

Synthesis, Characterization and Corrosion Inhibition Investigation of substituted triazines on aluminium and mild steel in 1M HCl: Experimental and Theoretical approach

By

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Declaration

I affirm that the research presented in this thesis is solely my own and was conducted under the guidance of Prof. L.C Murulana, Dr. C Fernandez, Prof. S.S Mnyakeni-Moleele, and Prof. M.M Kabanda as my co-supervisors. The information obtained from the literature has been appropriately acknowledged within the text, and a comprehensive list of references has been provided. This submission is intended to get a Doctor of Philosophy degree in Chemistry at the University of Venda. It has not been previously submitted for any other degree or examination at any other university.

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Dedication

This thesis is dedicated to my parents (**Tshikhudo Nndateni C and Tshikhudo Mbudzeni B**), for their support, endless encouragement, and boundless love have been my guiding light throughout this journey. Their sacrifices, wisdom, and faith in me have been the foundation upon which I have built my dreams.

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Abstract

Corrosion is the natural process through which refined metals are gradually converted to more chemically stable forms such as oxides, hydroxides, or sulphides. This process occurs because metals tend to return to their natural states. Proper selection and use of corrosion inhibitors can greatly extend the lifespan of metal components and reduce maintenance costs. This current study investigates the synthesized substituted triazines, namely 4,6-dichloro-2-morpholine-1,3,5-triazine (DMT), 4,6-dichloro-2-anilino-1,3,5-triazine (DPT), and 4,6-dichloro-N-methylanilino-1,3,5-triazine (DNT) as corrosion inhibitor on aluminium (Al) and mild steel (MS) in 1M hydrochloric acid (HCl). The substituted triazines were successfully synthesized and characterized using Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared (FT-IR) spectroscopy, and liquid chromatography-mass spectrometry (LCMS). Thermogravimetric analysis (TGA) was performed on the DMT, DPT, and DNT inhibitors to determine the degradation temperature. It was observed that the mass loss of DMT, DPT, and DNT begins when the temperature reaches 85.91°C, 181.007°C, and 253.82°C, respectively. Their anti-corrosive effect on Al and MS in 1M HCl was studied at a lower temperature using gravimetric analysis, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization curve (PDP), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX), and density functional theory approach (DFT). The weight loss measurement was carried out at different temperatures (303 to 323 K) and concentrations from 0.001M to 0.005M of the DMT, DPT, and DNT. The results obtained from the weight loss analysis revealed that the %IE of all the inhibitors is directly proportional to concentration on Al and MS. The highest inhibition efficiency of DMT, DPT, and DNT was observed at a concentration of 0.005M. On Al surface, the %IE of DMT and DPT decreased with increasing temperature, reaching 83.02% and 82.39% at 303 K, respectively. In contrast, DNT showed improved performance with rising temperature, achieving a maximum %IE of 95.02% at 313 K, making it the most effective inhibitor for Al under these conditions. On the MS surface, all three inhibitors exhibited a decrease in %IE with increasing temperature, with values of 93.87% (DMT), 90.20% (DPT), and 87.95% (DNT) at 303 K. The inhibitor adsorption on the Al and MS surface for all the inhibitors obeyed the Langmuir adsorption isotherm. The adsorption isotherm indicates the reaction is spontaneous, and inhibitor molecules adsorb onto Al and MS surface through weak force (Physisorption) and chemical bond (Chemisorption).

Based on EIS results, the Al impedance spectra consist of capacitive loops at a higher frequency and inductive loops at a lower frequency. In contrast, MS consists of a high-frequency capacitive loop. The capacitive loops represent the charge transfer resistance of the corrosion process and double layer. The inductive loops are attributed to the relaxation process in the oxide film covered on the metal surface. The PDP results revealed an increase in E_{corr} (a less negative value) was observed with a sustained rise in the DMT, DPT, and DNT concentration. For Al, all inhibitors are either anodic or cathodic inhibitors according to changes in E_{corr} and mild steel PDP, revealed that all the inhibitors are mixed typer inhibitors, implying that DMT, DPT, and DNT interfere with both the dissolution of the metal (anodic reaction) and the reduction of oxygen (cathodic reaction). The SEM/EDX confirms that DMT, DPT, and DNT inhibitors formed a protective film on the Al and MS surfaces, protecting them from a corrosive environment. From a water contact angle, the hydrophobicity of the Al and MS surfaces is enhanced in the presence of DMT, DPT, and DNT. The effect of graphene oxide (GO) into DMT, DPT, and DNT inhibitor in 1M HCl solution on MS as corrosion inhibitor was done using EIS and PDP. The modification of GO indicates an increase in the diameter of the Nyquist plot semi-circle and a shift in E_{corr} to more negative on the Tafel plot. DFT using the perdew-burke-ernzehof (PBE) in the DMol³ program was used to perform inhibitor...Al interactions to estimate the binding energies of the inhibitors on the Al(111) surface. The calculated binding energies value indicates that all inhibitor molecules physically bind on the Al(111) metal surface. For MS, the Perdew–Wang exchange (PW91) was used to perform inhibitor...Fe interaction. The binding energy calculation values indicate that all inhibitor molecules are chemically adsorbed onto the Fe(100) surface.

List of abbreviations

%IE	Inhibition efficiency
$\Delta G^{\circ}_{\text{ads}}$	Change in free energy of adsorption
ΔH_a	Enthalpy of activation
ΔS_a	Entropy of activation
A	Pre-exponential factor
Al	Aluminium
AO	Atomic Orbital
BSD	Backscattered detector
BCC	Body-centred cubic
BP	Becke-Perdew
CC	Coupled cluster
C_{dl}	Double-layer capacitor
Cl⁻	Chloride ions (Cl ⁻)
C_{inh}	Concentrations of inhibitors
COSMO	Conductor-like screening model
COSMO-RS	COSMO for real solvent
CPE	Constant-phase element
C_R	Corrosion rate
DC	Direct current
DCM	Dichloromethane
DFT	Density functional theory
DPT	4,6-dichloro-2-anilino-1,3,5-triazine
DMT	4,6-dichloro-2-morpholine-1,3,5-triazine

DNT	4,6-dichloro-N-methylanilino-1,3,5-triazine
DND	Double-numerical +d
DNP	Double numeric with polarization functions
DSPP	DFT semi-core pseudopotential
E_a	Activation energy
E_{ads}	Adsorption energy
$E_{binding}$	Binding energy
E_{corr}	Corrosion potential
EEC	Equivalent electric circuit
EIS	Electrochemical impedance spectroscopy
Eocp	Evolution of open-circuit potential
Eocp	Open circuit potential
E_w	Equivalent weight
f_a	Anodic interaction coefficient
f_c	Cathodic interaction coefficient
FCC	Face-centred cubic
Fe	Iron
$Fe(OH)_2$	Ferrous hydroxide
$Fe(OH)_3$	Ferric hydroxide
FT-IR	Fourier-transform infrared spectroscopy
GDP	Gross domestic product
GGA	Generalized gradient approximation
GRP	Glass-fiber reinforced polymers
GTO	Gaussian-type orbitals
GO	Graphene oxide
HCl	Hydrochloric acid
HF	Hartree-Fock

I	Electric current
i_{corr}	Corrosion current density
K_L	Dimensionless constant; separation factor
L	Inductance
LC/MS	Liquid chromatography/mass spectrometry
LDA	Local density approximation
Meta-GGA	Meta-generalized gradient approximation
MNDO	Modified Neglect of Diatomic Overlap
MS	Mild steel
MP	Møller-Plesset perturbation
MW	Molecular weight
n	CPE exponent
NACE	National Association of Corrosion Engineers
NAO	Numerical atomic orbitals
NCPP	Norm-conserving pseudopotentials
NDDO	Neglect of differential diatomic overlap
NMR	Nuclear magnetic resonance spectroscopy
O₂	Oxygen
OCP	Open-circuit potential
PAC	Performance, availability, and cost
PBC	Periodic boundary conditions
PBE	Perdew-Burke-Ernzerhof
PDP	Potentiodynamic polarization
PW86	Perdew-Wang 86
PW91	Perdew-Wang

Q_{ads}	Heat of adsorption
QM	Quantum mechanical
R	Resistance
R_{ct}	Charge transfer resistance:
RE	Reference electrode
RHF	Restricted Hartree-Fock (RHF)
R_L	Inductive resistance
R_p	Polarization Resistance
RPBE	Revised Perdew-Burke-Enzerhof
RT	Retention time
SCE	Saturated calomel electrode
SCF	Self-consistent field
SEM/EDS	Scanning electron microscopy/energy dispersive X-ray spectroscopy
SHE	Standard hydrogen electrode
TGA	Thermogravimetric analysis
TNP	Triple numerical polarized
UPLC	Ultra-performance liquid chromatography
UK	United Kingdom
US	United States
VCA	Video contact angle system
VCl_s	Volatile corrosion inhibitors
VP	Variable pressure detector
β_a	Anodic Tafel constant/slope
β_c	Cathodic Tafel constant/slope
τ	Relaxation time constant

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Chapter 1: Introduction

This chapter sets the stage for the research by providing a comprehensive overview of the background, objectives, and significance of the study.

1.1. Introduction

The world's economic development depends on its natural resources, production activities, and infrastructures that account for goods' exploitation, processing, and marketing. Those infrastructures (roads, bridges, airport air transport, school buildings, etc.) are affected by corrosion. Corrosion is one of the growing issues that greatly impact the country's economy and safety; the impact on the country's economy becomes the most important measure of corrosion in the country. A report developed by Corrosion Map of South Africa's macro atmosphere in 2019 states that according to the Worldwide Corrosion Authority, the cost of corrosion is estimated to be ZAR166 billion per annum which costs 5-7% of Gross Domestic product[1] and for the U.S is approximately 4.2% [2, 3]. These figures are likely underestimates, as they primarily reflect losses in large industries like oil and gas, while everyday corrosion-related costs remain largely unaccounted for.

Corrosion is a spontaneous, thermodynamically driven process involving electrochemical reactions, often accelerated by environmental conditions[4, 5]. Corrosion is something hoped to be avoided, but in the end, it is not possible to change the fundamental laws of thermodynamics to stop the corrosion process because it cannot be created nor destroyed completely: however, it is possible to reduce its rate by making use of different techniques such as anodizing, and painting, coating, cathodic protection, and corrosion inhibitors. Among these, corrosion inhibitors are considered one of the most cost-effective and practical solutions for controlling metal degradation.

Organic corrosion inhibitors are of particular interest due to their molecular structures, which typically contain heteroatoms (such as N, O, or S) and π -electron systems that enhance their ability to adsorb onto metal surfaces[6, 7]. This adsorption forms a protective barrier that reduces metal dissolution and inhibits further corrosion. However, many commercial organic inhibitors are toxic, expensive, or derived from non-renewable sources, which presents a significant limitation in their long-term industrial use.

Despite extensive research on organic inhibitors, there remains a need to develop new, more efficient, eco-friendly, and structurally tailored compounds that provide enhanced protection under aggressive acidic conditions. Current research is therefore focused on the design and synthesis of drug organic molecules with specific functional groups that promote strong adsorption, improved thermal stability, and high inhibition efficiency.

In this study, newly synthesized triazine derivatives are investigated as corrosion inhibitors for mild steel and aluminium in acidic media. The novelty of this research lies in the introduction of unique substituent groups designed to optimize the electronic and steric interactions between the inhibitor and metal surface. These compounds are evaluated using both experimental techniques and computational methods to provide a deeper understanding of their inhibition mechanisms, adsorption behavior, and structure activity relationships.

1.2. Scope of the study

Over a billion tons of metals are produced every year to construct plenty of products from different industries[8, 9]. There are countless uses of mild steel and aluminium in every industry, and they play a vital role in people's lives as they are used or form part of most equipment that humans use. This could be in the form of machinery such as the ones used in the medical field, gadgets such as smartphones, laptops, and vehicles that people use on their daily basis. Metals are also employed in the oil and gas industries, which normally operate at high temperatures. Their functions also involve the use of a corrosive solution like hydrochloric acid. The occurrence of corrosion in the field weakens metal over time. It frequently results in structural failure, leading to the shutdown of plants or industries and affecting their day-to-day operational activities.

South Africa is currently facing challenges associated with its aging infrastructure, including roads, bridges, air transport systems, and public buildings. These structures are increasingly affected by corrosion, leading to costly maintenance, structural failures, and safety risks such as building closures, bridge collapses, pipeline leaks, and chemical plant hazards. These problems not only threaten public health and safety but also impede the country's technological progress and economic growth.

Globally, corrosion prevention remains a major industrial and scientific concern, given the critical role metals play in infrastructure and manufacturing. Among the various corrosion control strategies, organic corrosion inhibitors have attracted significant attention due to their efficiency, ease of application, and cost-effectiveness. While many studies have reported inhibition efficiencies above 98%, these often involve structurally complex or expensive molecules, limiting their practical applicability.

This study addresses this gap by synthesizing and investigating three novel, structurally simpler triazine-based compounds: 4,6-dichloro-2-morpholine-1,3,5-triazine (DMT), 4,6-dichloro-2-

anilino-1,3,5-triazine (DPT), and 4,6-dichloro-N-methylanilino-1,3,5-triazine (DNT). These molecules were selected based on due to the triazine core's known coordination ability and chemical versatility. The novelty of this research lies in the rational design and modification of the triazine ring with different substituents to investigate their influence on corrosion inhibition performance. A combined experimental (weight loss, EIS, PDP, SEM-EDX, contact angle) and theoretical (DFT) approach is employed to thoroughly evaluate the inhibition efficiency and elucidate the adsorption mechanisms. This integrated study provides valuable insights into structure activity relationships and demonstrates a pathway toward developing cost effective and environmentally friendly corrosion inhibitors tailored for real-world application.

The framework of the investigation is based on the following objectives:

1. Synthesize and characterize substituted triazine derivatives (DMT, DPT, and DNT) as corrosion inhibitors using NMR, FTIR, and LC-MS.
2. Evaluate the thermal stability and decomposition behavior of the synthesized inhibitors using Thermogravimetric Analysis (TGA).
3. Investigate the corrosion inhibition efficiency and adsorption behavior of triazine derivatives through gravimetric analysis, electrochemical techniques (EIS, PDP), and surface characterization (SEM, EDS, FTIR).
4. Analyze the thermodynamics and kinetics of inhibitor adsorption on metal surfaces under varying conditions.
5. Assess the hydrophobicity and wettability effects of the inhibitors using contact angle measurements.
6. Utilize quantum chemical calculations and theoretical modeling to predict molecular interactions, electronic properties, and inhibition mechanisms

Chapter 2: Literature Review

The purpose of this chapter is to provide a comprehensive review of the existing literature relevant to corrosion inhibitors. This chapter aims to offer a thorough understanding of the key concepts, theories, and empirical findings that form the foundation of this study. By critically evaluating previous research, this chapter explores the key theories and models that underpin the research. It will also identify and discuss the literature's main themes and concepts that justify the present study's need.

2.1. Introduction to corrosion

Corrosion is viewed as a universal phenomenon, omnipresent and omnipotent; people know it as rust. Corrosion is generally taken as a spontaneous process that damages the material by reacting with a corrosive agent that tends to transform pure material into an undesirable substance[10]. Corrosion brings an entire change within the properties of metals; it negatively affects industries differently. Just like other natural hazards the damage that corrosion makes is very clear. Corrosion causes extensive damage to infrastructure, railroads, pipeline breakage, ships, aircraft, mining, petrochemical production, food processing, mining, agricultural production, etc.

One of the largest sectors of the world economy is the agriculture industry, in which their investments depend on the type of activities involved. In agriculture, corrosive chemical compounds are widely used in various farming activities. These include fertilizers, chemicals for pest, disease, and weed control (herbicides and pesticides), grain and silage preservatives, salts and weak acids, sterilizing chemical solutions for cleaning purposes, and solutions containing sulphates and chlorides[11, 12]. The corrosive attack of agricultural environments on machines leads to damage and a variety of defects. Also, agricultural buildings and their fittings are vulnerable to corrosion. Animal houses especially experience severe corrosion attacks due to the atmosphere, which contains ammonia, weak acids, sulphur compounds, salts, and moisture in high concentrations.

Corrosion affects domestic water supplies. Corrosive chemical slowly dissolves into metal, causing plumbing pipes, fixtures, and water-using equipment to deteriorate and fail. It can affect domestic water supply differently; the entire metal surface becomes thin, and red stains appear in iron and steel plumbing systems or metals oxidize in a process, which often reduces water flow through the line supply and destroys water valves or water surface control, creating leaks inside and outside of valves. This type of corrosion is caused by water chemistry and by exposure to soil or other corrosive environments. Another is when it forms deep pits that can penetrate pipe or tank walls; this makes a hole in a pipe or tank and causes serious water damage to the home or business[13].

2.2. Corrosive environmental

A corrosive environment refers to an environment in which materials, especially metals, are exposed to conditions that accelerate the corrosion process. As mentioned, corrosion is the deterioration of materials, typically metals, due to chemical or electrochemical reactions with their surrounding environment. A corrosive environment can involve various factors that contribute to the degradation of materials. Here are some common features of corrosive environments:

2.2.1. Temperature

Temperature extremes can influence the corrosion of materials in several ways. Both high and low temperatures can affect the rate and mechanisms of corrosion, depending on the specific environment and the type of materials involved. High temperatures can accelerate the kinetics of chemical reactions, including corrosion reactions[14, 15]. Fluctuations in temperature, especially if they involve rapid heating and cooling cycles, can contribute to thermal cycling corrosion. The expansion and contraction of materials can create stress, making them more susceptible to corrosion. Some metals form protective oxide layers at room temperature, but these oxide layers may break down or become less effective at elevated temperatures, exposing the metal to corrosion[15-19]. Low temperatures generally slow down electrochemical reactions, which can reduce the corrosion rate. However, this does not mean that corrosion is entirely halted, especially in the presence of corrosive agents. Some metals, particularly those that become brittle at low temperatures, may be more susceptible to stress corrosion cracking[20-24]. The combination of low temperatures and tensile stress can promote crack formation and propagation.

2.2.2. Moisture

Moisture serves as an electrolyte, providing the medium through which ions can move. In the presence of moisture (water or humidity), metals can undergo electrochemical reactions that lead to corrosion. The moisture facilitates the flow of ions, enabling the movement of electrons between anodic and cathodic sites on the metal surface. Water is involved in various corrosion reactions, such as oxidation and reduction. For example, in the presence of oxygen and water, iron can oxidize to form iron oxide (rust). Corrosion reactions often involve the evolution of

hydrogen gas. Moisture is necessary to form hydrogen ions, which can participate in reactions leading to hydrogen gas generation [25-30].

2.2.3. Chemical agents

Chemical agents such as acids, bases, etc., significantly influence corrosion by accelerating or initiating corrosion reactions on metal surfaces. The interaction between metals and specific chemicals can lead to the deterioration of the metal, compromising its structural integrity. Acids can react with metals, leading to the formation of metal salts and the release of hydrogen gas. Strong acids, such as hydrochloric or sulfuric acid, can be highly corrosive to certain metals. Bases can also corrode metals, particularly aluminum and mild steel. The formation of complex hydroxide compounds during the reaction contributes to corrosion[31-38].

2.3. Electrochemical Corrosion

Electrochemical corrosion is when metal corrodes in a corrosive environment. This happens when metal meets conducting fluid or when two heterogeneous metals are dipped in a solution[39-41]. On the surface of the metal, according to electrochemical corrosion, there is the formation of a galvanic cell, where anodic and cathodic reactions are always necessary if corrosion takes place since metal cannot lose electrons unless other substances can accept those electrons. Anodic electrode undergoes oxidation, resulting in corrosion[42].



In acidic solutions with a pH less than 4, the primary common cathodic reaction during the corrosion of metals involves the reduction of protons (hydrogen ions) and the gain of electrons to produce a molecule of hydrogen gas.



In strongly acidic solutions, the reduction of protons to form hydrogen gas (H_2) is often a dominant cathodic reaction. However, as the pH increases or is neutral to alkaline solutions, the reduction of oxygen becomes more favorable and can play a significant role as the primary cathodic reaction. In the absence of dissolved oxygen, the reduction of water can serve as an alternative cathodic reaction. The direct reduction of water involves the gain of electrons and protons, forming hydroxide ions[43-48]. The reaction can be represented as follows 2.3:



2.3.1. Corrosion of mild steel

Mild steel is probably a material used frequently in the construction industry. Mild steel is an affordable, adaptable, and useful material in a wide range of applications, such as producing automobile components, pipelines, mining, construction, etc. Unfortunately, it is also prone to corrosion. When mild steel is exposed to an environment that contains oxygen or water, it corrodes. When these elements come into contact with the surface of the mild steel, they react with the iron atoms in its surface layer, causing oxidation. In addition to water and oxygen, other substances, such as chloride or sulphide ions from acid, can speed up corrosion.

When iron corrodes, iron particles undergo oxidation, releasing electrons. These electrons accumulate within the metal, resulting in a buildup of negative charge. This process is known as an anodic reaction and leads to the formation of ferrous ions[49].



The electron released at the anodic area migrates to the cathodic area. Faraday's principles dictate that the speed of anode and cathode reactions must be directly proportional and determined by the corrosion current, which represents the overall flow of electrons from anodes to cathodes[50-52]. When the iron is immersed into hydrochloric acid at the cathode, hydrogen ions' reduction produces hydrogen gas, as shown in equation 2.2. The overall chemical reaction is given in equation 2.5.



For aqueous solutions, the adsorption of hydrogen ions (H^+), is involved in the surface of the solid, followed by the release of protons (H^+) and the formation of ferrous ions and water. The equilibrium expression for this reaction can be written as follows:



Aqueous solutions containing Cl^- ions, the type of reaction occurring here involves the dissolution of a complex ion $[FeClOH]$, the release of protons (H^+), and the formation of ferrous ions (Fe^{2+}), chloride ions (Cl^-), and water (H_2O).



