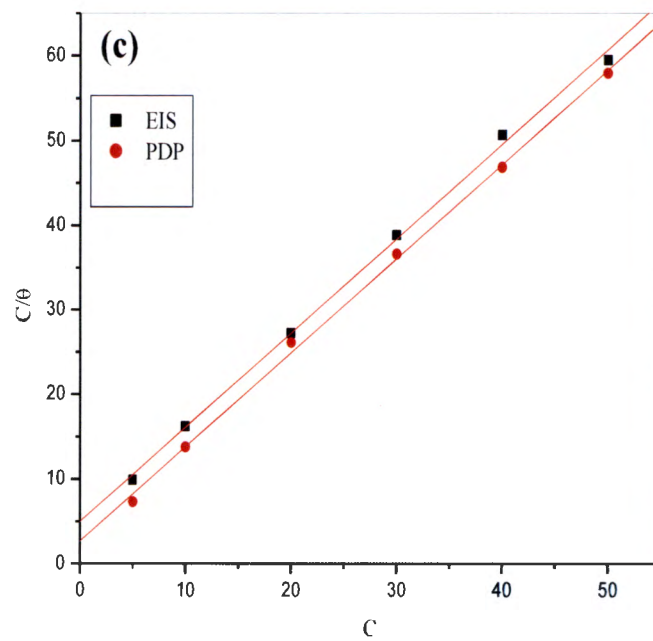
$$\frac{C'}{\theta} = mC' + \frac{1}{K_{ads}} \quad (3)$$

Where K_{ads} is the equilibrium constant for the adsorption of inhibitor molecules on the mild steel surface, C is the molar concentration of inhibitor molecules and θ is the degree of surface coverage of inhibitor molecules on the mild steel surface. The Langmuir adsorption isotherm plots are represented in Figure 4.13. The adsorption equilibrium constant, K_{ads} is related to the change in Gibbs free energy of adsorption (ΔG_{ads}) as :

$$\Delta G_{ads}^o = -RT \ln(55.55 K_{ads}) \quad (4)$$

Where ΔG_{ads} is the Gibbs free energy of adsorption, the value 55.55 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. The negative value of Gibbs free energy of adsorption shows a spontaneous process while positive value indicates non-spontaneous. Generally, the values of ΔG_{ads} up to -20 kJ. mol^{-1} are attributed to physisorption while those around -40 kJ mol^{-1} or more negative are associated with chemisorption process^{84,85}. From table 4.3 below, it is evident that ΔG_{ads} values ranges between $-25.23 \text{ kJ. mol}^{-1}$ to -23 kJ. mol^{-1} , which means that the adsorption of the hydantoin and its derivatives in this study as inhibitors on mild steel surface belongs to the physisorption and the adsorptive film has an electrostatic character⁸⁶.