2.3.2. Corrosion of aluminium

Aluminum is produced by extracting bauxite, a material obtained by mining, in order to obtain usable aluminum. Aluminum possesses the qualities of being lightweight, strong, and resistant to corrosion. This is attributed to the inert and protective nature of the aluminum oxide film that forms on the surface of the metal. Although aluminium is resistant to corrosion when exposed to a very strong acid or alkaline environment outside the pH range from 4 to 9, pitting corrosion will occur. The rate of corrosion of aluminum is also reduced rapidly with time.

During a corrosion process, aluminum loses electrons and is oxidized to form aluminum ions with a positive charge at the anode in equation 2.8. After aluminum loses electrons, another species must undergo reduction, accepting the electrons that aluminum is releasing at the cathode



The corrosion of aluminum in an aqueous solution of hydrochloric acid, aluminum reacts with the hydrogen ions from hydrochloric acid, leading to the formation of aluminum ions and the release of hydrogen gas.



The aluminum ions formed in the dissolution step react further with chloride ions from hydrochloric acid to produce aluminum chloride.



2.4. Classification of Corrosion

Corrosion is a process involving intricate chemical reactions that can be triggered by many factors, depending on the surrounding environment. This has led to the emergence of different categorizations of corrosion. Corrosion can manifest in two broad manners: as generalized corrosion, affecting the entire metal surface, or as localized corrosion, confined to specific

regions or sections. Metals can corrode in several ways depending on environmental conditions or design-related issues.

2.4.1. Generalized corrosion

General corrosion is also known as uniform attack corrosion, which is the most common type of corrosion caused by a chemical or electrochemical reaction, resulting in the deterioration of the entire exposed metal surface. This type of corrosion increases with an increase in acidity concentration. Because this type of corrosion occurs in a specific corrosive environment, estimating the lifetime of a material is easy; it can be estimated by measuring the corrosion rate. In most cases, generalized corrosion on metal surfaces manifests as visual damage before it compromises the metal's structural integrity. As a result, maintenance usually takes place long before this kind of rust destroys an item. However, if consistent corrosion is not stopped, an asset will eventually completely degrade[53-55].

2.4.2. Localized corrosion

Localized corrosion is the accelerated deterioration of passive metals in corrosive settings. This phenomenon is distinguished by a concentrated assault on specific regions of surface components, whereas the rest of the surface experiences corrosion at a somewhat slower pace. This can occur as a result of environmental factors or the inherent qualities of the component material, such as in the formation of a protective oxide film. Localized corrosion occurs when the surface of a material is effectively protected against corrosion, but there are specific areas where the corrosion protection is no longer effective, leading to deterioration in those localized spots. Pitting, crevice, and stress corrosion cracking are the three most prevalent forms of localized corrosion[56-59]. In pitting, the metal is attacked at certain fixed sites on the metal surface where the otherwise protective oxide film breaks down locally, usually due to the action of chloride ions[59-61]. In crevice corrosion, the metal within narrow clearances undergoes localized attack. In stress-corrosion cracking, the combined action of applied stress and a chemical environment causes the initiation and propagation of cracks in the metal[20, 62-64].

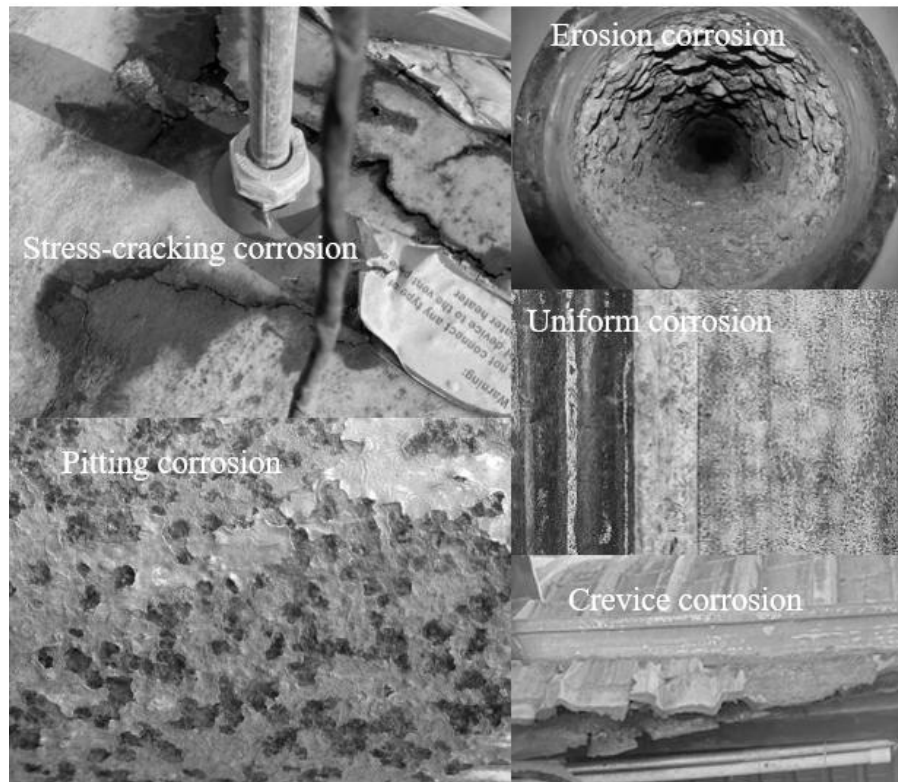


Figure 2. 1: Different types of corrosion.

2.5. Cost of Corrosion

Corrosion incurs significant expenses and has the potential to cause substantial harm. Corrosion gives rise to three primary areas of concern: economic implications, safety risks, and environmental harm. Within this particular framework, the malfunction or collapse of operational machinery or buildings, such as bridges, due to corrosion can result in catastrophic consequences, such as harm to individuals or even loss of life.

2.5.1. Economic cost

The financial cost of corrosion involves both direct and indirect expenses, which can be classified into four primary categories: capital costs include expenses related to the replacement and refurbishment of corroded equipment, as is shown in Figure 2.2, there is a need for replacement and refurbishment of the corroded pipeline, control costs are related to efforts aimed at managing and mitigating corrosion, design costs are incurred during the initial planning and construction phases future corrosion related, and associated costs are indirect cost related to corrosion including the supplementary service and risk management[65]. The global cost of corrosion is estimated to be around \$3 trillion USD annually, equivalent to about 3-4%

of the world's GDP. Africa faces a substantial portion of this burden due to its industrial and environmental conditions[66]. In 2017, Baorong Hou estimated that the cost of corrosion in China was over 2127.8 billion RMB, approximately equivalent to 310 billion USD. This amount accounted for around 3.34% of the country's gross domestic product[67]. The cost of corrosion in South Africa is a significant economic burden, estimated to account for over 5% of the country's GDP. This translates to more than R130 billion annually[68]. Corrosion affects various sectors beyond mining, including infrastructure and water supply systems. Studies indicate that up to 25% of water is lost due to leaks caused by corrosion in the supply chain. To mitigate these costs, advanced materials like glass-fiber reinforced polymers (GRP) are being used, especially in extreme environments, as they offer superior resistance to corrosion compared to traditional materials[69, 70].



Figure 2. 2: Corroded water supply system[71]

2.5.2. Human safety

In addition to financial losses, corrosion can also pose a risk to human safety, making it crucial for industry people to be vigilant about this occurrence. Death can be caused by the failure of steam pipes in nuclear power plants, bridge collapses, gas pipeline breaches, and airplane catastrophes. Moreover, the corrosion of iron-based hulls in ships presents a peril to the crew.

Lead-based pipes were often used for water transportation for a long time. However, it was later discovered that lead can contaminate the water due to corrosion, leading to lead poisoning in humans. Corrosive substances used in industrial processes can pose a threat to workers and the surrounding population if harmful chemicals spill, resulting in health problems and potential deaths. Weichen Xu documented in 2024 that in 2021, a total of 98 individuals perished due to the collapse of a condominium in Miami, Florida, with corrosion being a likely factor. The collapse of a 200-meter portion of a road bridge and one of its three supporting towers in Genoa, Italy, in 2018, resulting in the death of 43 individuals, was likely caused by corrosion[66].

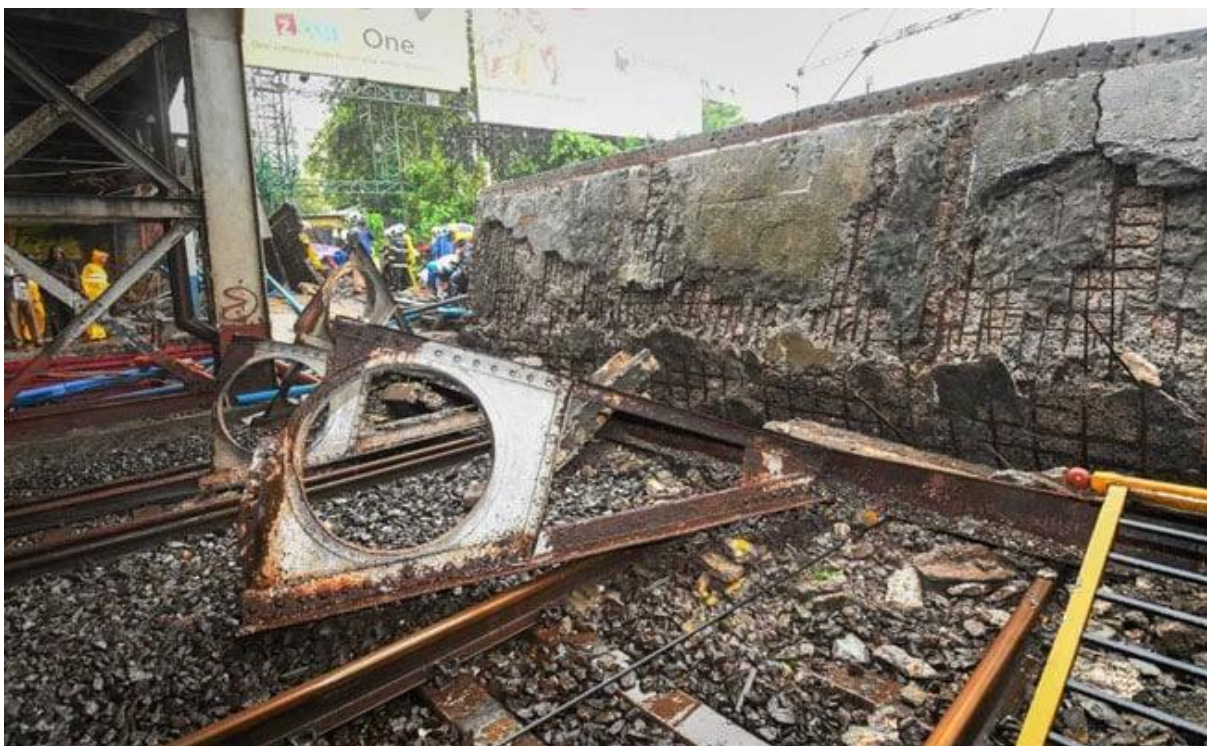


Figure 2. 3: Mumbai bridge collapse due to corrosion [72]

2.5.3. Impact of environmental

A significant example of environmental damage caused by corrosion is oil spills from corroded pipelines. For instance, the 2010 oil spill in the Gulf of Mexico, although primarily caused by a blowout, highlighted the potential for corrosion in aging infrastructure to exacerbate environmental disasters. Oil spills result in widespread ecological damage, affecting marine and coastal ecosystems and leading to long-term environmental and economic consequences[73]. Corroded materials often need to be disposed of, contributing to waste management challenges. The extraction of raw materials needed to replace corroded

components can lead to habitat destruction, affecting biodiversity and disrupting ecosystems. The production and transportation of new materials to replace corroded ones consume significant amounts of energy, leading to increased greenhouse gas emissions and further environmental degradation. Corrosion can lead to the release of harmful substances into the environment, causing air pollution and water and soil contamination, as shown in Figure 2.3[65].



Figure 2. 4: Disaster caused by oil spill in the Gulf of Mexico[73].



Figure 2. 5: External corrosion of oil & gas pipelines [74].

2.5. Corrosion control

Corrosion control is essential for maintaining the integrity and longevity of materials, particularly metals, that are prone to degradation through chemical or electrochemical reactions with their environment. Effective corrosion control strategies can prevent significant economic losses, safety hazards, and environmental damage.

2.5.1. Material selection

Material selection involves the choice of materials that are inherently resistant to corrosion or can be effectively protected against it. Engineers must consider performance, cost, and availability when choosing materials for corrosion management. Each metal and alloy exhibit distinct responses when exposed to different corrosive conditions; comprehending these interactions is crucial. Chromium improves strength under high temperatures and is resistant to oxidation and sulfidation. Nickel enhances the metal's stability, weldability, and resistance to stress corrosion[75-78]. Aluminum accelerates the process of age hardening and increases resistance to oxidation at elevated temperatures. Titanium improves age hardening and reduces the overall weight of the material. Molybdenum contributes to the strength at high temperatures and reduces the effects of acids. Niobium increases resistance to pitting and crevice corrosion. Tungsten improves weldability and strength. Cobalt makes the alloy resistant to carburization

and sulfidation[79-82]. Nitrogen provides metallurgical stability and strength. The costs associated with acquiring high-quality alloys are directly proportional to the desired level of performance. In addition, the process of selecting a material result in finding a suitable material solution. This selection must take into consideration several elements, such as national rules, international standards, operational experience, and prior goods. Typically, carbon steel is the preferred choice for all systems unless it can be proven that corrosion-resistant alloys are more efficient, resulting in significant cost savings. Low-cost alternatives for hydrate control include the use of low alloyed stainless steels with protective painting, carbon steel with polymer materials, or pipe-in-pipe solutions[79, 83-86].

2.5.2. Environmental control

Environmental control involves modifying or controlling the environment to reduce corrosive elements. The corrosion rate can be reduced by controlling the factors that influence corrosion rate, such as humidity and moisture, temperature, atmosphere, and chemical environment control. Humidity and moisture can be controlled by dehumidification, and outdoor areas should be designed with proper grading and sloping to ensure water runoff and prevent water accumulation around structures[87, 88]. For temperature, by making use of thermal insulation materials to maintain consistent temperatures and prevent condensation on pipes, tanks, and other equipment, the atmosphere is controlled by design structures with adequate openings and vents to promote natural airflow and reduce the concentration of corrosive gases and use air filters to capture and remove particulate matter and corrosive substances from the air in an industrial setting[89, 90]. In a chemical environment, the corrosion rate is controlled by maintaining a neutral pH in aqueous environments to minimize acidic or alkaline corrosion and by adding corrosion inhibitors into water systems to prevent the corrosion of metal components[29, 54, 91-95]. Corrosion inhibitor is the central theme of this thesis and, therefore, it is discussed further in the following sections

2.6. Corrosion inhibitors

The use of corrosion inhibitors is one of the most economical and practical methods of reducing corrosion attacks on metals. When a suitable concentration of corrosion inhibitor is added in a corrosive environment, the rate of corrosion is reduced. The corrosion inhibitor can be solid, liquid, or gas. It can be used in solid media (concrete, coal slurries, or organic coating), liquid media (water, aqueous solution, or organic solvent), and gaseous (atmosphere or water

vapor)[93, 96-99]. Corrosion inhibitors are used in oil and gas exploration and production, petroleum refineries, chemical manufacturing, heavy manufacturing, water treatment, and product additive industries. Water transmission and distribution systems use corrosion inhibitors like phosphates and amine volatiles (cyclohexylamine, morphine), pH adjusters, and alkalinity controls for efficient protection[100, 101]. Thermoelectric uses Ammonia, Cyclohexylamine, alkanol, and morphine as inhibitors in boilers in various processes. Corrosion inhibitors are added to the hydrochloric acid used for the solubilization of limescale to prevent an attack on pipes. Inhibitors can be organic or inorganic compounds usually dissolved in an aqueous environment[102-104].

2.6.1. Classification of inhibitors

Corrosion inhibitors are classified based on their mode of action, chemical nature, or the environment in which they are used. Here are the main classifications

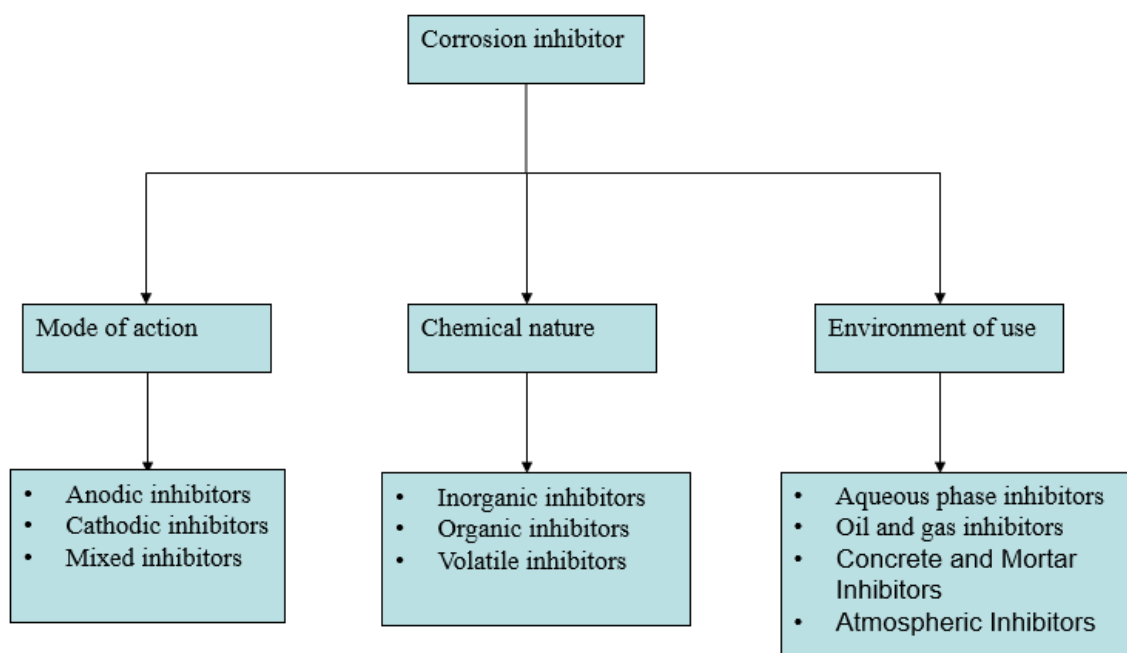


Figure 2. 6: Classifications of corrosion inhibitors

2.6.1.1. Anodic inhibitors

Anodic inhibitors interfere with the anodic process by increasing the anodic polarization. They work by shifting the anodic potential to enable passive film, which is formed on the surface of the metal by inhibiting the anodic metal. Although these inhibitors are widely used, they are

known as dangerous inhibitors because if certain areas are left unprotected by the depletion of the inhibitors, severe local attacks can occur. When the passivation inhibitors such as phosphates, tungstate, and molybdates do not reach the concentration level to block off all anodic sites, localized attacks such as pitting corrosion can become a serious problem[29].

2.6.1.2. Cathodic inhibitors

Cathodic inhibitors reduce corrosion by slowing the reduction reaction rate at the cathode or precipitate cathodic areas to increase the resistance on the surface, so diffusion of reducible ions is limited[105-108]. In a typical electrochemical corrosion process, two primary reactions occur: the anodic reaction, where the metal loses electrons and dissolves into the solution, and the cathodic reaction, where these electrons are consumed by a reduction process, often involving oxygen or hydrogen ions in the electrolyte[54, 55, 109-111]. Cathodic inhibitors function through multiple mechanisms: Certain cathodic inhibitors promote the formation of a protective layer on the surface of the metal. For example, compounds such as phosphates and carbonates can undergo a chemical reaction with metal ions, forming insoluble precipitates. These precipitates then cover the surface, which subsequently reduces the available area for the cathodic reaction[112-115]. Some other cathodic inhibitors have the ability to adhere to the surface of a metal, forming a protective layer that limits the exposure of corrosive substances to the metal. These compounds frequently consist of functional groups that exhibit strong bonding with the metal, forming a protective layer. Other cathodic inhibitors function by diminishing the concentration of the reactants engaged in the cathodic process. For example, oxygen scavengers eliminate dissolved oxygen from the electrolyte, hence reducing the rate of oxygen reduction, which is a frequently occurring cathodic reaction[115-119].

2.6.1.3. Mixed inhibitor

Mixed inhibitors involve the simultaneous inhibition of corrosion for both anodic and cathodic reaction rates. This type of inhibitor works by forming a film compound that indirectly blocks both anodic and cathodic sites through the formation of precipitates on the surface. Compared to the pure anodic inhibitors, mixed inhibitors are less dangerous[29, 120-124]. Many mixed inhibitors adsorb onto the metal surface, forming a protective barrier that reduces the accessibility of both anodic and cathodic sites to corrosive agents. This barrier can decrease

the rate of both metal dissolution (anodic reaction) and the reduction of oxidizing agents (cathodic reaction)[122, 125, 126]. Other mixed inhibitors can form a passivating film over the metal surface. This film can be either organic or inorganic and serves to protect the metal by physically blocking corrosive substances from reaching the surface. Some mixed inhibitors may chemically react with the metal surface to form a stable compound less susceptible to corrosion[93, 114, 116].

2.6.1.4. Inorganic inhibitors

Inorganic inhibitors are compounds used to prevent or slow down corrosion by forming protective films or layers on metal surfaces. These inhibitors are typically more stable at higher temperatures and in harsh chemical environments compared to organic inhibitors. However, careful selection and management are crucial to maximize their effectiveness while minimizing environmental and operational risks. Because some inorganic inhibitors, such as chromates, are toxic and pose environmental risks. May not be suitable for all types of metals and applications. Some inhibitors can lead to scaling or deposition problems if not properly managed[113, 127, 128].

2.6.1.5. Volatile inhibitors

Volatile corrosion inhibitors (VCIs) are a class of corrosion inhibitors that protect metal surfaces by releasing vapor-phase compounds that condense and form a protective molecular layer on the metal. These inhibitors are beneficial for protecting metal parts in enclosed environments, such as during storage and shipping. VCIs are simple to apply; they protect without the need for direct application of coatings or oils, which can be difficult to remove. However, most VCIs are effective in sealed or enclosed environments where the vapor can accumulate. Some VCI compounds can be hazardous and require proper handling and ventilation[29, 116, 129, 130]. Not all VCIs are suitable for all metals; selection must be based on the specific metal and environmental conditions.