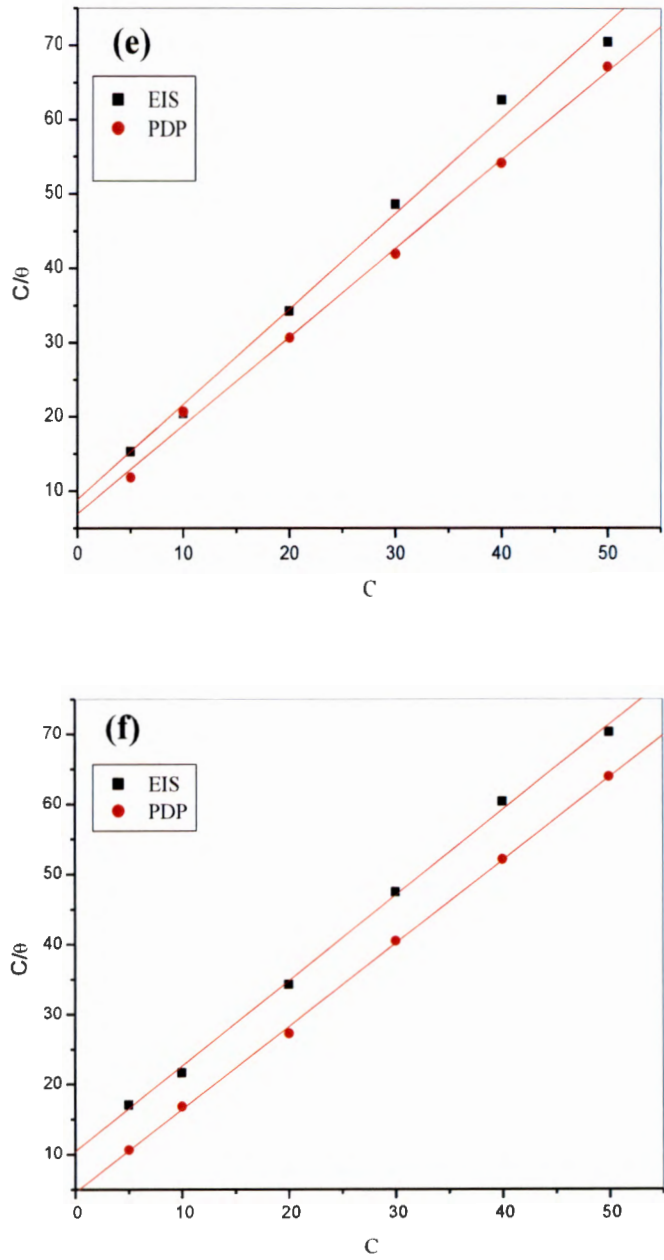


Figure 4.13: Langmuir adsorption isotherm plots for (a). [HYD], (b). [MHYD], (c). [DMHYD], (d). [DBDMHYD], (e). [MPHYD] and (f). [HYDAC] using the Tafel and EIS experimental data respectively.

Table 4.3: Adsorption parameters derived from the Langmuir isotherm plots for the inhibitors.

Inhibitor	PDP		EIS	
	$K_{ads} (\times 10^3)$	$\Delta G_{ads} (\text{kJ. mol}^{-1})$	$K_{ads} (\times 10^3)$	$\Delta G_{ads} (\text{kJ. mol}^{-1})$
[HYD]	285.71	- 23.96	71.43	- 20.53
[MHYD]	100.00	- 21.36	68.49	- 20.43
[DMHYD]	400.00	- 24.80	200.00	- 23.08
[DBDMHYD]	197.24	- 23.06	66.67	- 20.36
[MPHYD]	250.00	- 23.63	111.11	- 21.62
[HYDAC]	476.19	- 25.23	90.91	- 21.13

4.3. ULTRAVIOLET-VISIBLE SPECTROPHOTOMETRY (UV/VIS)

This technique was employed with a sole objective of giving us the interaction between mild steel and the inhibitor molecules. The UV-Visible absorption spectra for 0.5 M HCl solution with and without a maximum concentration of the inhibitor molecules of 50 mM before and after 6 hours of mild steel immersion at room temperature are shown in figures 4.14 – 4.19. It is very clear from the figures that the spectra of mild steel immersion in acid solution is different from the untreated solution. The untreated solution shows a maximum peak at 244 nm throughout while the spectra of mild steel immersion displays an intense adsorption at 251 nm, the observed change indicates the interaction of the between the inhibitor molecules with the metal iron (Fe). This confirms that a metal-inhibitor complex has been formed at the metal surface.

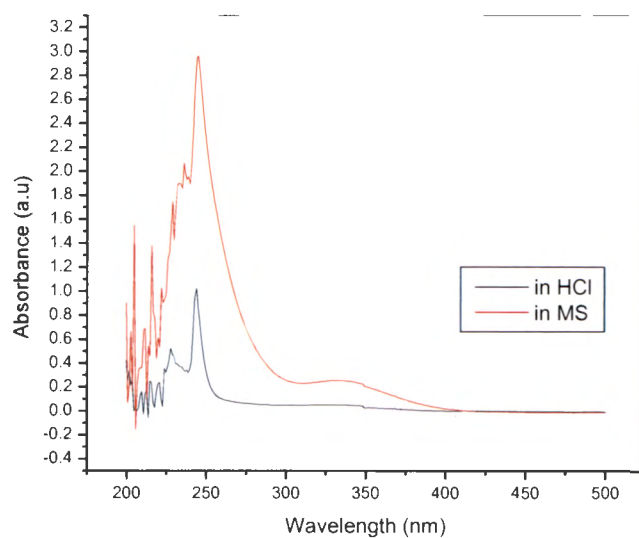


Figure 4.14: UV/Vis spectra of 50 mM [HYD] solution diluted in 0.5 M HCl and MS immersed for 6 hours.

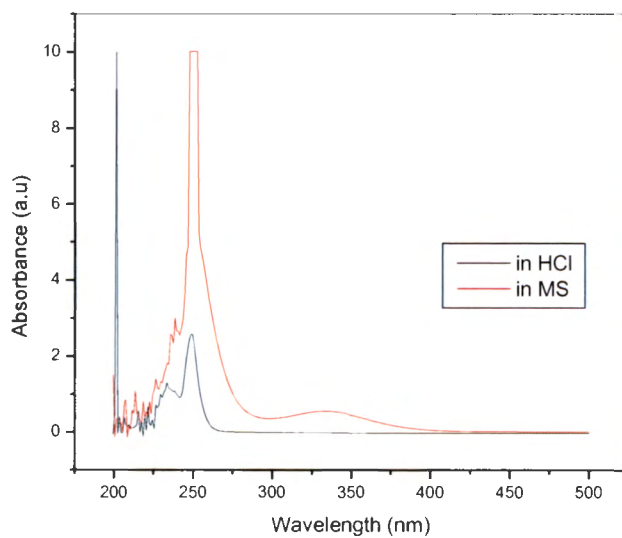


Figure 4.15: UV/Vis spectra of 50 mM [MHYD] solution diluted in 0.5 M HCl and MS immersed for 6 hours.