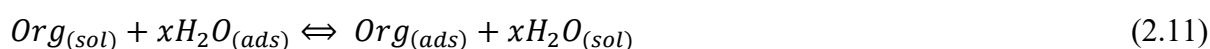
2.6.1.4. Organic inhibitors

Organic inhibitors are substances used to reduce the rate of corrosion by forming a protective film on the surface of metals. These inhibitors are often preferred due to their efficiency and relatively low environmental impact compared to inorganic inhibitors[113]. Organic inhibitors

can be used in oil and gas, water treatment, automotive, metalworking, and manufacturing industries. The presence of active functional groups is essential for the effectiveness of organic corrosion inhibitors[131]. These functional groups interact with the metal surface and form a protective layer, preventing further corrosion. The mechanism through which these functional groups act involves adsorption onto the metal surface, creating a barrier that inhibits the interaction of corrosive substances with the metal. The commonly employed active functional groups in organic corrosion inhibitors include: These functional groups contain nitrogen atoms that have the ability to form chelating agents when they react with metal ions. The dominating nitrogen atoms have the ability to create chelating agents with metal ions. The main nitrogen-containing functional groups used in corrosion inhibitors are amines, imides, and guanidines. Oxygen atoms in compounds can form a protective layer on metal surfaces, inhibiting further corrosion. Carboxylic acids, esters, and ethers are commonly used as oxygen-containing functional groups in substances that prevent corrosion. Sulfur-containing functional groups possess the capability to form a protective coating on the metal surface, preventing further corrosion. Sulfonic acids and thiols are commonly employed as sulfur-containing functional groups in corrosion inhibitors[132-139]. Phosphorus-derived functional groups have the ability to form a protective coating on metal surfaces, thereby inhibiting further corrosion. Phosphonic acids and phosphates are often employed as functional groups in phosphorus-containing corrosion inhibitors. Halogens, including chlorine, fluorine, and bromine, possess functional groups that can form a protective coating on metal surfaces, inhibiting further corrosion[131, 140-143].

2.7. Mechanism of corrosion inhibitor

The corrosion inhibitor (Org) can alternate between adsorbing onto the solid surface and being dissolved in the aqueous solution. This is a fundamental idea in corrosion inhibition: the inhibitor molecules may bind to the metal surface and slow down corrosion by creating a protective layer or preventing the electrochemical reactions that lead to corrosion. Equation 2.11 describes the reversible process of a corrosion inhibitor (Org) either adsorbing onto a solid surface or desorbing from that surface in the presence of water (H₂O)[144].



where $Org_{(sol)}/Org_{(ads)}$ It represents the corrosion inhibitor in the aqueous solution and is adsorbed onto a solid surface. $xH_2O_{(ads)}/xH_2O_{(sol)}$ Represents water molecules adsorbed onto

a solid surface and water molecules in the aqueous solution. The adsorption of inhibitor molecules onto a metal surface can involve physisorption and chemisorption mechanisms, often collectively referred to as physio-chemisorption or chemisorption.

Physisorption: in the presence of HCl solution, the Fe (iron) elements on the surface of mild steel can undergo excessive oxidation, which means they lose electrons and become positively charged[145, 146]. The metal can dissolve as Fe^{2+} ions due to the acidic conditions. The positively charged Fe^{2+} ions attract negatively charged chloride ions (Cl^-) from the HCl solution. As a result, the metal surface becomes negatively charged due to the accumulation of chloride ions[144]. The inhibitor molecules can interact with the surface in this negatively charged environment on the metal surface. In acidic media, heteroatoms in the inhibitor molecules may become protonated and positively charged. The positive charge on the inhibitor molecules can lead to attractive forces between the inhibitor molecules and the negatively charged metal surface. The interaction between the positively charged inhibitor molecules and the negatively charged metal surface can form a bridge. This bridge represents the adsorption of inhibitor molecules onto the metal surface, with the positive and negative charges facilitating the binding[147-149].

Chemisorption: In an aggressive acidic environment, the surface iron atoms can undergo further oxidation, losing electrons and becoming positively charged. This oxidation can result from the corrosive action of the acid. The positively charged surface iron atoms can release electrons, which can be consumed by the inhibitor molecules in the vicinity. As a result, the inhibitor molecules become neutral again, losing their positive charge. This step is crucial for the subsequent chemisorption process. In inhibitor molecules with heteroatoms (N, O, S) with lone pairs of electrons, these lone pair electrons can be donated to the surface iron atoms. This electron transfer allows the inhibitor molecules to form chemical bonds with the metal surface. The transfer of electrons from the lone pairs of the inhibitor molecules into the d-orbitals of the surface iron atoms results in chemisorption[149, 150]. Chemisorption is a strong and stable adsorption mechanism involving the formation of covalent or ionic bonds between the inhibitor molecules and the metal surface[150-152]. This adsorption type is often more effective in providing corrosion protection than physisorption.

Inhibitors applied to the surface of a material reduce the rate of electrochemical reactions happening at the cathode and/or anode. In acidic solutions, inhibitors can affect the corrosion of metals through multiple interactions occurring at the same time. It is difficult to assign a

single mechanism of action to an inhibitor because its behavior can vary depending on different experimental conditions. The effectiveness of inhibitors with the same functional group can differ due to factors like the structure of the molecule and the electron density. Inhibition usually occurs through one or more of the following mechanisms.

2.7.1. Presence of surface charge on the metal

The adsorption process may be influenced by electrostatic forces of attraction between ionic charges or dipoles of the adsorbed inhibitor species and the electric charge on the metal at the metal/solution interface. The metal surface can carry a net electric charge due to various factors, such as the dissolution of metal ions, the formation of oxide layers, or the presence of reactive functional groups on the metal surface. Inhibitor molecules with ionic charges or polar functional groups can be attracted to the oppositely charged or polarized metal surface[153, 154]. Corrosion inhibitors often contain functional groups with ionic charges, such as amines, carboxylates, or phosphates. The positively or negatively charged groups on the inhibitor molecules can interact with the opposite charges on the metal surface[114, 144, 155].

2.7.2. Effect of functional group and structure of the inhibitor

This process is often favoured when the metal contains vacant electron orbitals of low energy, such as transition metals. The relatively loosely bound electrons in the metal facilitates electron transfer from the adsorbed species. Inhibitors with certain functional groups, such as nitrogen or oxygen-containing groups (e.g., amines, imines, hydroxyl groups), can donate lone pairs of electrons to the vacant orbitals on the metal surface. This donation of electron pairs leads to the formation of coordinate bonds between the inhibitor and the metal[156-159].

2.7.3. Interaction between inhibitor and water molecules

The displacement of adsorbed water molecules during the adsorption of an inhibitor is indeed a common occurrence. The change in interaction energy with water molecules, as the inhibitor transitions from the dissolved to the adsorbed state, plays a significant role in the overall free energy change associated with adsorption. When an inhibitor molecule adsorbs onto a metal surface, it can displace water molecules that may have been previously adsorbed on the metal. The displacement of water molecules and the establishment of new interactions between the inhibitor and the metal surface contribute to the overall free energy change[149, 160].

2.7.4. Interaction of adsorbed inhibitor compound

The interaction between adsorbed inhibitor species on a metal surface, often referred to as lateral interactions, becomes increasingly significant as the surface coverage and proximity of the adsorbed species increase[155]. These interactions can be either attractive or repulsive and play a crucial role in determining the overall behavior and effectiveness of the corrosion inhibitor film. Attractive lateral interactions involve forces that tend to bring adsorbed inhibitor molecules closer to each other. These interactions may enhance the stability and cohesion of the inhibitor film on the metal surface. Repulsive lateral interactions involve forces that push adsorbed inhibitor molecules away from each other. Repulsive interactions may prevent the close packing of inhibitor molecules and influence the structure and integrity of the inhibitor film[161, 162]. The interactions between adsorbed inhibitor species can exhibit synergistic or antagonistic effects. Synergistic effects enhance the overall corrosion inhibition efficiency, while antagonistic effects may diminish it. The interaction of adsorbed inhibitor species influenced adsorption isotherm, which describes the relationship between inhibitor concentration and the amount adsorbed on the metal surface[155, 161, 163, 164].

2.7.5. Reaction of adsorbed inhibitors

In certain cases, adsorbed corrosion inhibitors undergo electrochemical reduction on the metal surface, leading to the formation of a reaction product. This reaction product may also possess inhibitive properties, contributing to overall corrosion protection. The inhibition resulting directly from the added substance is referred to as primary inhibition, while the inhibition due to the reaction product is termed secondary inhibition[29, 93, 119, 162]. Primary inhibition refers to the direct inhibitive action of the adsorbed corrosion inhibitor on the metal surface, which forms a protective layer that hinders the corrosion process. Secondary inhibition occurs when the reaction product formed during the electrochemical reduction of the adsorbed inhibitor also exhibits inhibitive action[116, 162, 165, 166].

2.7.6. Formation of a diffusion barrier

The formation of a diffusion barrier is a common mechanism by which absorbed corrosion inhibitors provide protection to metal surfaces. When an inhibitor is adsorbed onto a metal surface, it can form a surface film that acts as a physical barrier, limiting the diffusion of ions

or molecules to and from the metal. This, in turn, retards the rate of corrosion reactions[114, 155].

2.7.8. Participation in the electrode reaction

In certain corrosion reactions, the formation of adsorbed intermediate species with surface metal atoms plays a significant role. Adsorbed inhibitors can hinder the formation of these adsorbed intermediates, but electrode processes may still proceed through alternative paths involving intermediates containing the inhibitors. Examples include adsorbed hydrogen atoms in the hydrogen evolution reaction and adsorbed species like $(\text{FeOH})_2$ in the anodic dissolution of iron[167-170].

2.7.9. Alteration of the electrical double layer

The alteration of the electrical double layer is an important mechanism through which the adsorption of ions or species on metal surfaces influences the rates of electrochemical reactions, particularly in the context of corrosion inhibition. The electrical double layer forms at the metal/solution interface and plays a crucial role in the electrochemical processes occurring during corrosion. Adsorption of cations or positively charged species, such as quaternary ammonium ions and protonated amines, tends to make the potential more positive at the metal surface. Conversely, the adsorption of anions or negatively charged species makes the potential more negative on the metal side of the electrical double-layer[155, 171].

2.8. Literature of corrosion inhibitors

2.8.1. Triazines derivatives

Triazine derivatives have a unique structure: a planar six-membered ring with alternating carbon and nitrogen atoms. The nitrogen atoms in the triazine ring possess lone pairs, making them capable of forming coordination bonds with metal ions in the corroding system. The heteroaromatic p-electrons in the triazine ring can interact with metal surfaces, creating protective layers on the metal's surface. This interaction can inhibit the corrosive attack by providing a barrier and altering the electrochemical processes at the metal surface. Additionally, the σ -backbone of the triazine molecule can participate in adsorption on the metal

surface, forming a protective layer and preventing further corrosion. Recently reported as organic promising corrosion inhibitors of steel in hydrochloric acid.

S. k Shukla et al. [172], synthesized triazine derivatives namely hexahydro-1,3,5-triphenyl-s-triazine(Inh-1), hexahydro-1,3,5-p-toyl-s-triazine(Inh-2), hexahydro-1,3,5-p-methoxyphenyl-s-triazine(Inh-3), Hexahydro-1,3,5-p-aminophenyl-s-triazine(Inh-4), and hexahydro-1,3,5,-p-nitrophenyl-s-triazine (Inh-5) and investigate as corrosion inhibitor of mild steel in HCl solution using weight loss, polarization resistance, Tafel polarization and electrochemical impedance spectroscopy techniques. The results reveal that Inh-4 is the best inhibitor with 97%, Tafel polarization suggests that the studied inhibitor is mixed-type in nature. The author also indicates that the inhibiting action of triazine depends on the electronic nature of functional groups present in triazine derivatives, The AFM technique was also used to confirm that the inhibitor protects the mild steel surface from HCl solution.

A El-faham et al. [173], studied the effects of hydrazine-methoxy-1,3,5-triazine derivatives of steel in acidic media namely 2-hydrazino-4,6-dimethoxy-1,3,5-triazine (DMeHT), 2,4-dihydrazino-6-methoxy-1,3,5-triazine (DHMeT), and 2,4,6-tridydrazino-1,3,5-triazine (TH₃) on steel. The results showed that DHMeT gave the best corrosion protection performance at low concentrations with 95%. In addition, Tafel polarization studies and electrochemical impedance spectroscopy (EIS) showed that the examined inhibitor shifted the corrosion potential anodically and cathodic, which means it is the mixed type and significantly enhanced the charge transfer resistance for corrosion of mild steel. The author also synthesized other triazines derivatives namely 2.4.6-tris(quinoline-8-yloxy)-1.3.5-triazine(T3Q), N²,N⁴,N⁶-tris(pyridine-2-ylmethyl)-1.3.5-triazine-2.4.6-triamine(T3AMPy), and 2.2'.2''-[(1.3.5-Triazine-2.4.6-tryl)tris(azanediyl)] tris(ethan-1-ol)(T3EA) and investigate their inhibition of steel corrosion in HCl solution using electrochemical technique. The corrosion protection of the prepared compounds increased with increasing concentration and reached up to 98% at 250ppm; their adsorption on the steel surface followed Langmuir adsorption isotherm. The electrochemical also revealed that it was mixed-type adsorption[174].

R Yildiz [175], investigated the adsorption and corrosion behavior of 1,3,5-triazines derivatives, namely 2,4-Diamino-6-methyl-1,3,5-triazine (2-DMT) on mild steel in HCl solution using experimental and theoretical studies. The results showed that the 2-DMT has an outstanding anti-corrosion performance of 94%. The PDP Tafel curves and Langmuir adsorption isotherm show that the studied inhibitor is classified as mixed type. The adsorption

of inhibitor molecules on the MS surface is discussed in more detail, and PZC results confirm the existence of electrostatic and chemical interactions. SEM and AFM images confirm the presence of inhibition by 2-DMT due to obtaining a smooth surface. Quantum chemical calculation manifested that the adsorption ability of inhibitor molecule is due to dipole moment and high value of ΔN . From the study conducted by Ifzan Arshad et al. [176], potentiodynamic polarization indicates that other substitution triazine can behave as a cathodic inhibitor type. The weight loss measurement results show that when the concentration of inhibitor increases, the IE% also increases, and their IE% is 92.07% at the highest concentration. The computational studies show that the energy gap of the inhibitor is small indicating higher inhibitory efficiency; this was also confirmed by the larger fraction of electron transport (ΔN) for the examined inhibitor.

2.8.2. Graphene oxide (GO)

Graphene is an impermeable material with an extremely tight hexagonal structure, which makes it an excellent barrier against the penetration of corrosive species like ions and gases[177]. When graphene is used as a coating or incorporated into a composite material, it can act as a physical barrier that prevents contact between the metal surface and corrosive agents, thereby reducing corrosion rates[178-180]. Graphene is an excellent conductor of electricity[181, 182]. When it is used as a corrosion inhibitor, it can help maintain the electrical continuity of a metal surface, preventing the formation of localized corrosion sites, such as galvanic cells[183, 184]. This is particularly important in applications where electrical conductivity is essential, such as in the aerospace and electronics industries. When graphene is combined with organic corrosion inhibitors, it can enhance the effectiveness of the inhibitor. Graphene can act as a support material for the organic inhibitor, increasing its adhesion to the metal surface and providing a controlled release mechanism for the inhibitor over time. This synergy can result in improved corrosion protection[185, 186].

K.R. Anasae et al.[187], designed graphene oxide derivatives and investigated their corrosion inhibition performance on mild steel corrosion in 1M HCl using EIS , PDP methods. From the results indicate that the inhibitors retard corrosion by adsorption mechanism. The PDP reveals that it's a mixed type. Surfactant-modified graphene oxide is a novel corrosion inhibitor for mild steels in acidic media. N.Baig et al.[188] evaluate the corrosion inhibition performance of diethylenetriamine functionalized graphene-oxide(DETA-GO) in 1 M HCL for mild steel. The DETA-GO behaves as efficient corrosion inhibition, as the electrochemical analysis showed it.

The inhibition efficiency increased with concentration, reaching 92.67% at 25mg/L. The tafel plot revealed that the inhibitor exhibits a mixed type of nature with cathodic predominance. The results were also confirmed by examining a protective film of the inhibitor over mild steel by SEM and FTIR-ATR. This study also made a comparison of the quantum chemical parameters of GO, DETA, and DETA-GO to determine the influence of the organic functionalization of GO on the corrosion inhibitor. From the result of DFT it was concluded that DETA-GO has a better capability of electron donating than GO and DETA alone.

2.9. Utilisation of computational methodologies in corrosion studies

Surface chemistry experiments can provide valuable information about the interaction between inhibitors and metals. Computational models can stimulate the interaction of corrosion inhibitors with metal surfaces, providing insight into how inhibitors bind to the surface and block the electrochemical reaction that produces corrosion. Computational models can provide information on the chemical composition and reactivity of the inhibitor as well as the potential for inhibiting corrosion. Different techniques are utilized to perform simulations of the interactions between the inhibitor and the metal surface. Some of these methods are based on molecular mechanics, and others are based on electronic structure approaches. Electronic structure methods are based on solving the Schrodinger equation in quantum mechanics. The following subsections will discuss some electronic structure methods, starting with the Schrödinger equation and the approaches utilized to approximate the Schrödinger equation for multi-electron systems.

2.9.1. Schrödinger equation

The Schrödinger equation, which defines the behavior of quantum systems such as atoms, molecules, and subatomic particles, is fundamental in quantum mechanics [189, 190]. The time-independent Schrödinger equation for a single particle is given by the following equation [191]

$$\hat{H}\Psi = E\Psi \quad (2.12)$$

where $\hat{H}$ represents the Hamiltonian operator, which represents the total energy of the system, $\Psi(\psi)$ is the wavefunction of the particle, which is a mathematical function that contains information about the particle's position, momentum, and other properties, and E represents the energy of the particle[192, 193].

The Hamiltonian operator, denoted by $\hat{H}$, is defined as:

$$\hat{H} = T + V \quad (2.13)$$

where T represents the kinetic energy operator, which is associated with the motion of the particles in the system, and V represents the potential energy operator, which arises from the interaction of particles with each other and with external fields or potentials[192].

The kinetic energy operator, T , is given by

$$T = \frac{-\hbar^2}{2m} \nabla^2 \quad (2.14)$$

where $\hbar$ is the reduced Planck's constant ($h/2\pi$), which h is 1.055×10^{-34} Js, m is the mass of the particle. ∇^2 is the Laplacian operator, which represents the second derivative of the wavefunction with respect to the spatial coordinates.

Therefore, equation 2.13 can be written as:

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V \quad (2.15)$$

Equation 2.12 can be given as:

$$\hat{H}\varphi_{ele,nuc}(r,R) = E\varphi_{ele,nuc}(r,R) \quad (2.16)$$

The Schrödinger equation is a partial differential equation that relates the spatial behavior of the wavefunction to the energy of the system. Solving the Schrödinger equation allows us to determine the allowed energy states and corresponding wavefunctions of the system, however solving the Schrödinger equation exactly for systems with many atoms becomes computationally demanding. Approximation approaches are often utilised to overcome this challenge. Among the approximation approaches utilized include the Born-Oppenheimer approximation and the Hartree-Fock approximation.

2.9.2. Born-Oppenheimer approximation

The Born-Oppenheimer approximation simplifies the description of a molecule's behavior by separating the motion of electrons and atomic nuclei [194]. From Hamiltonian operator denoted by

$$\hat{H} = T + V \quad (2.17)$$

where, for a system with electrons (e) and nuclei (n), the kinetic energy operator T is defined as:

$$T = \frac{\hbar^2}{2} \sum_{i=1}^e \frac{1}{m_i} \nabla_i^2 - \frac{\hbar^2}{2} \sum_{I=1}^n \frac{1}{M_I} \nabla_I^2 \quad (2.18)$$

where the first sum runs over all electrons i and the second sum runs over all nuclei I . m_i is the mass of the electron i and M_I is the mass of the nucleus I . The Laplacian operators ∇_i^2 and ∇_I^2 involve differentiation with respect to the coordinates of the i th electron and the I th nucleus [195].

The potential energy operator V consists of the Coulomb interactions:

$$V = \sum_{i=1}^e \sum_{i < j}^e \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^e \sum_{I=1}^n \frac{Z_I e^2}{4\pi\epsilon_0 r_{iI}} + \sum_{I=1}^n \sum_{I < J}^n \frac{Z_I Z_J e^2}{4\pi\epsilon_0 R_{IJ}} \quad (2.19)$$

where $r_{ij} = |r_i - r_j|$, $r_{iI} = |r_i - R_I|$, $R_{IJ} = |R_I - R_J|$. Electron-electron repulsion term is $\sum_{i=1}^e \sum_{i < j}^e \frac{e^2}{4\pi\epsilon_0 r_{ij}}$. This term accounts for the repulsion between different pairs of electrons (i and j) in the system. The numerator e^2 represents the charge of an electron squared and the denominator $|r_i - r_j|$ represents the distance between the electron positions. The permittivity of vacuum (ϵ_0) [196].

$\sum_{i=1}^e \sum_{I=1}^n \frac{Z_I e^2}{4\pi\epsilon_0 r_{iI}}$ is the electron-nucleus attraction term describing the attraction between each electron (i) and each nucleus (I) in the system. The numerator $Z_I e^2$ represents the charge of nucleus I multiplied by the elementary charge squared, and the denominator $|r_i - R_I|$ represents the distance between the electron and the nucleus [197].