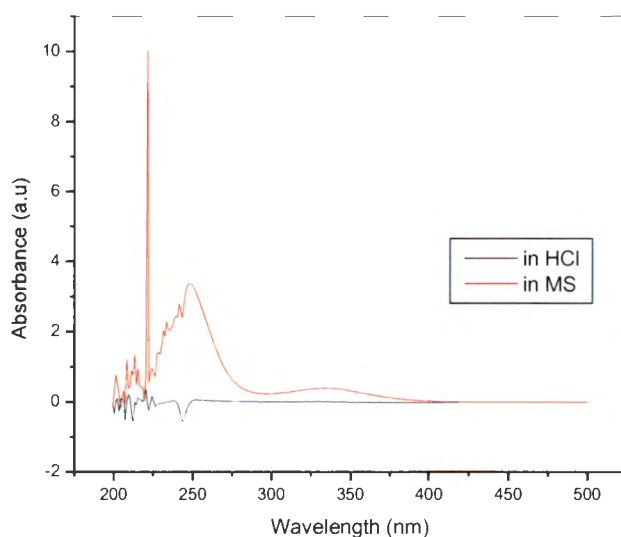


Figure 4.16: UV/Vis spectra of 50 mM [DMHYD] solution diluted in 0.5 M HCl and MS immersed for 6 hours.

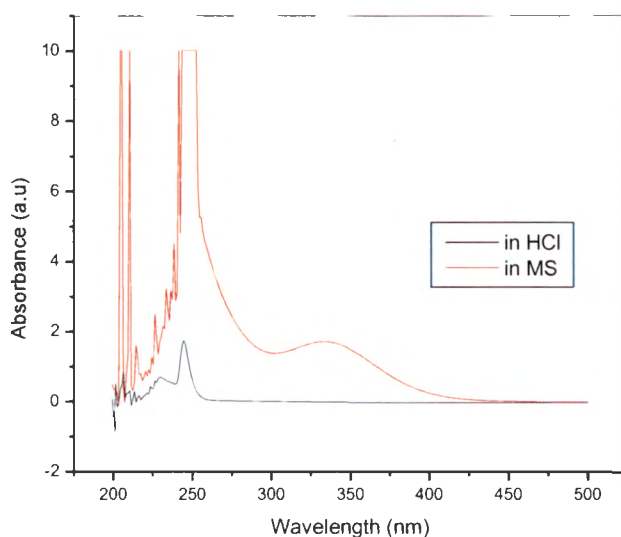


Figure 4.17: UV/Vis spectra of 50 mM [DBDMHYD] solution diluted in 0.5 M HCl and MS immersed for 6 hours.

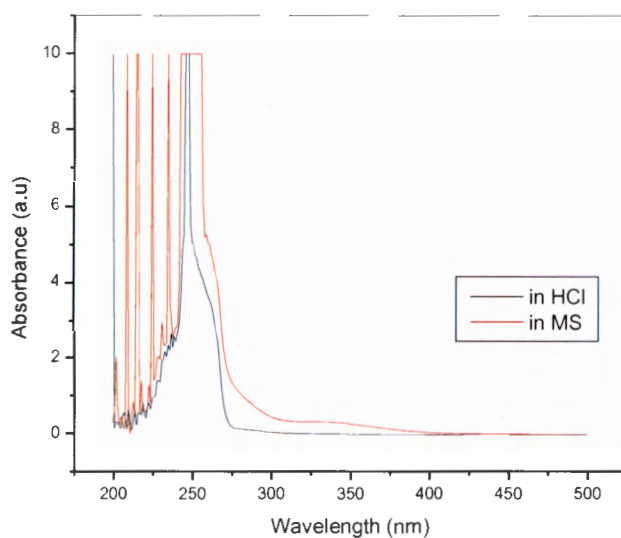


Figure 4.18: UV/Vis spectra of 50 mM [MPHYD] solution diluted in 0.5 M HCl and MS immersed for 6 hours.

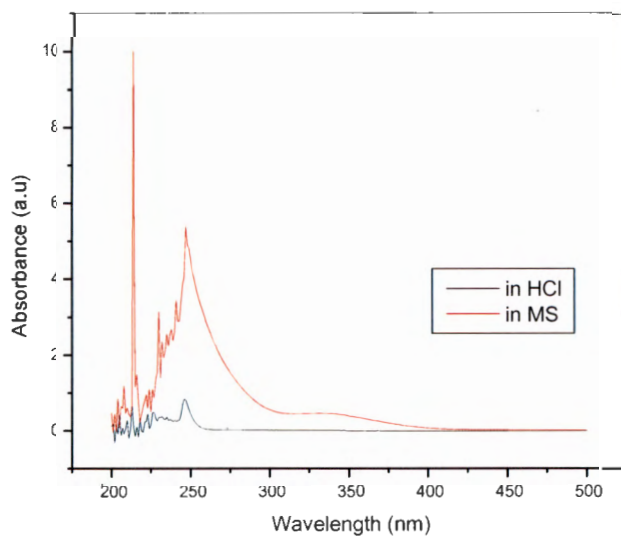


Figure 4.19: UV/Vis spectra of 50 mM [HYDAC] solution diluted in 0.5 HCl and MS immersed for 6 hours.

4.4. QUANTUM CHEMICAL CALCULATIONS

Quantum chemical studies were carried out in order to relate corrosion inhibition properties of the studied compounds to their molecular orbital (energy) parameters and other quantum chemical descriptors. The optimized structures of the hydantoin derivatives are shown in Figure 4.20. One salient observation in the structures is the torsional displacement of the phenyl substituent in MPHYD and the dimethyl substituents in DMHYD and DBDMHYD out of the plane of the ring.

The HOMO and LUMO electron density distribution isosurfaces are also shown in Figure 4.26. In all the molecules, the HOMO and LUMO are distributed over the five-membered imidazole ring such that N1, N3, C2 and C5 atoms in the ring are involved in the frontier molecular orbitals. It appears that C4 atom is not as strongly involved in HOMO electron density distribution as it does in the LUMO. Both O6 and O7 atoms feature in the HOMO and LUMO electron density distributions. The C8 atom in MHYD involved in the HOMO but not in the LUMO. The dimethyl substituents in DMHYD contribute to HOMO and LUMO, while those of DBDMHYD only feature in the HOMO. The carboxyl group in HYDAC is not involved in the HOMO but features in the LUMO. The wide spread of the frontier molecular orbitals electron density in these molecules is suggestive of efficient donor-acceptor interactions with metallic atom.

Selected quantum chemical parameters of the optimized structures are listed in Table 4.4. High value of E_{HOMO} connotes high tendency of a molecule to donate its HOMO electron to a suitable vacant orbital of the metal, while low value of E_{LUMO} implies high susceptibility of the molecule to electron-acceptance from appropriate occupied orbital of the metal. A molecule with lower energy gap (ΔE) is generally expected to have higher reactivity¹⁰¹⁻¹⁰⁵. The results in Table 4 revealed that there are no simple trends for most of the parameters in relation to the order of experimental inhibition efficiencies. However, DBDMHYD has the lowest E_{LUMO} and ΔE , which suggests that it is more disposed to electron-acceptance from a donor site than the other molecules and also more reactive. In addition, it also has the least value of η and highest value of χ . All these are in support of its highest inhibition efficiency as observed from experimental studies. Though the use of dipole moment (μ) to support inhibitive action of a corrosion inhibitor is often seen in two different ways, the highest value of dipole moment for DBDMHYD might favour strong dipole-dipole interactions between its molecules and metallic surface. This might inform enhanced adsorption of DBDMHYD molecules on mild steel surface and its high inhibition efficiency.