Nucleus-nucleus repulsion term is described by $\sum_{I=1}^n \sum_{I < J}^n \frac{Z_I Z_J e^2}{4\pi\epsilon_0 R_{IJ}}$. This term accounts for the repulsion between different pairs of nuclei (I and J) in the system. The numerator $Z_I Z_J e^2$ represents the product of the charges of nuclei I and J , and the denominator $|R_I - R_J|$ represents the distance between the nuclear positions [197].

Solving the Schrödinger equation with the potential energy operator, along with the kinetic energy operator, allows for the determination of the electronic wavefunction and energy of the

molecular system within the Born-Oppenheimer approximation. A significant simplification within the Born-Oppenheimer approximation arises from the fact that the mass of the electrons is much smaller than that of the nuclei. This mass imbalance allows for the separation of electronic and nuclear motions, treating them as independent variables. As a result, one can approximate the electronic motion as instantaneous, adjusting rapidly to changes in nuclear positions. First approximation, one can focus on solving the electronic Schrödinger equation while treating the nuclear positions as fixed, where the nuclear-nuclear repulsion is a constant. Therefore, the electronic Hamiltonian can be:

$$\hat{H}_{ele} = -\frac{\hbar^2}{2} \sum_{i=1}^e \frac{1}{m_e} \nabla_i^2 + \sum_{i=1}^e \sum_{i < j}^e \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^e \sum_{l=1}^n \frac{Z_l e^2}{4\pi\epsilon_0 r_{il}} \quad (2.20)$$

and the electronic Schrödinger equation become:

$$\hat{H}_{ele} \varphi_{ele}(r, R) = E_{ele}(R) \varphi_{ele}(r, R) \quad (2.21)$$

The electronic wavefunction $\varphi_{ele}(r, R)$ describes the motion of the electrons in a molecule. It explicitly depends on the electronic coordinates r (positions of the electrons) and parametrically depends on the nuclear coordinates R (positions of the nuclei)[198]. After obtaining the electronic wavefunction, the nuclear motion can be treated separately by solving the nuclear Schrödinger equation.

$$\hat{H}_{ele,nuc} \varphi_{ele,nuc}(R) = E_{ele,nuc} \varphi_{ele,nuc}(R) \quad (2.22)$$

$$\text{where: } \hat{H}_{ele,nuc} = -\frac{\hbar^2}{2} \sum_{l=1}^n \frac{1}{M_l} \nabla_l^2 + E_{ele}(R) + \sum_{l=1}^n \sum_{l < j}^n \frac{Z_l Z_j e^2}{4\pi\epsilon_0 R_{lj}} \quad (2.23)$$

2.9.3. Hartree-Fock approximation

Hartree-Fock (HF) is when an electronic structure theory has an acceptable accuracy, and each electron is defined by an orbital and the total wave-functions are given because of orbit. HF have two methods which is Restricted Hartree-Fock (RHF) and Unrestricted Hartree-Fock (UHF) methods. Restricted Hartree-Fock (RHF) methods are for open shell systems, where electrons with α spin are constrained to occupy the same spatial orbitals as electrons with β spin. Unrestricted Hartree-Fock this method is for systems with unpaired electrons[199], such

as molecules with odd numbers of electrons, excited states, unusual electronic structures (two or more unpaired outer electrons), and bond dissociation. The HF equation is written as:

$$\hat{f}(i)|x_a\rangle = \epsilon|x_a\rangle \quad (2.24)$$

where: $\hat{f}(i)$ is the one-electron fock operator [199] and defined for each electron as

$$\hat{f}(i) = \hat{h}(i) + \hat{V}_{Hf}(i) \quad (2.25)$$

where: $\hat{h}(i)$ is the core Hamiltonian operator consisting of kinetic and nuclear energies terms and defined as:

$$\hat{h}(i) = \frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \quad (2.26)$$

where $\frac{1}{2}\nabla_i^2$ represents the kinetic energy operator for particle i. The symbol ∇_i denotes the gradient operator with respect to the coordinates of particle i, and ∇_i^2 represents the Laplacian operator, which calculates the second derivative of the wavefunction with respect to the spatial coordinates of particle i. $\sum_{A=1}^M \frac{Z_A}{r_{iA}}$ represents the potential energy operator for particle i due to its interaction with other particles in the system. Here, M represents the total number of particles in the system, Z_A represents the charge or atomic number [199] of particle A, r_{iA} represents the distance between particle i and particle A.

$\hat{V}_{Hf}(i)$ from one-electron fock operator is the HF potential, defined as:

$$\hat{V}_{Hf}(i) = \sum_{b \neq a} \hat{J}_{ab}(i) + \sum_{b \neq a} \hat{K}_{ab}(i) \quad (2.27)$$

where $\sum_{b \neq a} \hat{J}_{ab}(i)$ represents the Coulomb interaction term that involves a summation over all other particles b (where b is not equal to a) and includes the operator $\hat{J}_{ab}(i)$ which is defined by equation 2.17. This operator calculates the Coulomb interaction between particles a and b, with particle a being the one for which the potential is being evaluated particle i. And $\sum_{b \neq a} \hat{K}_{ab}(i)$

represents the exchange interaction term involves a summation over all other particles b (where b is not equal to a) and includes the operator $\hat{k}_{ab}(i)$ [199] in equation 2.29. This operator calculates the exchange interaction between particles a and b , considering the antisymmetric of the wavefunction due to the indistinguishability of identical particles.

$$\hat{j}_{ab}(1) = \int |x_b(2)|^2 r_{12}^{-1} dx_2 \quad (2.28)$$

$$\hat{k}_{ab}(1)x_a(1) = \int [x_b(2)^* r_{12}^{-1} x_a(2) dx_2] x_b(1) \quad (2.29)$$

The Unrestricted Hartree-Fock (UHF) n -electron wavefunction can be written as:

$$\varphi_{UHF} = \frac{1}{\sqrt{n}} \det |\phi_1^\alpha \phi_2^\beta(2) \phi_3^\alpha(3) \dots \phi_n^\beta(n)| \quad (2.30)$$

The Restricted Hartree-Fock (RHF) n -electron wavefunction for closed-shell systems is usually described for a single-state [199] and can be denoted as:

$$\varphi_{RHF} = \frac{1}{\sqrt{n}} \det |\phi_1^\alpha \phi_1^\beta(2) \phi_2^\alpha(3) \phi_2^\beta(4) \dots \phi_n^\beta(n)| \quad (2.31)$$

2.9.4. Molecular orbital approximation from atomic orbitals

The molecular orbital (MO) approximation is a theoretical approach used to describe the electronic structure of molecules by combining atomic orbitals (AOs) to form molecular orbitals, different key features of molecular orbitals are as follows:

- The number MO formed is equal to the number of atomic orbitals used in the combination. These molecular orbitals can be filled with electrons according to the Aufbau principle, Pauli exclusion principle, and Hund's rule, just like in the atomic orbital case.

- A molecular orbital is categorized as a bonding orbital when it facilitates the formation of a chemical connection between two atoms. Typically, a bonding molecular orbital has a substantial concentration of electron charge in the area between the nuclei, which consequently diminishes their mutual repulsion. An antibonding orbital is a chemical orbital that has minimal impact on nuclear shielding[159].

The MO approximations are further done using the Hartree–Fock (HF) or the density functional theory (DFT) models to the Schrödinger equation [200]. In the MO approximation, the AOs of the constituent atoms are combined to form bonding and antibonding molecular orbitals. The process of combining AOs is known as a linear combination of atomic orbitals (LCAO).

$$\psi = C_1\phi_1 + C_2\phi_2 \quad (2.32)$$

where ψ is the MO, and ϕ_1 and ϕ_2 are the AOs. The energy expectation value of this approximate MO is:

$$E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{C_1^2 H_{11} + 2C_1 C_2 H_{12} + C_2^2 H_{22}}{C_1^2 S_{11} + 2C_1 C_2 S_{12} + C_2^2 S_{22}} \quad (2.33)$$

where $\langle \psi | \hat{H} | \psi \rangle$ represents the expectation value of the Hamiltonian operator ($\hat{H}$) for the wave function ψ . It corresponds to the average value of the energy when the system is described by the wave function ψ . The normalization factor of the wave function ψ is represented by $\langle \psi | \psi \rangle$, is the overlap integral of ψ with itself and represents the probability amplitude of finding the system in the state described by ψ . C_1 and C_2 represent the coefficients or expansion coefficients associated with the molecular orbitals in the linear combination of atomic orbitals (LCAO) approach. C_1 corresponds to the coefficient for the first molecular orbital, and C_2 corresponds to the coefficient for the second molecular orbital.

H_{11} , H_{12} , and H_{22} are the matrix elements of the Hamiltonian operator in equation 2.34 between the atomic orbitals or molecular orbitals where H_{11} corresponds to the element associated with the first atomic or molecular orbital interacting with itself, H_{12} corresponds to the element

associated with the interaction between the first and second orbitals. The element associated with the second orbital interacting with itself is represented by H_{22} . The S_{11} , S_{12} , S_{22} terms represent the matrix elements of the overlap operator (S) between the atomic orbitals or molecular orbitals. S_{11} corresponds to the overlap element associated with the first atomic or molecular orbital overlapping with itself, S_{12} corresponds to the overlap element associated with the overlap between the first and second orbitals, and S_{22} corresponds to the overlap element associated with the second orbital overlapping with itself. If AOs are normalized the $S_{11}=S_{22}=1$ and S_{12} is between 0 and 1 [201], they are considered as S_{ij} which are overlap integrals written in equation 2.35.

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \quad (2.34)$$

$$S_{ij} = \langle \phi_i | \phi_j \rangle \quad (2.35)$$

The linear-combination coefficients C_1 and C_2 are determined by energy minimization. C_1 and C_2 are optimal that give a ψ that satisfies the time-independent Schrödinger equation as best as possible.

$$\frac{\partial E}{\partial C_1} = 0 \text{ and } \frac{\partial E}{\partial C_2} = 0 \quad (2.36)$$

each of these equations results in a linear equation in C_1 and C_2 , giving a system of two linear equations.

$$(H_{11} - ES_{11})C_1 + (H_{12} - ES_{12})C_2 = 0 \text{ and } (H_{12} - ES_{12})C_1 + (H_{22} - ES_{22})C_2 = 0 \quad (2.37)$$

For matrix notation:

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad (2.38)$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (2.39)$$

Expanding equation 2.39 to get equation 2.40 below:

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{12} - ES_{12})^2 = 0 \quad (2.40)$$

Rearranging equation 2.40 to collect all terms of equal power in E gives the following quadratic equation for the energy below, by solving quadratic equation C_1 and C_2 can be calculated.

$$E^2(S_{11}S_{22} - S_{12}^2) + E(-H_{11}S_{22} - H_{22}S_{11} + 2H_{12}S_{12}) + H_{11}H_{22} - H_{12}^2 = 0 \quad (2.41)$$

For a homo-diatomic molecule $H_{11}=H_{22}$ and assuming AO normalization $S_{11}=S_{22}=1$, the two solutions (MOs and associated energies) can be given as:

$$\psi_g = \frac{1}{\sqrt{2+2S_{12}}}(\phi_1 + \phi_2), E_g = \frac{H_{11}+H_{12}}{1+S_{12}} \quad (2.42)$$

$$\psi_u = \frac{1}{\sqrt{2-2S_{12}}}(\phi_1 - \phi_2), E_g = \frac{H_{11}-H_{12}}{1-S_{12}} \quad (2.43)$$

where ψ_g and ψ_u define as ground state and excited state wave function. E_g and E_u is the ground state and excited state energy.

2.9.5. Basis sets

Basis sets are sets of mathematical functions used to approximate the wavefunctions of electrons in molecules. These basis functions provide a representation of the electronic wavefunction within a given approximation scheme. Different types of basis sets are employed depending on the level of accuracy desired and the size of the system being studied. There are those that are referred to as Pople type and those that are referred to as Dunning type. We provide a brief description of both types in the subsections that follows.

2.9.5.1. Atomic Orbital (AO) Basis Sets

Quantum chemistry often uses Atomic Orbital (AO) basis sets to accurately describe the electronic wavefunctions of atoms within molecules. The basis sets comprise atomic orbitals localized on individual atoms and are utilized as fundamental units for generating molecular orbitals. Two often utilized types of atomic basis functions are the Slater Type Orbitals (STO). STOs are commonly employed in atomic and diatomic systems that demand high precision, as well as in semi-empirical methods that disregard three- and four-center integrals. They can also be utilized with density functional approaches that do not require accurate exchange and calculate the Coulomb energy by fitting the density into a set of auxiliary functions. STO is denoted as

$$\phi_i(\zeta, n, l, m; r, \theta, \phi) = N r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi) \quad (2.44)$$

here Y_{lm} is the angular momentum part, r , and θ are the spherical coordinates, N is a normalization constant, and ζ is called the exponent dependence on the distance between the nucleus and electron mirrors the exact orbitals for the hydrogen atom. The n , l , and m are quantum numbers: principal, angular momentum, and magnetic respectively[202].

The second type is Gaussian Type Orbital (GTO) atomic basis functions which have a mathematical form that resembles a Gaussian distribution and provide a flexible and computationally efficient representation of atomic orbitals. GTO is given by equation.

$$g(\alpha, l, m, n; x, y, z) = N e^{-\alpha r^2} x^l y^m z^n \quad (2.45)$$

where (x, y, z) represents the Cartesian coordinates, N is a normalization constant, α is a parameter related to the size of the orbital, and (l, m, n) are the angular momentum quantum numbers determining the shape and orientation of the orbital[202].

2.9.5.2. Split-valence Pople type basis sets

Split-valence basis sets are a sort of basis set that, when compared to minimal basis sets, provides a more accurate description of molecular electrical structure. Split-valence basis sets split each atomic orbital into two parts, allowing for a more flexible and refined description of electron density. Split-valence basis sets are made up of a dual basis in which each atomic orbital is split into two components.

A core component that represents the inner portion of the atomic orbital nearest the nucleus. The core functions have been simplified Gaussian functions that closely approximate the behavior of atomic orbitals around the nucleus. The electron density in the more localized and firmly bound region, as well as a valence component, are captured by the core function. The valence component, on the other hand, describes the atom's outer region and is often more diffuse. Split-valence basis sets are frequently expressed using notation such as $X-nY$, where X signifies the core functions, n the number of valence functions, and Y the kind of valence functions. For example, 6-31G is a split-valence basis set. The core orbitals are made up of six primitive gaussian functions, whereas the inner and outer valence orbitals are made up of three and one primitive gaussian function, respectively [195].

2.9.5.3. Polarization Pople type basis sets

Polarization basis sets include extra functions (polarization functions or diffuse functions) in addition to the core and valence functions to better characterize the behavior of electrons in the outside regions of atoms and molecules. Polarization and diffuse functions are often more diffuse than valence functions, allowing for a more realistic depiction of electron correlation effects. Polarization basis sets frequently include the addition of greater angular momentum functions than ordinary basis sets.

These higher angular momentum functions allow for a more flexible description of the electron density distribution and better capture the anisotropic nature of electron correlation effects. Polarization basis sets are often denoted by additional letters or numbers in their notation to indicate the inclusion of polarization functions. For instance, 6-31G(d,p) basis set includes

diffuse functions (d functions) as well as polarization functions (p functions) to the split-valence 6-31G basis set for the description of each heavy (non-hydrogen) atom and hydrogen atom, respectively[195].

2.9.5.4. Diffuse Pople type basis sets

Diffuse basis sets describe the behavior of electrons in the outer regions of atoms and molecules, where electron density is more diffuse or spread out. Diffuse basis sets include additional functions that capture the diffuse electron density and allow for a more accurate representation of molecular electronic structure known as diffuse functions. This is accomplished by appending a "+," such as 6-31+G(d,p), which signals that four very diffuse functions (s,px,py,pz) are added to the 6-31G(d,p) basis set for each non-hydrogen atom in the second row of the periodic table.

2.9.5.5. Dunning basis sets

Dunning basis sets, also known as correlation consistent basis sets are a class of systematically optimized basis sets that are commonly utilized in quantum chemistry calculations, particularly in atomic and molecular electronic structure predictions[203]. There are several commonly used types of dunning basis sets that have been employed in corrosion inhibitor research, each designed to provide a specific level of accuracy and computational efficiency.

a) Dunning's Augmented correlation consistent (aug-cc-pVXZ) basis sets

The aug-cc-pVXZ series is one of the most widely used Dunning basis sets. It includes polarization and diffuse functions and provides accurate descriptions of electron correlation effects. These basis sets are especially effective for systems with high electron correlation, such as metal complexes or transition metal systems. "P" denotes the basis set polarisation functions that account for electron density polarisation in response to external fields or interactions. The X in the notation denotes the level of approximation, such as single, double, triple, quadruple, etc and the "Z" represents the size of the basis set. A study conducted by Iain D. Mackie and Gino A. DiLabio used Mp2 coupled-cluster single double and CCSD method with the combination with aug-cc-PVDZ, aug-cc-PVTZ, and aug-cc-PVQZ basis sets to obtain electronic energies [204].

b) Dunning's correlation consistent polarized (cc-pVXZ) basis sets

Another collection of regularly used Dunning basis sets is the cc-pVXZ series. It incorporates polarization functions, like the aug-cc-pVXZ series, to capture electron correlation effects[205]. The symbol "cc" denotes that these basis sets have been optimised to incorporate suitable levels of electron correlation effects. "p" denotes the basis set's polarisation functions, which account for electron density polarisation in response to external fields or interactions. The "XZ" portion denotes the amount of approximation as well as the size of the basis set.

c) Dunning's correlation consistent (cc-pCVXZ) basis sets

The cc-pCVXZ series expands the cc-pVXZ basis sets by include core-valence correlation functions, which account for electron correlation in atoms' inner core orbitals. These basis sets are very useful for performing accurate computations with transition metals and heavier elements[206]. The cc-pCVXZ basis sets, the "CV" stands for "core-valence," suggesting the inclusion of additional functions to account for electron correlation effects in atoms' inner core orbitals. These core-valence correlation functions are critical for accurately modelling systems including heavy elements or transition metals that have strong electron correlation in the core orbitals.

2.9.6. Post Hartree-Fock methods

Each electron is considered to move independently in an average field created by all other electrons in the HF approach. This average field allows for electron electrostatic repulsion, but it ignores the dynamic and non-local character of electron correlation effects. By ignoring the dynamic and non-local features of electron correlation, some properties are limited in their description. Post-HF procedures must be used to handle electron correlation accurately. These methods go beyond the mean-field treatment of HF by explicitly incorporating electron correlation effects via various mathematical and computational techniques such as coupled cluster, Møller-Plesset perturbation theory, or density functional theory with appropriate correlation functionals.

2.9.6.1. Coupled cluster

Coupled cluster (CC) theory is highly accurate and widely used method for describing dynamical electron correlation effects within the realm of modern quantum chemistry. It can

be formulated to include various levels of approximation, such as CCSD (coupled cluster with singles and doubles), CCSD(T) (including perturbative triples), and higher-level variants like CCSDT, CCSDTQ, and so on, to improve accuracy. The CC theory expression can be written starting by an exponential ansatz for the wave function[207].

$$|\varphi_{CC}\rangle = e^T |\phi\rangle \quad (2.46)$$

where ϕ is the reference obtained from a Hartree-Fock calculation, and T is the cluster operator. The cluster operator T is responsible for including electron correlation effects and is expressed as a sum of excitation operators.

$$T = T_1 + T_2 + T_3 + \dots + T_N \quad (2.47)$$

here T_1 represents first-order excitations, T_2 represents second-order excitations, and so on. Each term in the cluster operator excites electrons from occupied orbitals to virtual orbitals.

Solving the coupled-cluster equations, which are obtained by projecting the time-independent Schrödinger equation onto the exponentially parameterized wavefunction, yields the cluster operator T[207, 208]. Solving these equations returns the amplitudes of each excitation operator as well as the electronic energy and other system parameters.

where T_1 in the expression is the cluster operator for the single excitations, which can be written in a second-quantization formalism as:

$$T_1 = \sum_a^{occ} \sum_r^{vir} t_a^r \hat{a}_r^+ \hat{a}_a \quad (2.48)$$

where t_a^r is the excitation amplitudes, representing the contribution of the excited determinants to the wavefunction. These amplitudes determine the excitation of an electron from an occupied MO (a) to a virtual MO (r). The expression $\hat{a}_r^+$ is the creation operator for a particle in the virtual MO (r), and $\hat{a}_a$ is the annihilation operator for a particle in the occupied MO (a).

T_1 is the cluster operator for the double excitations, which is written as

$$T_1 = \frac{1}{4} \sum_{a,b}^{OCC} \sum_{r,s}^{vir} t^{sr}_{ba} \hat{a}_r^+ \hat{a}_a^+ \hat{a}_b \hat{a}_a \quad (2.49)$$

where t^{sr}_{ba} is excitation amplitudes, representing the contribution of the doubly excited determinants to the wavefunction. These amplitudes describe the simultaneous excitation of two electrons from occupied MOs (a and b) to virtual MOs (r and s). $\hat{a}_s^+$ is creation operator for a particle in the virtual MO(s) and $\hat{a}_b$ is annihilation operator for a particle in the occupied MO(b)[208].

from equation 2.46 operator e^T the exponential can be expanded and rearranged the operators in terms as[209]:

$$\begin{aligned} e^T &= 1 + T + \frac{T^2}{2!} + \frac{T^3}{3!} + \dots \\ &= 1 + C_1 + C_2 + \dots + C_N \end{aligned} \quad (2.50)$$

where the operator C_1 generates single excitations, C_2 generates double excitations and $T_1=C_1$ and $C_2 = T_2 + \frac{1}{2}T_1^2$

2.9.6.2. Møller-Plesset perturbation (MP) theory

In terms of electron-electron interactions, MP Theory increases the wavefunction and energy as a power series. MP2 contains second-order disturbance, whereas MP3 has third-order contributions. MP methods are less computationally expensive than CC approaches and can produce accurate findings for a wide range of systems. MP2 and higher orders can be utilised to investigate corrosion inhibitors to comprehend the electronic structure and properties associated with inhibitor-metal interactions. MP considers small perturbations to an unperturbed Hamiltonian operator[210].