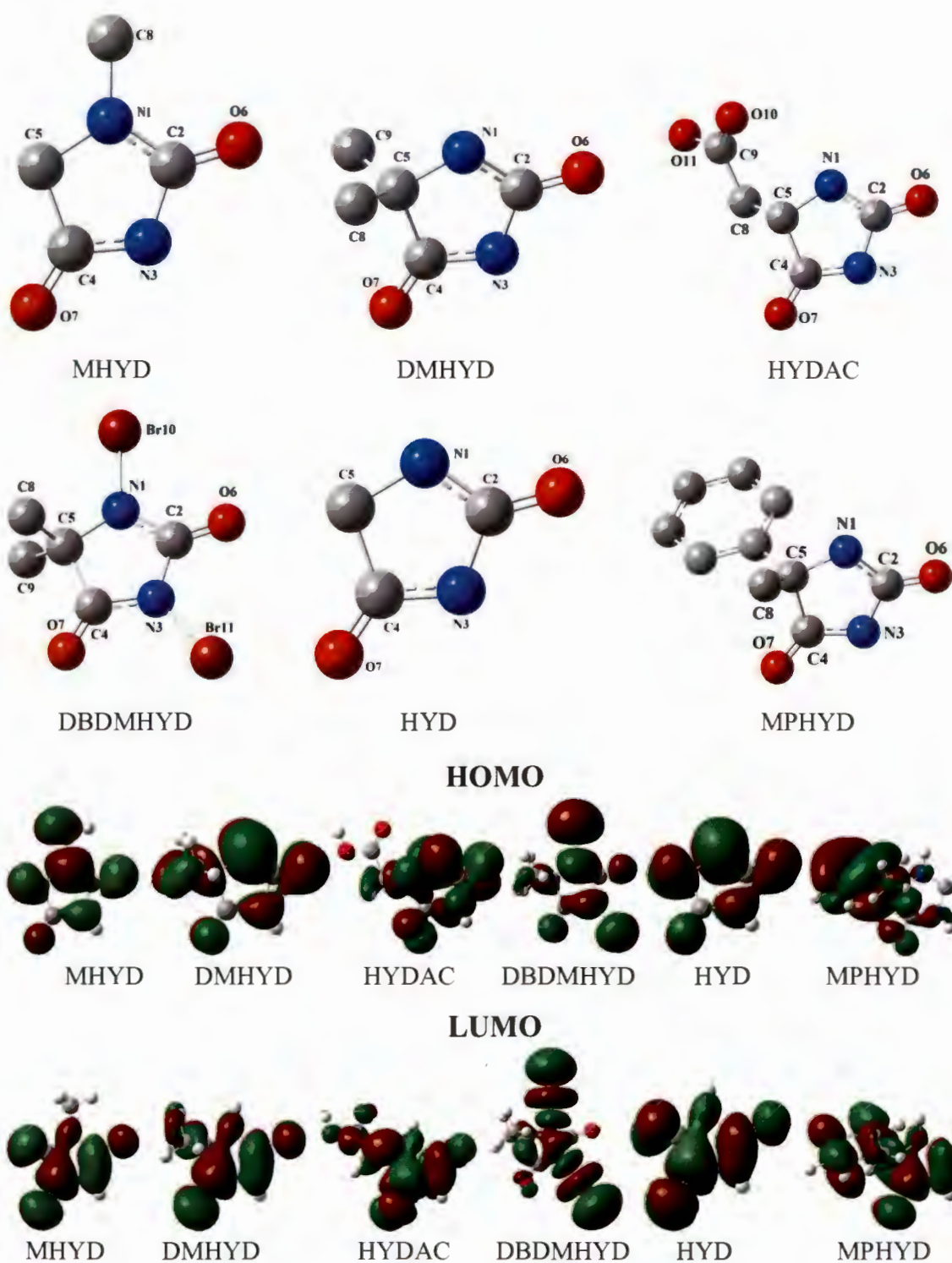


Figure 4.20: Optimized structures and HOMO and LUMO electron density isosurfaces of the studied hydantoin derivatives obtained using B3LYP/6-31G+(d,p) model in water phase.

Since a straight forward correlation could not be established between the individual quantum chemical parameters and the trend of inhibition efficiency, attempt was made to correlate experimental inhibition efficiencies with composite molecular descriptors (*vide infra* quantitative structure activity relationship). The results depicted in Table 4.4 showed that the values of quantum chemical calculation parameters did not show any regular trend, however, the lowest value of energy band gap (ΔE) for DBDMHYD suggests that it is most reactive and efficient inhibitor among the tested molecules. Moreover, DBDMHYD is associated with lowest hardness value (η) suggesting that it is most potent to transfer its electrons to the d-orbitals of the surface iron atoms resulting into strong metal-inhibitor interactions as compared to other remaining inhibitor molecules. In addition to the energy band gap (ΔE) and hardness (η) values, the highest inhibition efficiency of the DBDMHYD observed by experimental methods can be supported by its dipole moment value (μ). From the results it can be seen that DBDMHYD has maximum value of dipole moment suggesting that it is more polarizable when come in contact with metal surface and thereby cover larger surface area during metal-inhibitor interactions as compared to the other tested inhibitor molecules.

Table 4.4: Quantum chemical parameters for the hydantoin derivatives obtained using B3LYP/6-31G+(d,p) model in water phase.