MP theory starts with an unperturbed Hamiltonian, denoted as H_0 , which typically corresponds to a solvable or known system. The eigenstates and eigenenergy's of H_0 are assumed to be known. The perturbation to the unperturbed Hamiltonian is represented by an operator V . This perturbation operator introduces deviations from the idealized, solvable system described by

H_0 . V is assumed to be a small or "small enough" perturbation, ensuring that the perturbation theory approach is valid. Full Hamiltonian operator is denoted as:

$$H = H_0 + V \quad (2.51)$$

The unperturbed Hamiltonian (H_0) is taken to be the Fock operator, which is a mean-field approximation to the true electronic Hamiltonian. The Fock operator represents the one-electron part of the Hamiltonian.

$$H_0 = F + \langle \phi_0 | (H - F) | \phi_0 \rangle \quad (2.52)$$

where F is the Fock operator, which is a mean-field approximation to the electronic Hamiltonian. It represents the one-electron part of the Hamiltonian. H is the full electronic Hamiltonian, which includes both the one-electron and two-electron terms, representing the electron-electron interactions. ϕ_0 is the unperturbed wavefunction.

The perturbation from a full Hamiltonian operator can be defined as the correlation potential:

$$V = H - (F + \langle \phi_0 | (H - F) | \phi_0 \rangle) \quad (2.53)$$

The second order (MP2) is expressed as:

$$E_{MP2} = \frac{1}{2} \sum_{i,j,l} \frac{\langle \phi_i \phi_j | V | \phi_k \phi_l \rangle \langle \phi_k \phi_l | V | \phi_i \phi_j \rangle}{E_i + E_j - E_k - E_l} \quad (2.54)$$

where i, j, l indices representing molecular orbitals. i and j refer to occupied orbitals, while k and l refer to virtual orbitals. E_i, E_j, E_k, E_l are the orbital energies of the corresponding molecular orbitals [211, 212].

2.9.6.3. Density functional theory (DFT)

Density functional theory (DFT) is a powerful computational method used to study materials and molecules' electronic structure and properties. It is widely employed in the field of corrosion inhibition to understand the interactions between corrosion inhibitors and metal surfaces at the quantum level. The DFT approach is based on the principle that the energy of a molecule's ground-state energy can be derived by solving the Schrödinger equation in terms of electron probability density parameters rather than wave function parameters(ψ)[192]. The molecule's energy is expressed as a function of the electron density and is denoted as $E(\rho)$, where E is the molecule's energy and ρ is the electron density. The electron density varies with position and is indicated as $\rho(r)$.

The electron density is calculated from the occupied orbitals using the following equation:

$$\rho(r) = \sum_m |\varphi_m(r)|^2 \quad (2.55)$$

where $\rho(r)$ term represents the probability density function, which describes the probability of finding a particle at a specific position r in space. $\sum_m$ this indicates the summation over all orbitals, denoted by the index m . Each orbital φ_m contributes to the overall probability density. This $|\varphi_m(r)|^2$ term represents the squared magnitude of the wave function φ_m evaluated at position r . The wave function φ_m describes the spatial distribution of the particle associated with the orbital m .

The Kohn-Sham equations are used to calculate the occupied orbitals that are used to build the electron density. The Hartree-Fock equations are extended or modified by the Kohn-Sham equations[213, 214]. The word V_{xc} which stands for the exchange-correlation potential, is used in the modification.

$$\left\{ h_1 + j_0 \int \frac{\rho(2)}{r_{12}} d\tau_2 + V_{xc}(1) \right\} \varphi_m(1) = E_m \varphi_m \quad (2.56)$$

h_1 represents the one-electron Hamiltonian operator for the electron in the molecular system, electron in orbital $\varphi_m(1)$ and the electron density $\rho(2)$, and second electron denoted as $d\tau_2$. E_m term represents the energy eigenvalue associated with the m th molecular orbital $\varphi_m(1)$.

a) Local density approximation (LDA)

The LDA is the simplest and earliest form of DFT approximation which assumes that the exchange-correlation energy density depends only on the local electron density at each point in space[215]. LDA provides reasonable results for many systems but may not accurately capture certain interactions and properties. The LDA is represented by the equation below:

$$E_{xc}[p] = \int p(r)E_{xc}(p)dr \quad (2.57)$$

where the integration is over all space, $E_{xc}[p]$ is the exchange-correlation energy density depends on the electron density at each point in space and contains information about the exchange and correlation effects. And the integral of $p(r)E_{xc}(p)$ over space represents the total exchange-correlation energy of the system[216, 217]

b) Generalized gradient approximation

GGAs was created by Perdew, Burke, and Ernzerhof[218], which improves upon the LDA by considering not only the electron density but also its spatial gradient. By incorporating information about the density gradient, GGAs provide better descriptions of molecular systems, chemical reactions, and properties like bond lengths and energies.

$$E_{xc}[p] = \int f(p(r), |\nabla_p(r)|)dr \quad (2.58)$$

where the function $f(p(r), |\nabla_p(r)|)$ represents a general form of the exchange-correlation energy density functional, which depends on both the electron density $p(r)$, and its gradient $|\nabla_p(r)|$ [219, 220].

c) Meta-generalized gradient approximation (meta-GGA)

Meta-GGAs go beyond the GGA because it allows for better treatment of non-local effects and improves the description of systems with nonuniform electron densities by considering not only the density and its gradient but also the kinetic energy density. Meta-GGA is denoted by:

$$E_{xc}[p] = \int p(r)E_{xc}(p, |\nabla_p|, \nabla^2 p, \tau)dr \quad (2.59)$$

$E_{xc}[p]$ represents the exchange-correlation energy functional, in terms of the electron density $p(r)$, and the gradient ∇p , Laplacian $\nabla^2 p$, and the kinetic energy density (τ).

Where the kinetic energy is denoted by

$$\tau = \frac{1}{2} \sum_i |\nabla \varphi_i|^2 \quad (2.60)$$

d) Hybrid functionals

Hybrid functionals combine DFT with a fraction of exact exchange, typically derived from Hartree-Fock theory. These functionals incorporate both local and non-local contributions to the exchange-correlation energy and are often more accurate than pure GGA or LDA functionals.

$$E_{ex} = \frac{1}{2} \int dr dr_i \int_{\lambda}^i d \lambda \frac{\lambda e^2}{|r - r_i|} [\langle p(r)p(r_i) \rangle_{p,\lambda} - p(r)\delta(r - r_i)] \quad (2.61)$$

the exchange energy is denoted as E_{ex} , $p(r)$ and $p(r_i)$ is electron densities, and the positions of the electrons r and r_i . $\int dr dr_i \int_{\lambda}^i d \lambda \frac{\lambda e^2}{|r - r_i|}$ this part represents a double integration over the spatial coordinates of the electrons (r) and the spin variables (λ). The term $\frac{\lambda e^2}{|r - r_i|}$ represents the electron-electron interaction energy, where λ represents the spin and e^2 is the elementary charge squared. The denominator $|r - r_i|$ represents the distance between the positions of the electrons r and r_i [217].

This $\langle p(r)p(r_i) \rangle_{p,\lambda}$ term represents the correlation between the electron densities $p(r)$ and $p(r_i)$ at positions r and r_i , respectively. The brackets $\langle \rangle_{p,\lambda}$ indicate the average over all possible electron configurations, considering both spin variables (λ) and the electron density (p) [217]. This correlation term captures the tendency of electrons to avoid each other due to their Coulomb repulsion.

$p(r)\delta(r - r_i)$ represents the product of the electron density $p(r)$ at position r and the Dirac delta function $\delta(r - r_i)$, which enforces the constraint that the electron density is nonzero only at the position r_i . This term accounts for the Pauli exclusion principle, which states that two electrons cannot occupy the same quantum state.

2.9.7. Quantum chemical properties with relevance for corrosion inhibitors binding on metal surfaces.

DFT approaches have been shown to be effective in delivering information about chemical reactivity indices such as global hardness (η), global softness (σ), Frontier Orbital Energies, electronegativity (χ), electro affinity (A), ionization potential (I), electrophilicity (ω).

Global hardness is a measure of the resistance of a molecule or system to undergo changes in its electronic structure. It is related to the ionization potential (I) and electron affinity (A) of a molecule through the below equation[221-223].

$$\eta = \frac{I-A}{2} \quad (2.62)$$

The global hardness provides insights into the stability and reactivity of a system. Molecules with high hardness values are generally more stable and less prone to undergo chemical reactions or interactions with other systems. On the other hand, molecules with low hardness values are more reactive and tend to readily participate in chemical reactions or engage with other molecules or environments.

Global softness is the reciprocal of global hardness which provides complementary information to hardness and helps in understanding the reactivity of a system[221, 222]. Global softness is calculated as the inverse of hardness:

$$\sigma = \frac{1}{\eta} \quad (2.63)$$

Molecules with high softness values are more reactive and exhibit greater susceptibility to undergo chemical reactions or interact with other systems. Conversely, molecules with low softness values are less reactive and exhibit higher stability.

Frontier orbital energies include HOMO energies, the highest occupied molecular orbital and the lowest unoccupied molecular orbital called LUMO energies. The energy gap between these orbitals, denoted by the equation below[221, 222], determines the reactivity and stability of molecules and their ability to undergo electron transfer, charge transfer, or participate in various chemical reactions. Higher reactivity is molecules with small values of ΔE , whereas those with high values are normally associated with poor reactivity[224, 225].

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (2.64)$$

The tendency of an atom to attract electrons toward itself is measured as electronegativity (χ)[221, 222]. The equation below of electronegativity makes the frontier molecular orbital

related to electronegativity. Electronegativity differences between atoms in a molecule determine the polarity and reactivity of chemical bonds.

$$\chi = -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \quad (2.65)$$

Electro affinity (A) denotes the energy change when an electron is added to an atom or a molecule. Electron affinity reflects the tendency of a species to accept electrons and engage in electron transfer processes[226, 227].

$$A = -E_{LUMO} \quad (2.66)$$

Ionization potential (I) represents the energy required to remove an electron from an atom or a molecule[221, 225]. It provides information about the ability of a species to donate electrons and participate in electron transfer reactions.

$$I = E_{HOMO} \quad (2.67)$$

Electrophilicity (ω) provides valuable information about the reactivity and behavior of molecules by characterizing their ability to accept or react with electrons. Molecules with higher values of electrophilicity are associated with a good electrophile, while molecules with small or lower values are associated with being good nucleophiles. The electrophilicity of the molecule is related to the electronegativity and the global hardness[223, 225] as illustrated in the equation below.

$$\omega = \frac{\chi^2}{2\eta} \quad (2.68)$$

Furthermore, the total amount of electronic charge transferred (ΔN) from the inhibitor to the surface of the metal is calculated by the equation below of Pearson theory[222, 225]:

$$\Delta N = \frac{X_M - X_{INH}}{2(\eta_M + \eta_{INH})} \quad (2.69)$$

From Fukui's analysis, the partial atomic charge for the neutral molecule is $q_k(N)$ [227]. when a molecule accepts an electron is defined by $q_k(N+1)$, and when a molecule loses an electron is denoted by $q_k(N-1)$ [222, 225]. calculations for nucleophilic attack Fk^+ and electrophilic attack Fk^- followed equation below:

$$Fk^+ = q_k(N + 1) - q_k(N) \quad (2.70)$$

$$Fk^- = q_k(N) - q_k(N - 1) \quad (2.71)$$

Bind energy: Binding energy for quantum chemistry represents the energy difference between the bound state and the separated, non-interacting constituents which refers to the energy associated with the stability of a bound system, such as a molecule or a complex. The binding energy provides valuable insights into the stability, reactivity, and physical properties of molecules[228]. For corrosion inhibitor studies, the binding energy is a key quantity used to evaluate the strength of the interaction between the inhibitor molecule and the metal surface.

Binding energy in molecular system arises from the attractive forces between atoms that hold them together in a stable configuration. The electrons in the molecular orbitals contribute to the binding energy through their interactions with the atomic nuclei and with each other. The total binding energy of a molecule is the sum of the electronic energy, which accounts for the electron-electron and electron-nucleus interactions, and the nuclear repulsion energy, which arises from the Coulomb repulsion between the atomic nuclei. In corrosion inhibitor the binding energy can be defined as the difference energy between the total energy of the system when the inhibitor molecule is adsorbed on the metal surface and the total energy of the isolated inhibitor molecule[229, 230] which is expressed as:

$$BE = E_{total}(inhibitor + metal) - E_{total}(inhibitor) - E_{total}(metal) \quad (2.72)$$

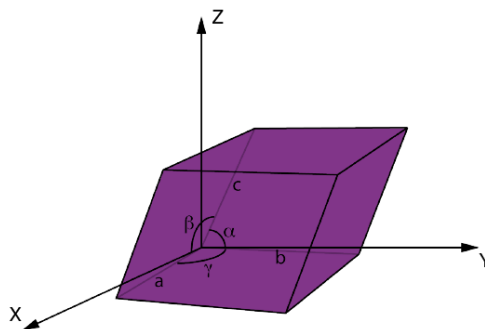
Moreover, the binding energy plays a significant role in intermolecular interactions and molecular recognition processes. It governs the strength of noncovalent interactions, such as hydrogen bonding, van der Waals forces, and π - π interactions[231]. These interactions are crucial in understanding the behavior of biomolecules, the formation of supramolecular assemblies, and the design of drugs and catalysts.

The binding energy is closely related to the stability and chemical reactivity of a molecule. Stronger binding corresponds to higher stability, as more energy is required to break the bonds within the molecule. Conversely, weaker binding may lead to increased reactivity, as the molecule is more susceptible to undergoing chemical transformations[232]. A negative binding energy indicates that the interaction between the inhibitor and the metal surface is favourable and stabilizing[233].

2.9.8. Crystal structure in relation to study of metal surface

When modeling metallic systems, it is crucial to have an understanding of the nature of the metal. It is understood that metal falls in the category of solid substances whose atomic composition is arranged in crystalline form. A crystal structure refers to the arrangement of atoms, ions, or molecules in a crystal lattice, forming a repeating pattern throughout the entire crystal. Crystal structures describe the geometric arrangement, connectivity, and symmetry of the constituent particles within a crystalline material. Crystal structure plays a crucial role in many areas of materials science, solid-state physics, and surface chemistry. In a crystal lattice, the unit cell is the smallest repeating unit. It is the primary building block upon which the complete crystal structure is built through repetition in various direction[234].

As illustrated in the figure below, a unit cell is fully characterised by six parameters: the lengths of the three edges (a , b , c) and the angles between them (α , β , γ). These parameters define the size and shape of the unit cell and can vary depending on the crystal structure.



2.9.8.1. Metallic crystal structures

Metallic crystal structures refer to the arrangement of atoms or ions in metallic materials. Metals are characterized by their high electrical and thermal conductivity, malleability, and ductility, which arise from the unique bonding and arrangement of atoms in their crystal structures. The following are some examples of common metallic crystal structures:

- **Body-Centered Cubic (BCC) Structure:** In the BCC structure, each atom is located at the center of a cube, with additional atoms situated at the corners of the cube. The coordination number (number of nearest neighboring atoms) in BCC structures is 8. iron, chromium, and some low-alloy steels adopted BCC structures.
- **Face-Centered Cubic (FCC) Structure:** The FCC structure is characterized by atoms located at the corners and in the center of each face of a cube. The coordination

number in FCC structures is 12, and the packing factor is 0.74. Stainless steels, aluminum, and copper, adopt the FCC crystal structure.

- **Hexagonal Close-Packed (HCP) Structure:** In an HCP structure, the third layer has the same arrangement of spheres as the first layer and covers all the tetrahedral holes. Since the structure repeats itself after every two layers, the stacking for HCP may be described as "a-b-a-b-a-b." The atoms in a hexagonal closest packed structure efficiently occupy 0.74 of space while 0.26 is empty space.

2.9.8.2. Crystallographic points, direction, and planes

Crystallographic points, also known as lattice points or lattice sites, represent specific positions within the crystal lattice where atoms, ions, or other structural units are located. Each lattice point corresponds to a repeating unit of the crystal structure. They form a three-dimensional array that defines the geometric arrangement of the crystal lattice.

The orientation and path of a line within the crystal lattice are described by crystallographic directions. They are represented by Miller indices, which are three integers (h , k , l) that define the direction relative to the crystallographic axes. The Miller indices (h , k , l) represent the reciprocals of the intercepts of the direction vector on the crystallographic axes.

Crystallographic planes represent two-dimensional surfaces within the crystal lattice. They are defined by their orientation and spacing with respect to the crystallographic axes. Crystallographic planes are described using Miller indices (h , k , l) as well. The Miller indices (h , k , l) of a plane represent the reciprocals of the intercepts of the plane on the crystallographic axes.

Miller indices for both directions and planes are determined by taking the reciprocals of the fractional intercepts of the direction or plane with the crystallographic axes. These indices represent the relative position and spacing of the lattice points along the corresponding direction or plane [235, 236].

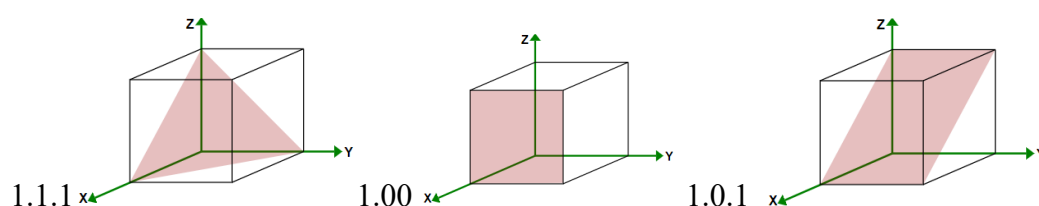


Figure 2. 7: Miller indices (h , k , l)

CHAPTER 3: EXPERIMENTAL PROCEDURES

This chapter details the methodologies employed in this study to investigate the synthesis of substituted triazines as corrosion inhibitors on aluminium and mild steel in 1M HCl, providing a comprehensive account of the experimental design, materials, and techniques used. The primary objective of this chapter is to ensure that the experiments can be replicated by other researchers, thereby validating the results and conclusions drawn from the study. By meticulously outlining each step of the experimental process, this chapter aims to provide a clear and transparent account of how the research was conducted. The chapter is organized as follows: Section 3.1 describes the method used to synthesize the substituted triazines. Section 3.2 describes the method used to study the thermal stability and decomposition of inhibitors. Section 3.3 details the electrode and solution preparation. Section 3.4 covers data collection methods for weight loss measurement, while Section 3.5 explains the experimental setup for electrochemical analysis techniques. Sections 3.6 to 3.8 cover the surface characterization methods. Finally, Section 3.9 discusses the Quantum Chemistry calculations.

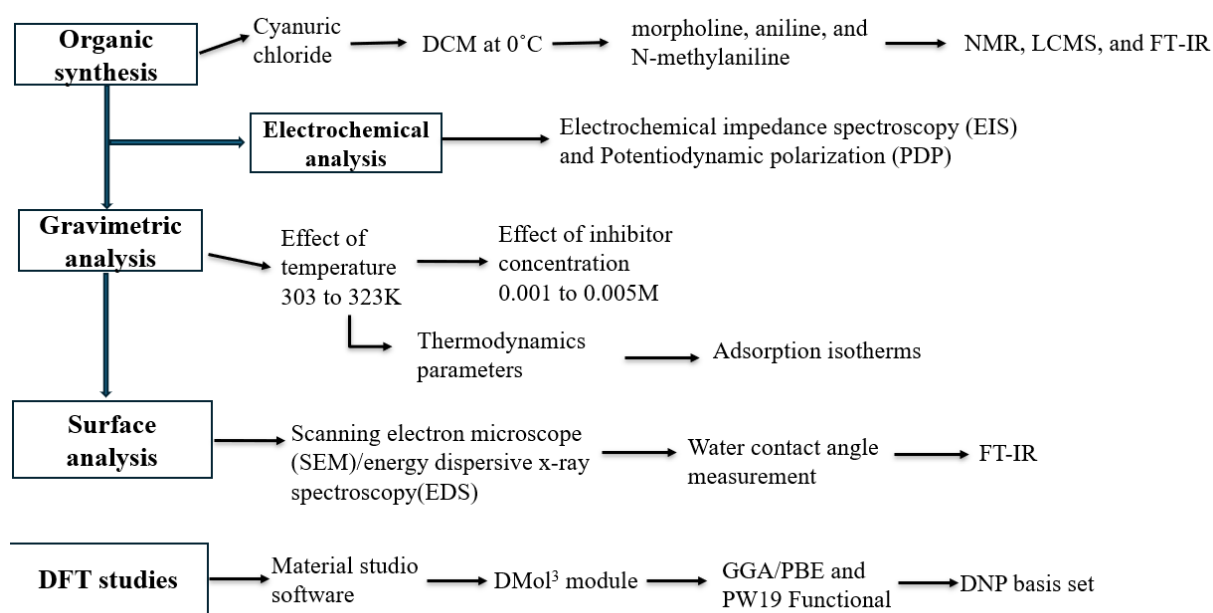
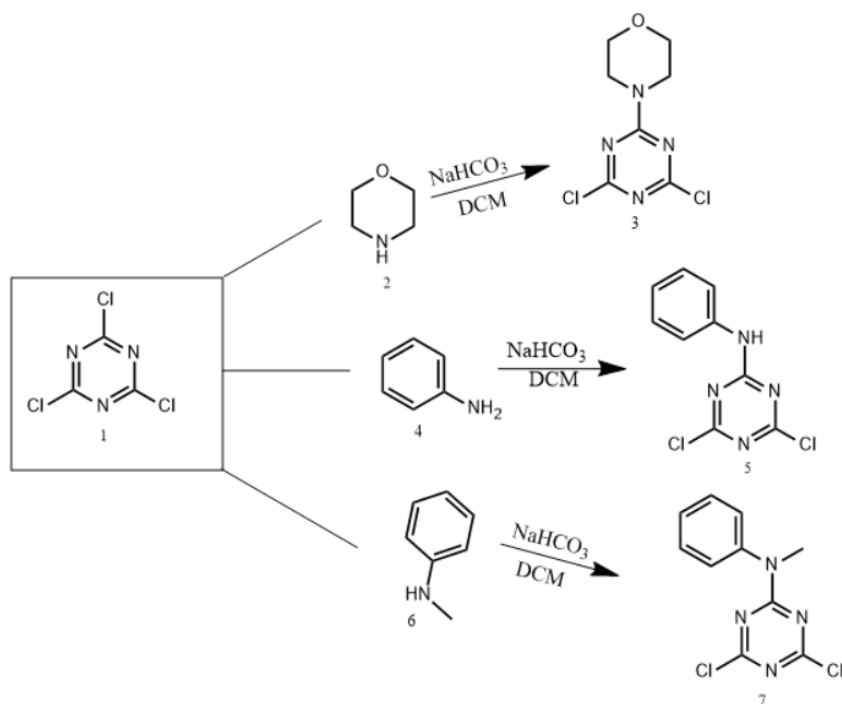


Figure 3. 1: Summary of experimental procedures

3.1. Synthesis of corrosion inhibitor

Organic inhibitor synthesis began with the one-step (substitution) synthesis, where cyanuric chloride was the starting material for all target compounds. Spectroscopic techniques were used to characterize ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra on a Bruker 400 MHz spectrometer using deuterated chloroform NMR solvent. Chemical shift values were expressed in parts per million (ppm). Bruker platinum 22-vector Fourier Transform spectrometer (FT-IR) was used to generate infrared spectra.

DMT 3, DPT 5, and DNT 7 were synthesized as depicted in scheme 1, whereby a mixture of cyanuric chloride and NaHCO_3 in 30ml DCM at 0°C was treated with appropriate amines (morpholine 2, aniline 4, and N-methylaniline 6) dropwise. The reaction mixture was kept at 0°C and monitored by thin-layer chromatography. After the completion of the reaction, the mixture was filtered, and the filtrate was left in the fume hood to dry; NMR, IR, and LCMS characterized the resultant solid products.



Scheme 1: Synthesis of substituted triazine

3.2. Thermogravimetric analysis (TGA)

Thermogravimetric Analysis (TGA) is an effective analytical method that can be used to assess the thermal stability of corrosion inhibitors. Through analysing the inhibitor's mass variation in response to temperature fluctuations. A thermogravimetric analysis (TGA) in this study was performed using the PerkinElmer Simultaneous Thermal Analyzer 6000. The measurements were taken from the initial temperature of the surroundings up to a temperature of 360°C. The heating rate used was 20°C per minute and the flow rate of nitrogen was 20ml per minute.

3.3. Electrode and solution preparation

3.3.1. Metallic materials used

Aluminium (Al) and mild steel (MS) were selected as the test metals with a composition of 3 x 2 cm dimensions. The coupons contained a hole with a radius of 0.375 cm, allowing for glass rods to be inserted to suspend the metals. The MS utilized in the studies has the following chemical composition: Mn = 0.37, Ni = 0.039, P = 0.02, S = 0.03, C = 0.21, Fe = 99.32, and Mo = 0.01. Aluminum coupons with an approximate content of 99% were also utilized. Before each test, the Al and Ms Coupon surface was polished using Struers LaboSystem and washed with distilled water. The metal coupons were dried using air.

3.3.2. Test settings with corrosive and inhibiting properties

The corrosive solution for this study was 1M HCl solution, prepared from the concentration of 32% HCl and distilled water for the corrosion analysis. The synthesized inhibitors (DMT, DNT, and DPT) were insoluble in water. To solve the issue, 1 ml of DCM was added during the preparation of the inhibitor using 1M HCl solution, obtaining different concentrations (0.001, 0.002, 0.003, 0.004, and 0.005M). Besides the performance of DMT, DPT, and DNT inhibitors, two drops of graphene oxide were added to each concentration of those inhibitors and stirred for more than 3 hours to investigate the effect of graphene oxide. This was done on mild steel only.

3.4. Weight loss measurements

The weight loss method involves exposing metal samples to a corrosive environment with and without a corrosion inhibitor and then measuring the metal's weight change after a certain exposure period[237, 238]. The mass loss experiments were performed under total immersion

into 1.0 M HCl solution (with or without different concentrations of DMT, DPT, and DNT) at various temperatures. A water thermostat controlled the temperature. After a six-hour immersion, the specimens were removed from the solution, washed with an acetone washed with an acetone polish using Struers LaboSystem under running water to remove the corrosion product shown in figure , dried in the air, and weighed accurately. The study was performed in the temperature range of 303 K to 323 K and the concentration range of 0.001M to 0.005M. Following schematic diagram in figure 3.1.

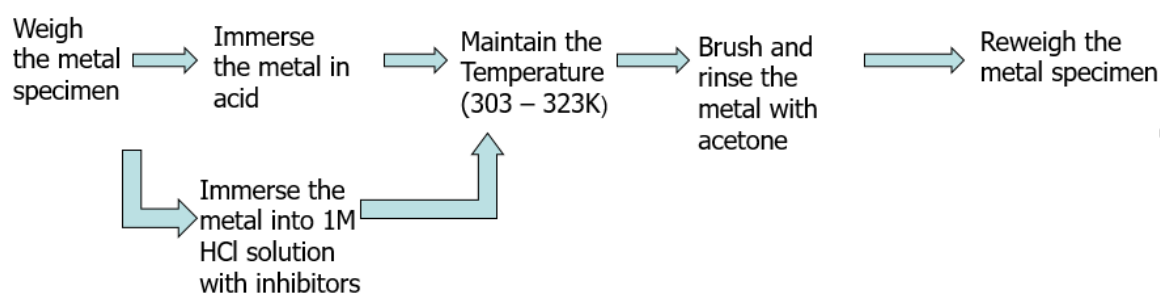


Figure 3. 2 weight loss Schematic diagram



Figure 3. 3: Polishing metal using Struers LaboSystem under running water



Figure 3. 4: weight loss set up

The weight loss data for each metal coupon was used to calculate the corrosion rate (C_R) equation 3.1[239].

$$C_R = \frac{\Delta W}{St} \quad (3.1)$$

where: the change in metal coupon mass before and after immersion into the solution is represented by ΔW . The total area of the metal coupon is denoted by s , and the immersion time is represented by t . Equations (3.2) and (3.3) were used to calculate the corrosion rate, percentage inhibition efficiency (%IE), and the degree of surface coverage (θ) for the metal coupons[240-244]:

$$\theta = 1 - \frac{C_{R_{inh}}}{C_{R_{Bla}}} \quad (3.2)$$

$$\%IE = 1 - \frac{C_{R_{inh}}}{C_{R_{Bla}}} \times 100 \quad (3.3)$$

where: $C_{R_{inh}} / C_{R_{Bla}}$ Represent corrosion rate in the presence and absence of inhibitors [245].

3.5. Electrochemical analysis

The electrochemical investigations were conducted in a three-electrode cell configuration at ambient temperature employing a potentiostat BioLogic–SP150 for all the metals test and an Electrochemical workstation Corrotest for mild steel using DMT, DPT, and DNT inhibitors with the modification of graphene. The working electrode shown in figure 3.3 consisted of mild steel/aluminium with surface area of 1 cm² of exposed surface area, a reference, and auxiliary electrodes, which were Ag/AgCl and graphite, respectively. Before the measurement of PDP and EIS, the working electrode was dipped in the test solution to stabilize the OCP. EIS measurements were carried out at OCP in a wide frequency of 100kHz to 100mHz, with a signal amplitude of 10mv to 10 mHz[246-248]. Reproducibility and repeatability were ensured by standardizing electrode surface preparation, using consistent experimental conditions and concentrations, conducting replicate measurements, and employing the same instrumentation and data analysis procedures. Measurements were repeated at least three times, and only consistent, stable data were considered for interpretation.



Figure 3. 5: The prepared working electrode used on BioLogic–SP150

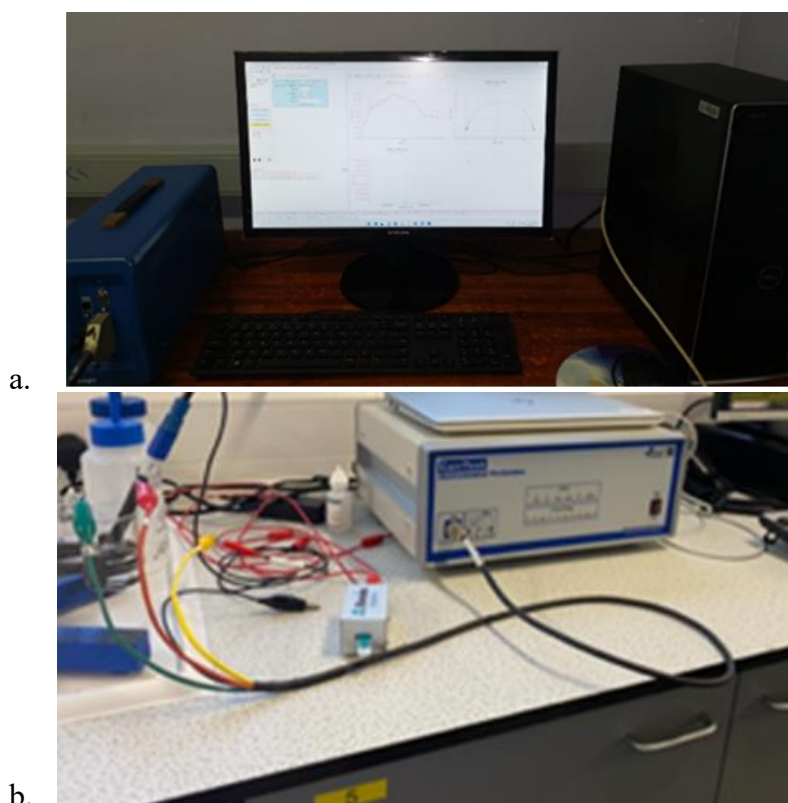


Figure 3. 6: a. Potentiostat BioLogic–SP150 for all the metals test and b. Electrochemical workstation Corrotest for mild steel using inhibitors with the modification of graphene.

The EIS data was fitted using Zfit EC-Lab software for aluminium, ZSimp software, and CS studios for mild steel. The inhibition efficiency (%IE_{EIS}), the double layer capacitance (C_{dl}), and the relaxation time constant (τ) were calculated using equations 3.4, 3.7, and 3.8

$$\%IE_{EIS} = \left(\frac{R_{P(inh)} - R_P}{R_{P(inh)}} \right) \times 100 \quad (3.4)$$

where $R_{p(inh)} / R_p$ represents the polarisation resistance with and without the inhibitor, which is calculated as follows[249, 250]:

$$R_p = R_1 + R_2 + R_3 \dots \quad (3.5)$$

$$\text{Or } \frac{1}{R_p} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} \dots \dots \dots \quad (3.6)$$

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (3.7)$$

$$\tau = C_{dl} \times R_{ct} \quad (3.8)$$

The polarization curves were run at a scan rate of 5 mVs^{-1} and in the potential range of 250 mv and the result of PDP was analyzed using EC-Lab software[247, 251-253]. The corrosion current densities (i_{corr}) were determined by extending the linear Tafel segments of the anodic and cathodic curves to the corrosion potential. Using equations 3.9, 3.10, and 3.11, the inhibition efficiency ($\%IE_{PDP}$), anodic interaction coefficient (f_a), and cathodic interaction coefficient (f_c)[254-256] were obtained respectively

$$\%IE = 1 - \frac{i_{corr}}{i_{corr}^o} \times 100 \quad (3.9)$$

$$f_a = \frac{i_{corr}}{i_{corr}^o} \exp \left(\frac{E_{corr}^o - E_{corr}}{\beta_a} \right) \quad (3.10)$$

$$f_c = \frac{i_{corr}}{i_{corr}^o} \exp \left(\frac{E_{corr} - E_{corr}^o}{\beta_c} \right) \quad (3.11)$$

where: i_{corr}/i_{corr}^o is the corrosion current densities in the presence and absence of the inhibitor, E_{corr}/E_{corr}^o is the corrosion potential in the presence and absence of inhibitors. β_a/β_c is the anodic and cathodic Tafel constant[245].

3.6. Scanning electron microscope/ energy dispersive x-ray spectroscopy (SEM/EDX) analysis

An investigation using scanning electron microscopy (SEM) was performed to evaluate the surface morphology of aluminum (Al) and mild steel (MS) before and after being exposed to a corrosive media (1 M HCl), both with and without DMT, DPT, and DNT, using a Phenom pro x for Al and Oxford instrument for MS. The images were captured using the variable pressure detector (VP) and the backscattered detector (BSD), in conjunction with an energy-dispersive X-ray Spectroscopy (EDX) detector, was utilized to evaluate the alterations in surface morphology of the Al and MS electrodes and examine their elemental composition. Before SEM/EDX investigation, the samples were subjected to gravimetric analysis, which entailed submerging them for 6 hours at a temperature of 303K. Afterwards, following this specific period, the samples were taken out from the reaction environment, washed with distilled water, and dried off using acetone. Photographs were taken of the precise portion of the samples from which more accurate data was obtained. The results were subsequently compared to the samples that were subjected to 1 M hydrochloric acid, both with and without different amounts of DMT, DPT, and DNT.

3.7. Water contact angle measurement

Using a smartphone to measure the contact angle of water on metal surfaces can be a cost-effective alternative to an expensive video contact angle system[257-259]. The impact of DMT, DPT, and DNT inhibitors on the wettability of Al and MS coupons was assessed by measuring the contact angle formed by water on the surfaces of the two metals. The water droplet image was captured in this study using a smartphone, pipette, macro lens, and lens mount. The data were examined using an open-source image editor (ImageJ version 1.53), which enables direct calculation of the contact angle from the image. After affixing it to the lens mount, the macro lens was attached to the smartphone's camera lens[260-263]. The sample was positioned adjacent to the edge of a well-illuminated workbench. A pipette dispensed a small droplet of ultrapure water, measuring one microliter near the foremost section of the sample to measure the static contact angle. Subsequently, they were submerged in corrosive solutions, uninhibited, and inhibited by 0.005M DMT, DPT, and DNT inhibitor concentrations for 6 hours. After 6 hours of immersion, the samples underwent scrubbing using a brush, were rinsed with distilled water, dried, and subsequently stored in a desiccator until they were ready for testing.

3.8. FT-IR Spectrometry

A Bruker spectrum analyzer was used to perform FT-IR spectroscopy analysis on compounds to identify the functional groups present. The technique was employed to analyze the corrosion products and inhibitory films that developed on the surface of metals. This analysis was conducted both in the presence and absence of the inhibitor solution's optimal concentration (0.005M). The metals were immersed in a 1 M HCl solution for 6 hours, along with the solutions of the inhibitors. The spectra were acquired within the room temperature range, specifically from 4000 to 400 cm^{-1} .

3.9. Quantum chemistry calculations

Surface chemistry experiments can provide valuable information about the interaction between inhibitors and metals. DFT is one of the computational procedures in the field of science that can stimulate the interaction of corrosion inhibitors with metal surfaces, providing insight into how inhibitors bind to the surface and block the electrochemical reaction that produces corrosion[264]. DMol³ module package was used for the DFT calculation using Material Studio with well-known generalized gradient approximation (GGA) and perdew-burke-ernzehof (PBE) for Al[152, 265] and Perdew–Wang exchange (PW91)[265-268] for MS. A double numerical plus polarization (DNP-3.5) base setting was set for effective core potentials[225, 269-271] and k -point $2 \times 2 \times 1$. The Al(111) and Fe(100) slab surface was built with a $5 \times 5 \times 1$ supercell with a vacuum thickness of 20.00 Å[272, 273] and with three layers where the uppermost layer of the Al(111) and Fe(100) slab was used as a target atom, and the remaining two layers were constrained[274]. The adsorption locator module was used to examine the adsorption of inhibitors on Al(111).

Adsorption energy(E_{ads}) and binding energy($E_{binding}$) of the inhibitors on the Al(111) and Fe(100) surfaces were calculated using equations 3.12 and 3.13, respectively.

$$E_{ads} = E_{inh-m} - (E_{inh} + E_m) \quad (3.12)$$

$$E_{binding} = -E_{ads} \quad (3.13)$$

where E_{inh-m} is the total energy of the adsorbed inhibitor on the Al and MS surface, E_m is the total energy of the metal(Al and MS) clean surface, E_{inh} is the total energy of the isolated

optimized inhibitor [269, 275-277]. The relative energy was calculated by subtracting the highest and lowest adsorption energy.

CHAPTER 4: Results and Discussion

The primary objective of this chapter is to detail the successful synthesis and characterization of target compounds used as corrosion inhibitors. This chapter is organized as follows: first, describe the synthesis process for the target compounds, followed by a detailed analysis of their structural characterization using NMR, FTIR, and mass spectrometry. TGA was performed on the compounds to determine the degradation temperature.

4.1. Characterization of inhibitors

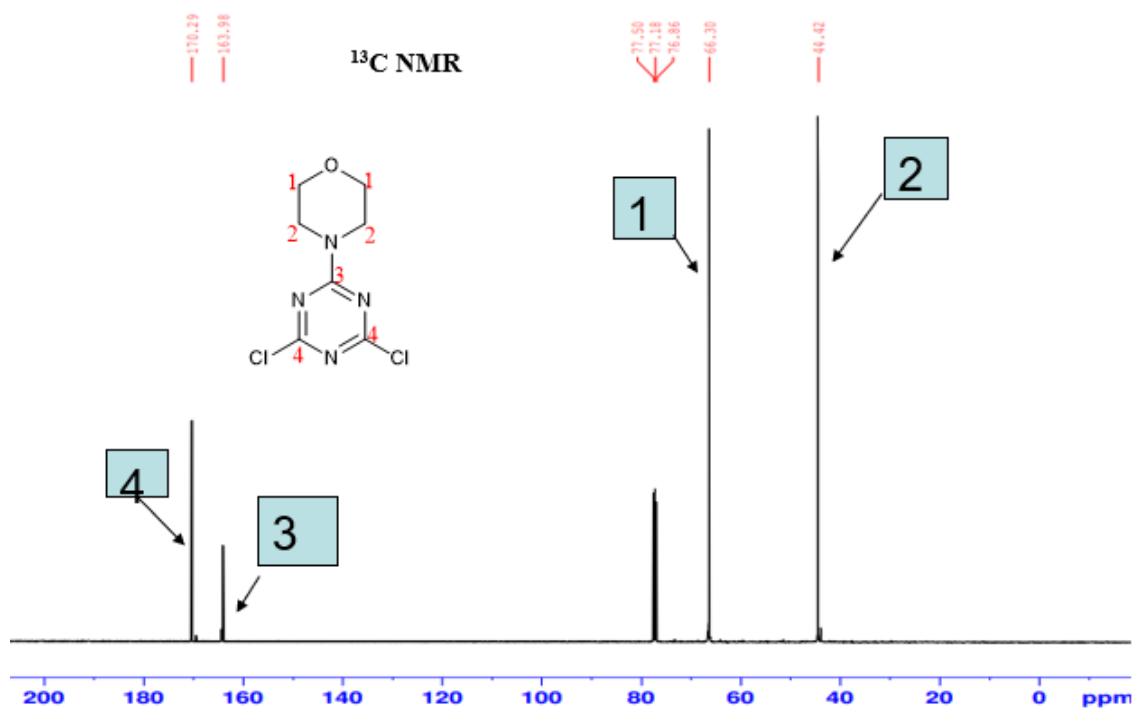
NMR, IR, and LCMS were used to characterize DMT, DPT, and DNT. Figure 4.1 shows ^{13}C NMR and ^1H NMR spectra of DMT, DPT (Figure 4.2) and DNT (Figure 4.3). ^{13}C NMR spectrum of DMT confirmed a mono-substituted 1,3,5-triazine with a peak at 170.29 ppm ascribed to equivalent carbons C4 and a peak at 163.98 ppm ascribed to C3. Two more peaks were observed in the ^{13}C NMR spectrum of DMT at 66.30 ppm and 44.42 ppm, confirming the methylene carbons C1 and C2, respectively. ^1H NMR spectrum of DMT revealed two triplets accounting for four protons each at 3.85 ppm and 3.69 ppm ascribed to Ha and Hb respectively.

^{13}C NMR spectrum of DPT revealed a total of four quaternary carbons at 166.62 ppm, 165.44 ppm, 159.37 ppm, and 130.96 ppm ascribed to C6, C7, C5, and C4, respectively. The spectrum also showed three methine carbon peaks at 124.56 ppm, 121.15 ppm, and 116.66 ppm ascribed to C2, C1, and C3, respectively. ^1H NMR spectrum of DPT revealed a broad singlet peak accounting for one proton at 7.83 ppm ascribed to Hd. The spectrum also showed three peaks in the aromatic region: a doublet accounting for two protons (Hc) at 7.56 ppm, a triplet accounting for two protons (Hb) at 7.43 ppm, and a quartet accounting for one proton (Ha) at 7.26 ppm.

^{13}C NMR spectrum of DNT revealed a total of four quaternary carbon peaks at 165.63 ppm, 165.21 ppm, 160.37 ppm, and 137.29 ppm due to C8, C7, C6, and C4, respectively. The spectrum also showed three methine carbon peaks at 124.82 ppm, 123.09 ppm, and 121.34 ppm C2, C1, and C3, respectively. Lastly, the spectrum revealed a methyl carbon peak at 34.50 ppm ascribed to C5. ^1H NMR spectrum of DNT revealed a singlet peak accounting for three protons at 3.51 ppm, which were ascribed to Hd. The spectrum also showed three peaks in the aromatic region: a doublet accounting for two protons (Hc) at 7.26 ppm, a triplet accounting for one proton (Ha) at 7.38 ppm, and a triplet accounting for two protons (Hb) at 7.59 ppm.