Compound	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	η (eV)	χ (eV)	ΔN	μ (Debye)	%IE*
MHYD	-7.214	-0.785	6.430	3.215	4.000	0.467	4.105	76.00
DMHYD	-7.599	-0.797	6.802	3.401	4.198	0.412	4.158	86.00
HYDAC	-7.778	-0.991	6.787	3.393	4.384	0.385	3.840	78.00
DBDMHYD	-7.261	-2.646	4.615	2.307	4.954	0.443	4.349	90.00
HYD	-7.671	-0.813	6.858	3.429	4.242	0.402	3.744	88.00
MPHYD	-7.102	-1.103	5.999	3.000	4.102	0.483	3.866	74.00

*Average values of experimental inhibition efficiency.

4.5. MONTE CARLO SIMULATION STUDIES

The adsorption of each inhibitor molecule on Fe (110) surface was modeled using molecular dynamic simulation approach. The equilibrium configurations of inhibitor/Fe (110) systems showing the adsorption of the inhibitor molecule on metallic surface are displayed in Figure 4.21. In all the systems, the hydantoin ring lies on Fe (110) surface in a near flat orientation. This is indicative of strong interactions between the molecules and metal surface. It is also evident that the methyl substituents in DMHYD, DBDMHYD and MPHYD are not interacting directly with the metal surface. Binding and interaction energies of the systems are listed in Table 4.5. The highest value of binding energy (232.03 kcal/mol) was recorded

for DBDMHYD+Fe (110) system, which is in support of the highest inhibition efficiency of DBDMHYD as obtained from experimental studies. Similar to DFT based parameters, the parameters derived from Monte Carlo simulations also did not show any regular trends, however maximum value of interaction energy (-232.03 kcal/mol) for DBDMHYD suggested that it has maximum tendency of adsorption towards mild steel surface.

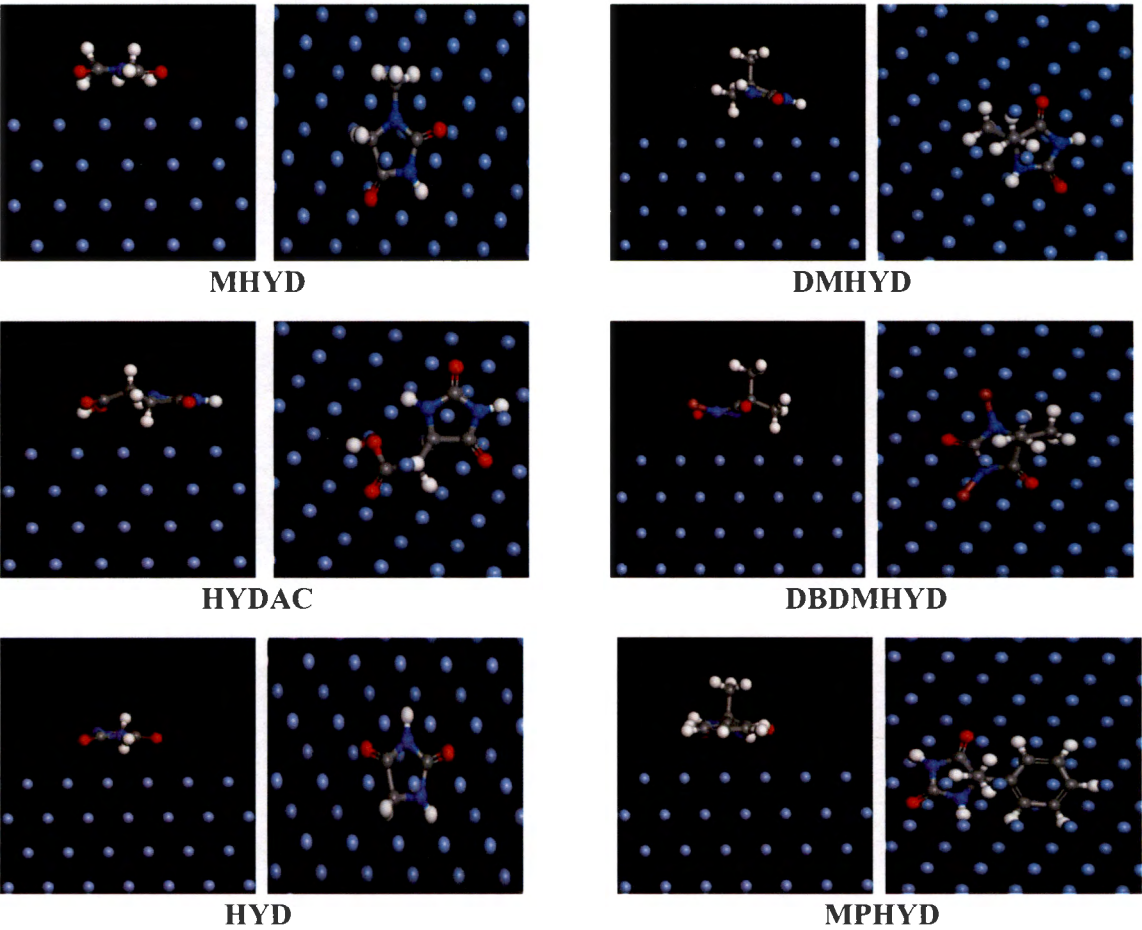


Figure 4.21: Top views (right-hand side) and side views (left-hand side) of equilibrium configurations

Table 4.5: Interaction energies between the inhibitors and Fe (110) surface (kcal/mol).

Systems	Interaction energy	Binding energy
Fe(110) + MHYD	-148.47	148.47
Fe(110) + DMHYD	-177.01	177.01
Fe(110) + HYDAC	-149.49	149.49
Fe(110) + DBDMHYD	-232.03	232.03
Fe(110) + HYD	-155.41	155.41
Fe(110) + MPHYD	-185.48	185.48

4.6 QUANTITATIVE STRUCTURE ACTIVITY RELATIONSHIP (QSAR) ANALYSIS

Quantitative structure activity relationship (QSAR) analysis is often employed to investigate the correlation of experimental data with molecular quantum chemical descriptors. QSAR proffers a way of observing how a particular (experimentally derived) activity of a set of compounds might vary with quantum chemical descriptors. It provides a robust statistical insight into the dependency of the observed corrosion inhibition activities of a set of molecules on multiple quantum chemical/molecular descriptors¹⁰⁶. In the present study, both quantum chemical parameters and the binding energies derived from the Monte Carlo simulations were utilized to correlate with the experimentally observed inhibition strength of the studied compounds. For this purpose, the average values of %IE obtained from the EIS measurements were utilized to correlate theoretical parameters and model equations were predicted based on multiple linear regression approach using the XLSTAT software¹⁰⁷. Different combinations of theoretical parameters were used to fit the experimental data. Linear and non-linear model equals were derived according to the propositions of Lukovits et al^{108,109}.

A wide search of different combination of parameters that best describe the average inhibition performances of the studied compounds was carried out. It was observed that the introduction of the binding energy to each composite parameters results in a better model compared to the ones without the binding energy. The best model was observed to be the one comprising the molecular weight (M.wt), ΔE , ΔN , and the binding energy (BE). The best three linear models as well as their corresponding plots of experimental and predicted %IE are shown in Figure 4.22. The model equations and associated statistical errors are listed in Table 4.6. The best linear fit suggests that the inhibition efficiency of the set of hydantoin derivatives studied in this work will increase with decreasing M.wt, ΔE , ΔN , and increasing BE.

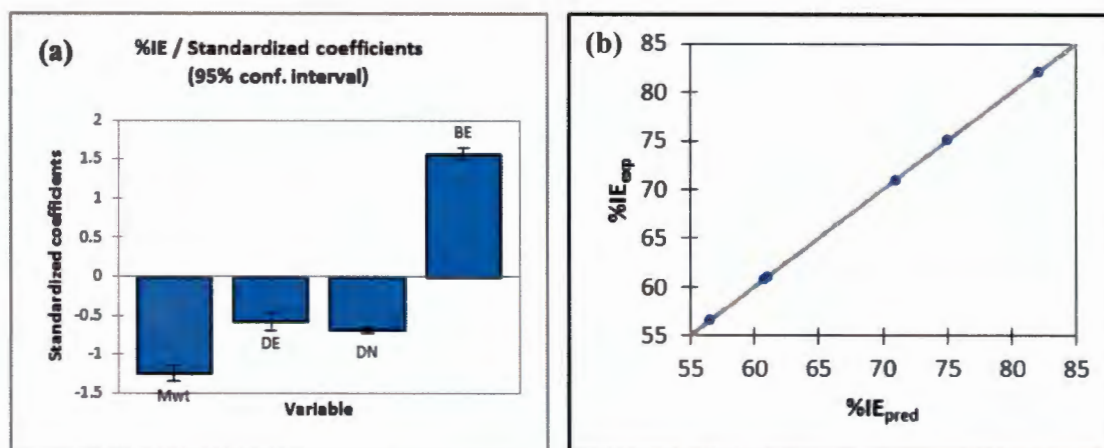


Figure 4.22: Standardized weights of parameters (a), and a linear plot of experimental and predicted %IE from the best linear model (b).

Table 4.6. QSAR composite parameters, model equations, correlation coefficients and root-means square errors.