Further characterization was done using LCMS in Figures 4.4a, b, and c to confirm the mono product of DMT, DPT, and DNT compounds. Additional characterization was conducted utilizing FT-IR in Figures 4.5-4.7 to verify the functional group present in the compounds. The FT-IR spectra exhibit a stretching vibration at around 2970cm^{-1} and 3000cm^{-1} , which is associated with the presence of a C-H group for DMT (Figure 4.5). The peak corresponding to the C-N bond was observed at around 1220cm^{-1} . The absorption peak at approximately 1200cm^{-1} was related to (C-O-C). Figure 4.6 displays a distinct stretching vibration at approximately 3208cm^{-1} , which is associated with the existence of hydrogen bound N-H group

and the peak of C-N at approximately 1157cm^{-1} . The FT-IR for DNT was characterized by the disappearance of N-H in Figure 4.7 and C-H peak around 3000cm^{-1} .



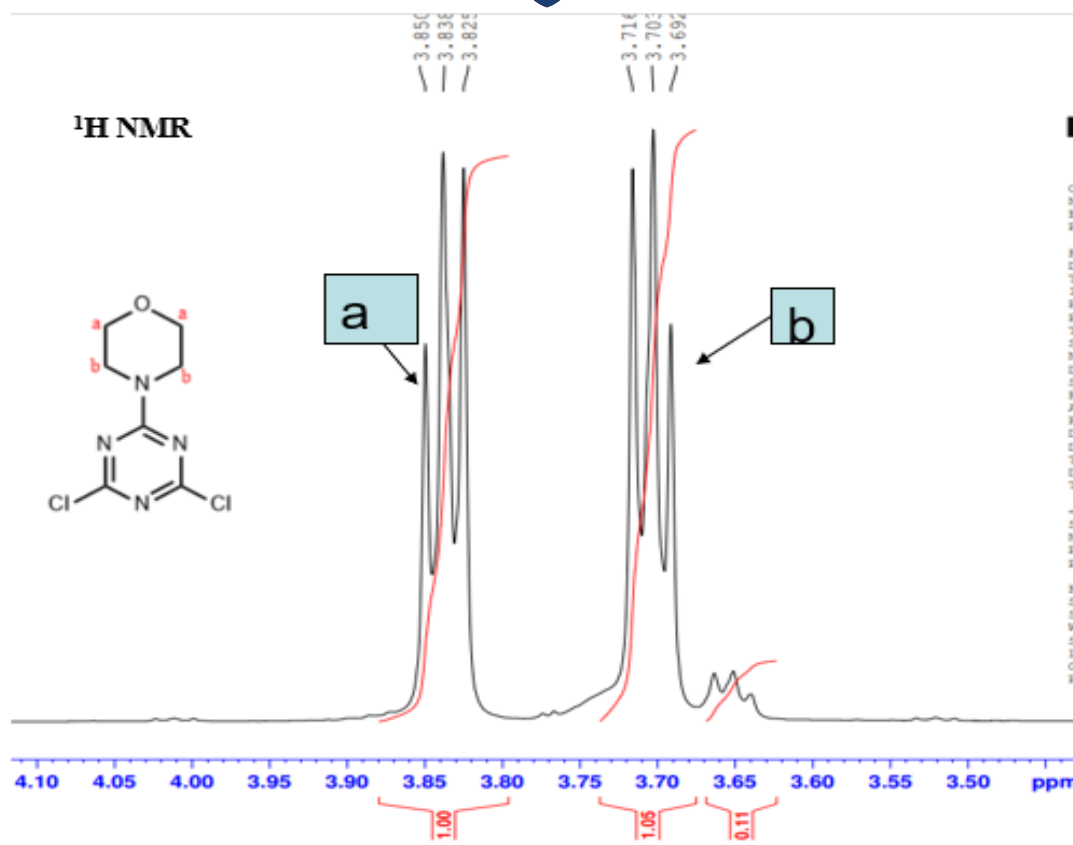
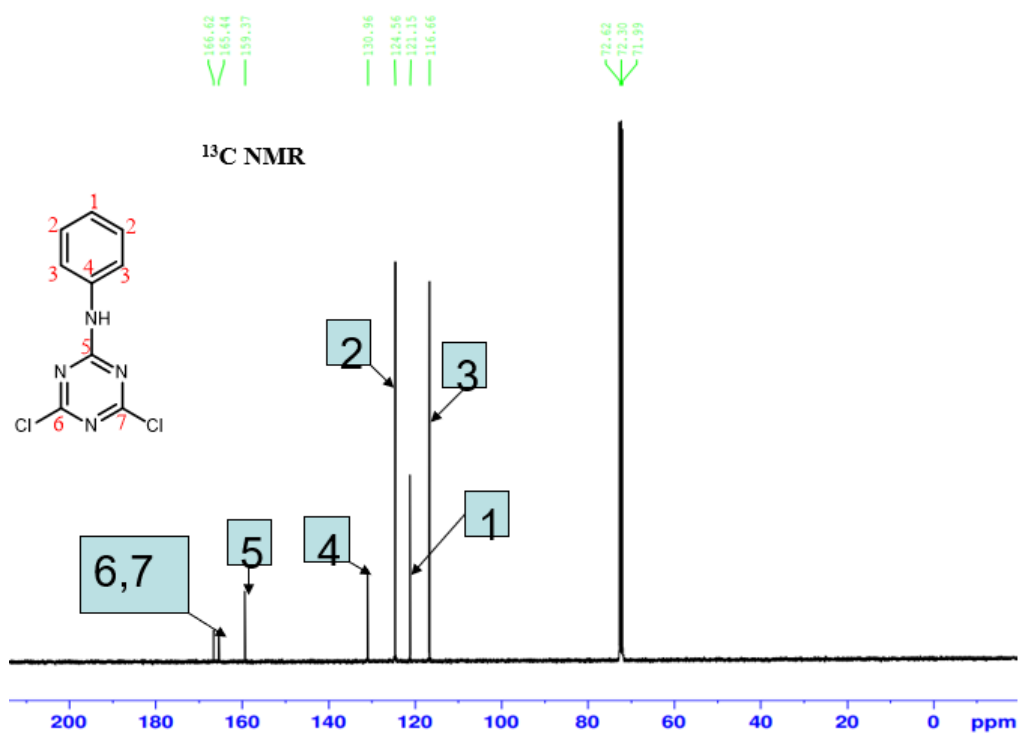


Figure 4. 1: ^{13}C NMR and ^1H NMR spectra for DMT



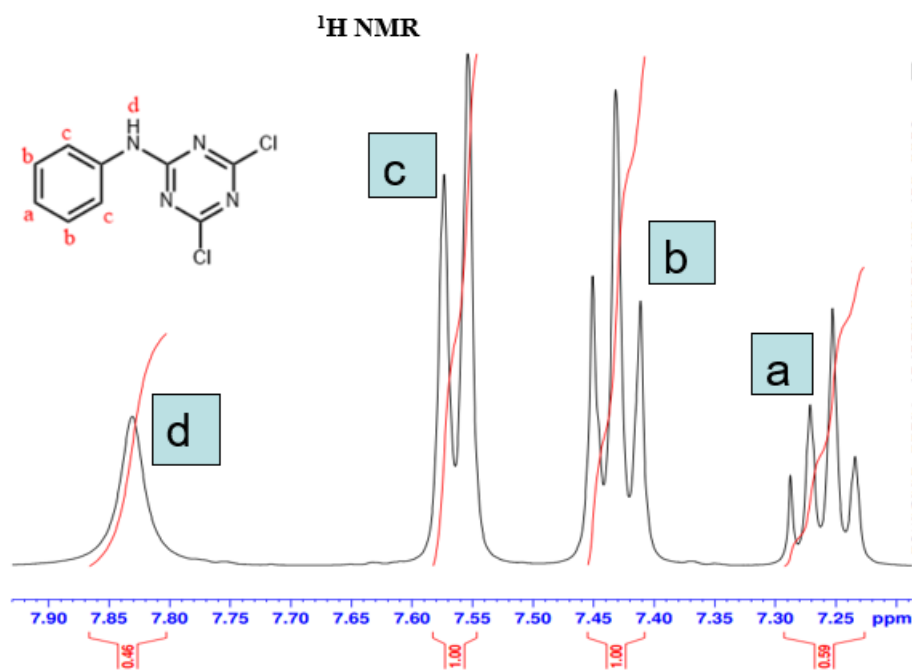
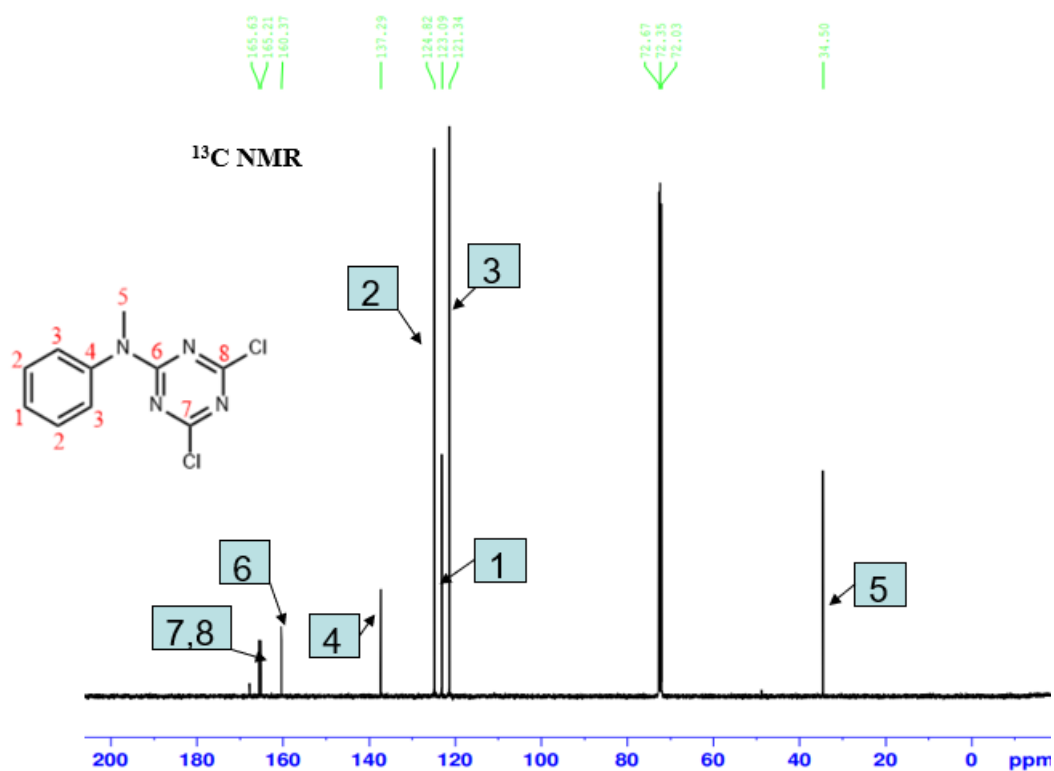


Figure 4. 2: ^{13}C NMR and ^1H NMR spectra for DPT



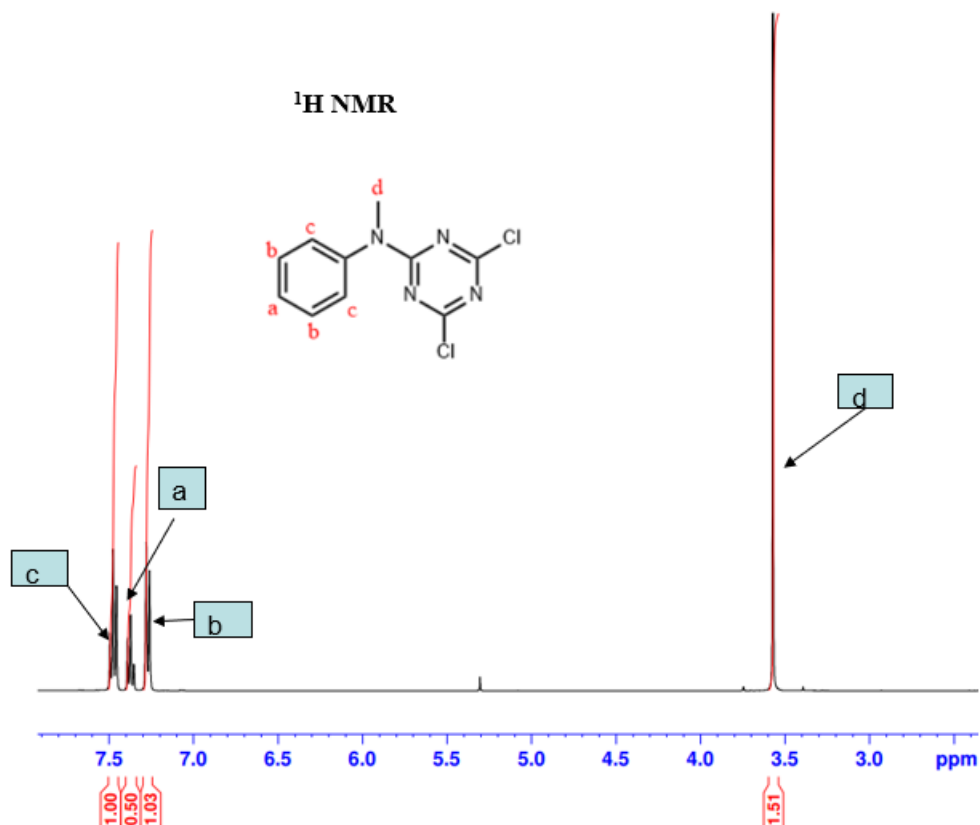
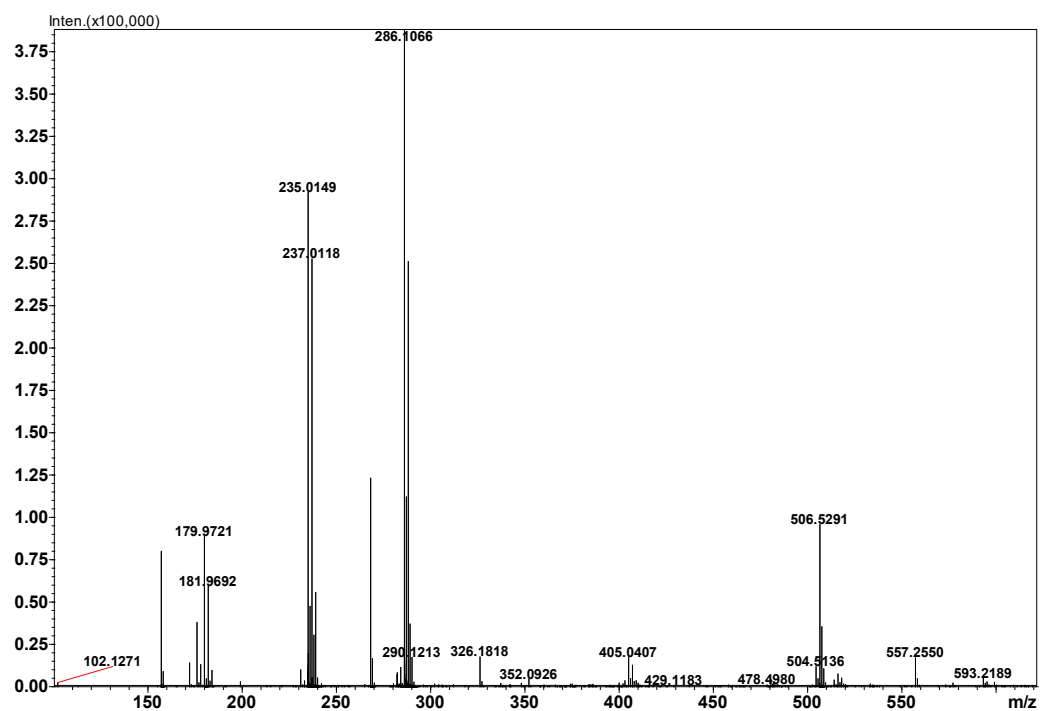
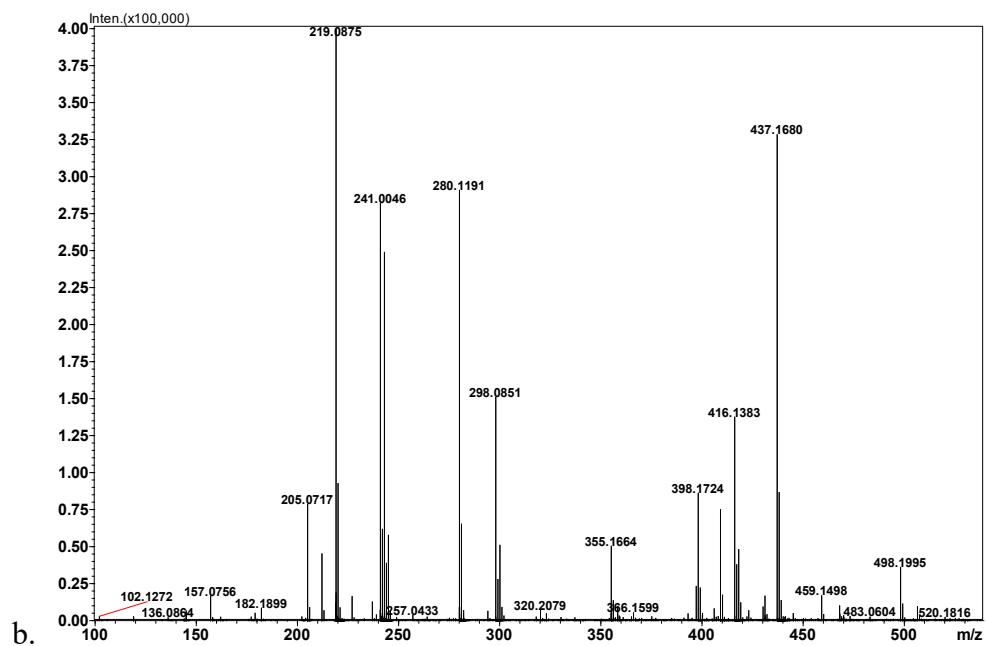


Figure 4. 3: ^{13}C NMR and ^1H NMR spectra for DNT



a.



c.

Figure 4. 4: LCMS for a) DMT, b) DPT, and c) DNT

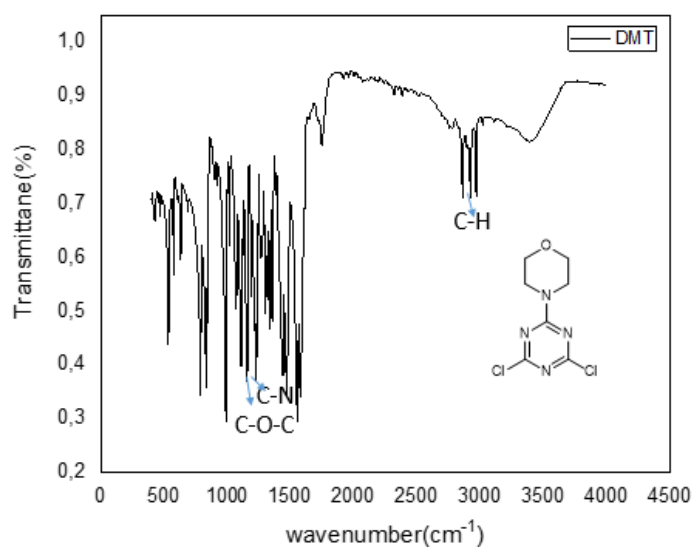
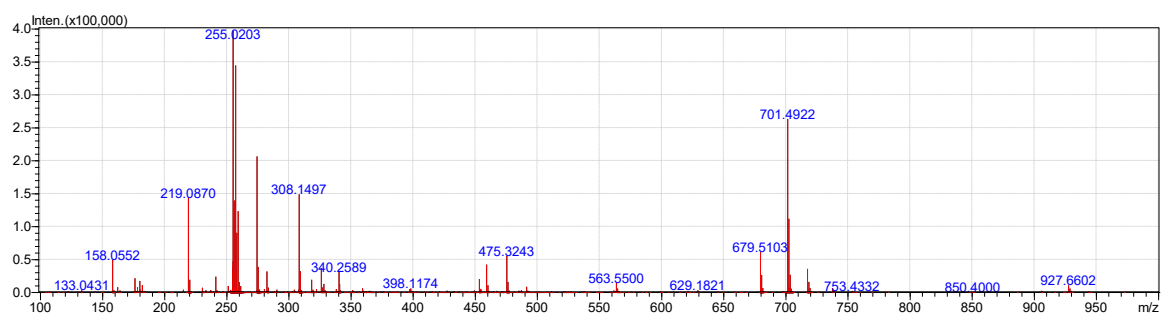


Figure 4. 5: FT-IR for DMT

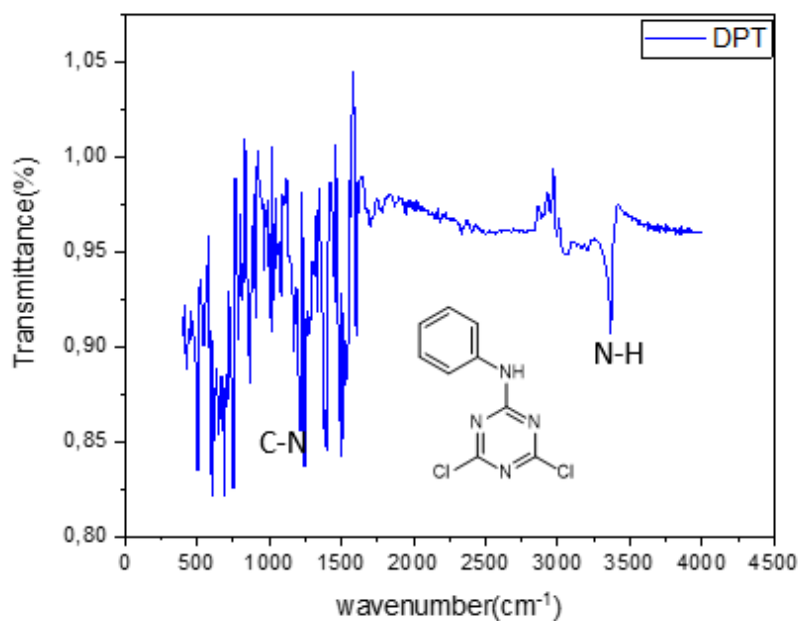


Figure 4. 6: FT-IR for DPT

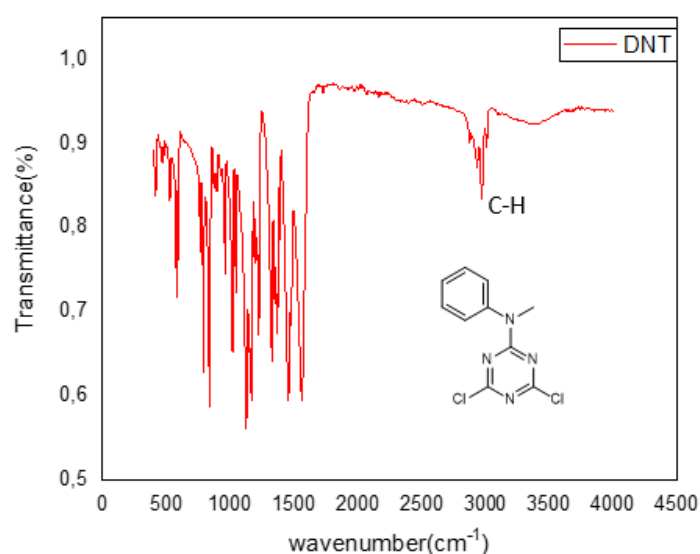


Figure 4. 7: FT-IR for DNT

4.2. Thermogravimetric Analysis

The Thermo-Gravimetric Analysis (TGA) is a method used to measure weight changes in a sample at a certain temperature. It is employed to evaluate the substances DMT, DPT, and DNT, as shown in Figures 4.8-4.10. The thermal breakdown curve offers valuable information about the inhibitor's decomposition with respect to temperature, highlighting significant points

of mass reduction. The results in Figure 4.8 indicate that there is a noticeable decrease in mass, amounting for 6.0066 wt% of the total, starting at 85.91°C. This decrease is due to the removal of surface water. The mass loss continues until 146.33°C, involving the removal of bound water. At temperatures ranging from 192.92°C to 276.87°C, there is a significant decrease in mass of 50.2421%. This decrease is directly related to the decomposition of the DMT inhibitor functional group[278-283]. The last weight loss of DMT was 12.7316% at a temperature ranging from 301.03°C to 334.94°C. The TGA curve for DPT in Figure 4.9 the weight loss begins to decompose at 181.007°C and ends at 312.4031°C with a mass loss of 75.6989%. The loss of DNT mass in Figure 4.10 begins at 253.82°C to 292.06°C with a mass loss of 27.989%.