Parameters		R^2	RMSE
Linear regression equations			
Mwt, ΔE , ΔN , BE	$\%IE_{pred} = 129.054 - 0.181Mwt - 6.550\Delta E - 174.884\Delta N + 0.484BE$	1.000	0.053
Mwt, E_{HOMO} , ΔN , BE	$\%IE_{pred} = 850.554 - 0.160Mwt + 75.209E_{HOMO} - 654.964\Delta N + 0.490BE$	0.999	0.768
Mwt, ΔN , BE	$\%IE_{pred} = 58.277 - 0.129Mwt - 145.025\Delta N + 0.533BE$	0.978	2.321
Mwt, E_{HOMO} , μ , BE	$\%IE_{pred} = -180.253 - 0.116Mwt - 21.265E_{HOMO} + 4.708\mu + 0.514BE$	0.971	3.775
Non-linear regression equation			
Mwt, ΔE , ΔN , BE	$\%IE_{pred} = (9.150 \times 10^{13}Mwt + 4.931 \times 10^{14}\Delta N + 9.701 \times 10^{13}\Delta E + 2.384 \times 10^{13}BE - 5.957 \times 10^{13}) \times 100 / (1 + 1.857 \times 10^{13}Mwt + 1.850 \times 10^{16}\Delta N + 8.102 \times 10^{14}\Delta E - 1.254 \times 10^{13}BE - 7.167 \times 10^{15})$	0.998	0.394
R^2 is the correlation coefficient, root-mean square error (RMSE) is defined as $\sqrt{\frac{1}{n} \sum_{i=1}^n (IE_{pred} - IE_{exp})^2}$ IE_{pred} = predicted average inhibition efficiency IE_{exp} = experimental average inhibition efficiency, $n = 6$ (number of observations)			

CHAPTER 5

CONCLUSION

5.1 CONCLUSION

In the present study, inhibition effect of hydantoin and its five derivatives have been investigated on mild steel corrosion in 0.5 M HCl solution using both experimental and theoretical methods. The following conclusions have been drawn from the studies:

- All the tested compounds inhibit mild steel corrosion and their inhibition efficiencies increase with increasing their concentration.
- Potentiodynamic polarization study suggested that tested compounds behaved as mixed type inhibitors, while MHYD, DMYD and HYD showed predominantly anodic inhibitive actions.
- The compounds inhibit mild steel corrosion in the acid by adsorbing on the steel surface to form protective film and their inhibitive action of did not change the corrosion mechanism.
- The adsorption behaviour of the compounds conforms to the Langmuir adsorption isotherm model and the mode of adsorption was inferred to be mainly physisorption.
- UV-Visible observation confirms the formation of a protective film of metal-inhibitor complex on the metal surface.
- Quantum chemical calculations and molecular dynamic simulations were carried out to corroborate experimental results. Quantitative structure activity relationship (QSAR) studies showed that the inhibitive performances of the studied compounds are well correlated with their molecular weights, frontier molecular orbitals energy gap, fraction of electron transferred and binding energy.
- Both experimental and theoretical studies revealed that DBDMHYD showed the highest protection efficiency for mild steel in 0.5 M HCl.

5.2 FUTURE RECOMMENDATION

Future work can be to perform surface analyses, such as SEM, TEM, etc on the inhibitor molecules and thermodynamic studies might also be worked on them. These compounds can be used in acid-pickling process owing to the high inhibition performance.

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APPENDICES

APPENDIX 1

Formulas used:

The parabolic rate law	:	$x^2 = k_p t - x_0$
Logarithmic rate law	:	$x = k_p \log(ct + b)$
Linear rate law	:	$x = k_L t$
Standard free energy change	:	$\Delta G^\circ = -nFE^\circ$
Inhibition efficiency (PDP)	:	$IE_{PDP} (\%) = \frac{(I'_{corr} - I_{corr})}{I'_{corr}} \times 100$
Inhibition efficiency (EIS)	:	$IE_{EIS} (\%) = \frac{(R_{ct} - R'_{ct})}{(R_{ct})} \times 100$
Global hardness	:	$\eta = -\frac{1}{2}(E_{HOMO} - E_{LUMO})$
Global electronegativity	:	$\chi = -\frac{1}{2}(E_{HOMO} + E_{LUMO})$
Fraction of electrons	:	$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}$
Interaction energy	:	$E_{interaction} = E_{total} - (E_{Fe-surface} + E_{inhibitor})$
Langmuir adsorption isotherm	:	$\frac{C}{\theta} = mC + \frac{1}{K_{ads}}$
Gibbs free energy of adsorption	:	$\Delta G^\circ_{ads} = -RT \ln(55.55K_{ads})$

APPENDIX 2

Paper submitted for publication from this thesis:

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“Experimental, quantum chemical, Monte Carlo simulations and QSAR studies on some hydantoin derivatives as corrosion inhibitors for mild steel in 0.5 M HCl solution”

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