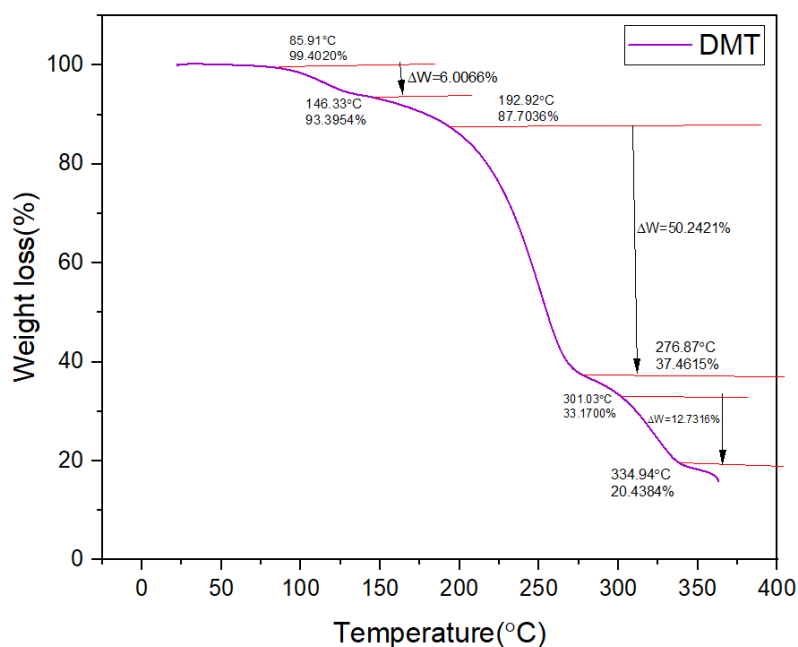
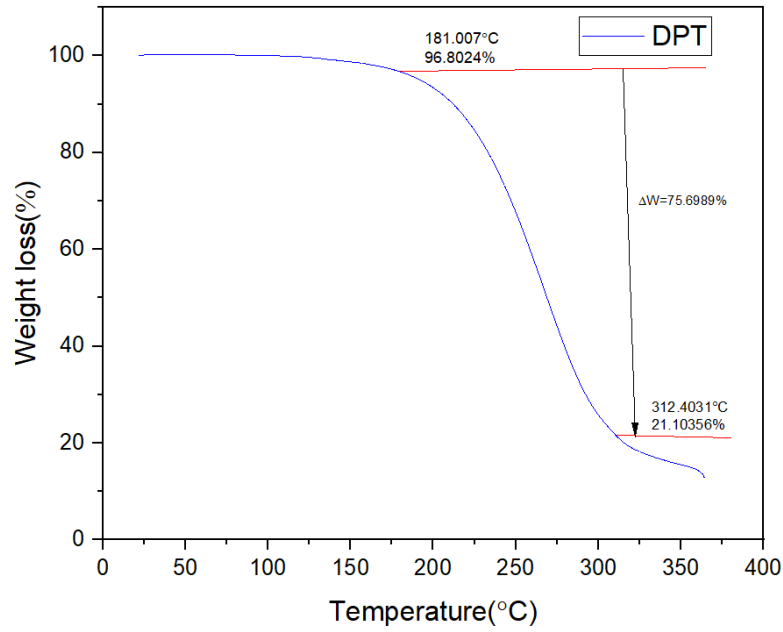
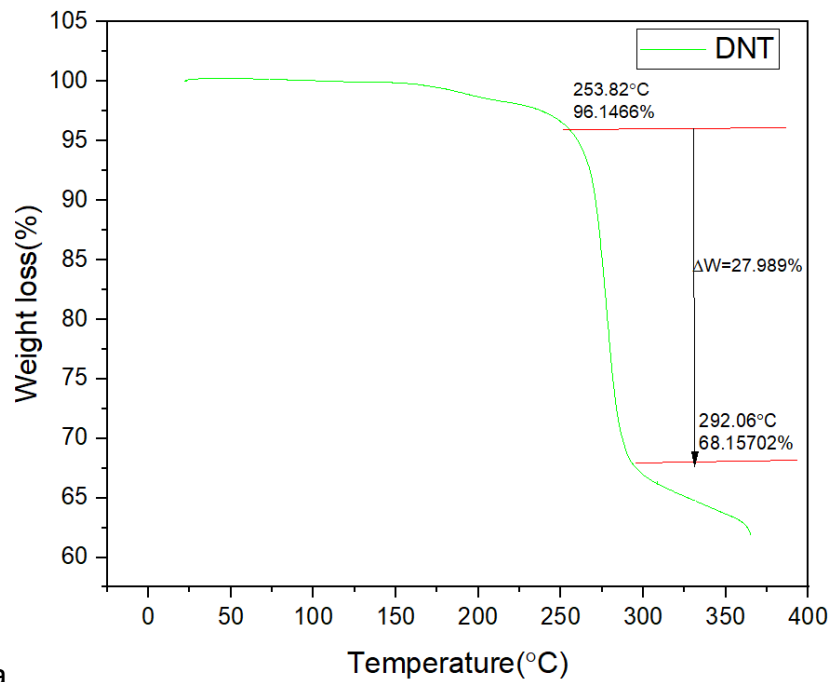


Figure 4. 8: TGA analysis of DMT



a.

Figure 4. 9: TGA analysis of DPT



a.

Figure 4. 10: TGA analysis of DNT

Chapter 5: Aluminium results and discussion

The results of aluminium (Al) are discussed and summarised in this chapter. The synthesized inhibitors were tested for their anticorrosive properties on aluminium in 1M HCl using weight loss analysis. The effects of temperature, inhibitor concentration, adsorption isotherms, and thermodynamic parameters were all examined. The inhibitors' mechanisms for inhibition, degradation, and resistance to corrosion were evaluated through the application of electrochemical techniques. Surface morphology, contact angle, and FTIR of the synthesized substitute triazine and aluminum surface were performed. The structures and binding energies for inhibitor -Al(111) were studied through computational methods.

5.1. Weight loss

Weight loss measurements provided a preliminary framework for the anti-corrosive nature of DMT, DPT, and DNT on Al in 1M HCl solution. By immersing the Al metal sample in 1 M HCl for six hours at various temperatures, weight loss analysis was used to assess the impact of DMT, DPT, and DNT concentration and temperatures against Al corrosion in a 1 M HCl solution.

5.1.1. Effect of inhibitor (DMT, DPT, and DNT) concentrations on aluminium metal in 1M HCl solution.

Table 5.1 shows the calculated C_R , θ , %IE from the weight loss measurements. Figures 5.1-5.3 shows the corrosion rate as a function of various inhibitor concentrations for aluminium samples at different temperatures. The varying inhibition efficiencies at 303–323 K for Al are displayed in Figure 5.4-5.6 concerning inhibitor concentrations. While aluminum has a natural oxide layer that provides some protection, it can be attacked by strong acids, particularly mineral acids such as hydrochloric acid, and undergo corrosion. This was seen in Table 5.1, where the HCl solution is available without the inhibitor, and the Al metal corrodes faster with a higher corrosion rate of 0.0159g/cm²h. The definition of corrosion inhibitor states that when a small amount is added to a corrosive environment, the corrosion rate is reduced. The result of this study proves the definition of a corrosion inhibitor; when DMT, DPT, and DNT inhibitor is introduced or added, it reduces the corrosion rate of Al corrosion by forming a protective layer. In the presence of 0.001, 0.002, 0.003, 0.004, and 0.005M DMT inhibitors, the corrosion rate was reduced to 0.0059, 0.0052, 0.0037, 0.0032, and 0.0027g/cm²h respectively. For DPT with the same concentration corrosion rate decreases to 0.0060, 0.0056, 0.0054, 0.0042, and 0.0028g/cm²h respectively. In the presence of DNT, the corrosion rate was reduced to 0.0080, 0.0074, 0.0052, 0.0035, and 0.0032g/cm²h respectively with 0.001, 0.002, 0.003, 0.004, and 0.005M concentration. The corrosion rate is inhibitor concentration dependent this can also be seen in Figures 5.1-5.3, for both inhibitors, the corrosion rate decreases with an increase in inhibitor concentration. When the inhibitor concentration increases it reduces the corrosion rate and simultaneously increases the inhibition efficiency(%IE) highlighted in Figure 5.4-5.6. The lowest corrosion rate and high inhibition efficiency were expressed in 0.005M inhibitor concentration due to the higher concentration of inhibitor molecules available to interact with the metal surface, effectively forming a more protective barrier against corrosion compared to 0.001M concentration.

Table 5. 1: Weight loss parameters of DMT, DPT, and DNT inhibitor on the corrosion of Al at various temperatures for 6 hours immersion.

Temperature (K)	Inhibitor concentration (M)	Weight loss (g)	Corrosion rate (g/cm ² h)	Surface coverage (θ)	%IE
DMT					
303	Blank	0.5736	0.0159	-	-
	0.001	0.2112	0.0059	0.6289	62.89
	0.002	0.1855	0.0052	0.6730	67.30
	0.003	0.1327	0.0037	0.7673	76.73
	0.004	0.1144	0.0032	0.7987	79.87
	0.005	0.0988	0.0027	0.8302	83.02
313.	Blank	0.7970	0.0221	-	-
	0.001	0.3316	0.0092	0.5837	58.37
	0.002	0.2775	0.0077	0.6516	65.16
	0.003	0.2077	0.0058	0.7376	73.76
	0.004	0.1888	0.0052	0.7647	76.47
	0.005	0.1724	0.0048	0.7828	78.28
323	Blank	0.9563	0.0265	-	-
	0.001	0.5509	0.0153	0.4226	42.26
	0.002	0.5313	0.0148	0.4415	44.15
	0.003	0.5093	0.0141	0.4679	46.79
	0.004	0.4661	0.0129	0.5132	51.32
	0.005	0.3721	0.0103	0.6113	61.13
DPT					
303	Blank	0.5736	0.0159	-	-
	0.001	0.2153	0.0060	0.6226	62.26
	0.002	0.2030	0.0056	0.6478	64.78
	0.003	0.1940	0.0054	0.6604	66.04
	0.004	0.1517	0.0042	0.7358	73.58
	0.005	0.1019	0.0028	0.8239	82.39
313	Blank	0.7970	0.0221	-	-
	0.001	0.3958	0.0110	0.5023	50.23
	0.002	0.3224	0.0090	0.5928	59.28
	0.003	0.2958	0.0082	0.6290	62.90
	0.004	0.2646	0.0074	0.6652	66.52
	0.005	0.1888	0.0052	0.7647	76.47
323	Blank	0.9563	0.0265	-	-
	0.001	0.4313	0.0120	0.5472	54.72
	0.002	0.4460	0.0124	0.5321	53.21
	0.003	0.3377	0.0094	0.6453	64.53
	0.004	0.3224	0.0090	0.6604	66.04
	0.005	0.3193	0.0089	0.6642	66.42
DNT					
303	Blank	0.5736	0.0159	-	-
	0.001	0.3092	0.0086	0.4591	45.91
	0.002	0.2673	0.0074	0.5346	53.46
	0.003	0.1888	0.0052	0.6730	67.30
	0.004	0.1278	0.0035	0.7799	77.99

	0.005	0.1139	0.0032	0.8010	80.10
313	Blank	0.7970	0.0221	-	-
	0.001	0.1507	0.0042	0.8099	80.99
	0.002	0.1055	0.0029	0.8688	86.88
	0.003	0.0865	0.0024	0.8914	89.14
	0.004	0.0675	0.0019	0.9140	91.40
	0.005	0.0411	0.0011	0.9502	95.02
323	Blank	0.9563	0.0265	-	-
	0.001	0.3905	0.0108	0.5607	56.07
	0.002	0.3163	0.0088	0.6684	66.84
	0.003	0.2987	0.0083	0.6869	68.69
	0.004	0.2050	0.0057	0.7849	78.49
	0.005	0.1123	0.0031	0.8825	88.25

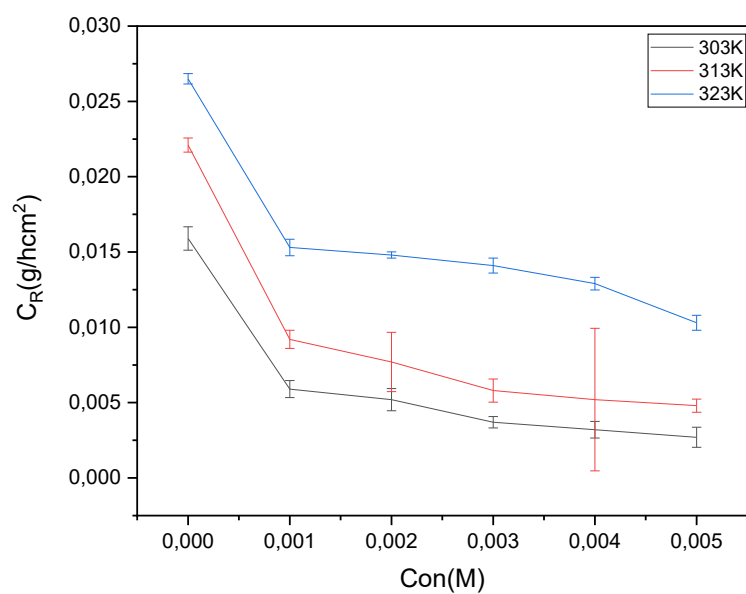


Figure 5. 1: Corrosion rate variation as a function of different DMT inhibitor concentrations for Al metal sample at 303 to 323 K.

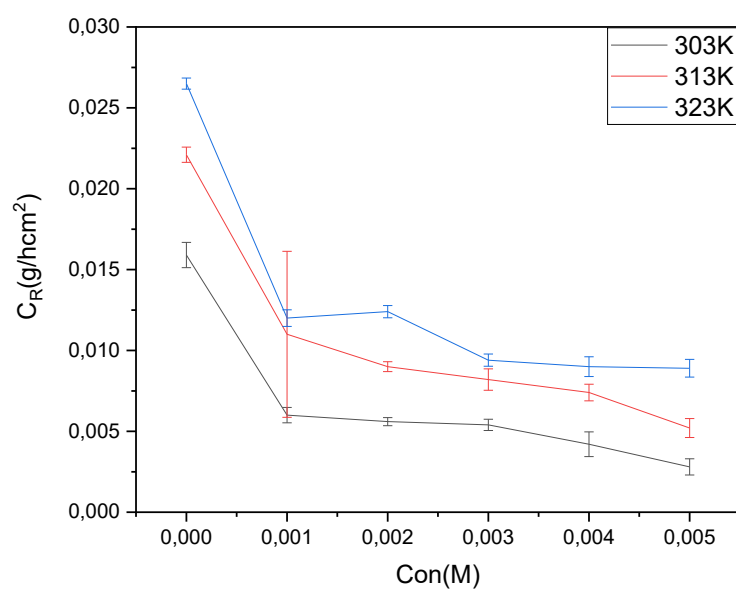


Figure 5. 2: Corrosion rate variation as a function of different DPT inhibitor concentrations for Al metal sample at 303 to 323 K.

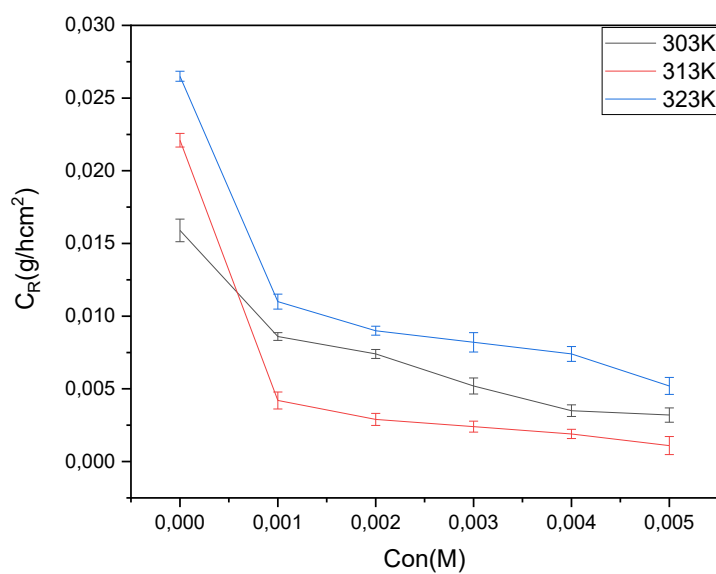


Figure 5. 3: Corrosion rate variation as a function of different DNT inhibitor concentrations for Al metal sample at 303 to 323 K.

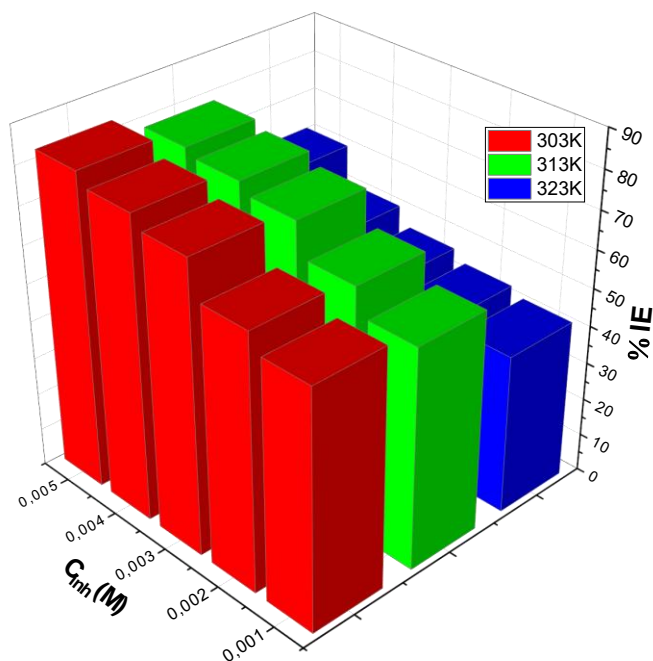


Figure 5. 4: The inhibition efficiency- DMT inhibitor concentration at different temperatures (303K, 313K, and 323K).

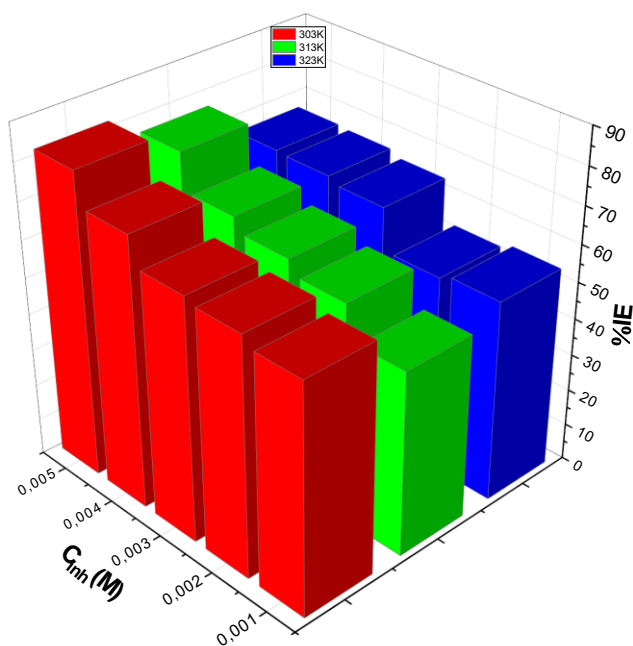


Figure 5. 5: The inhibition efficiency-DPT inhibitor concentration at different temperatures (303K, 313K, and 323K).

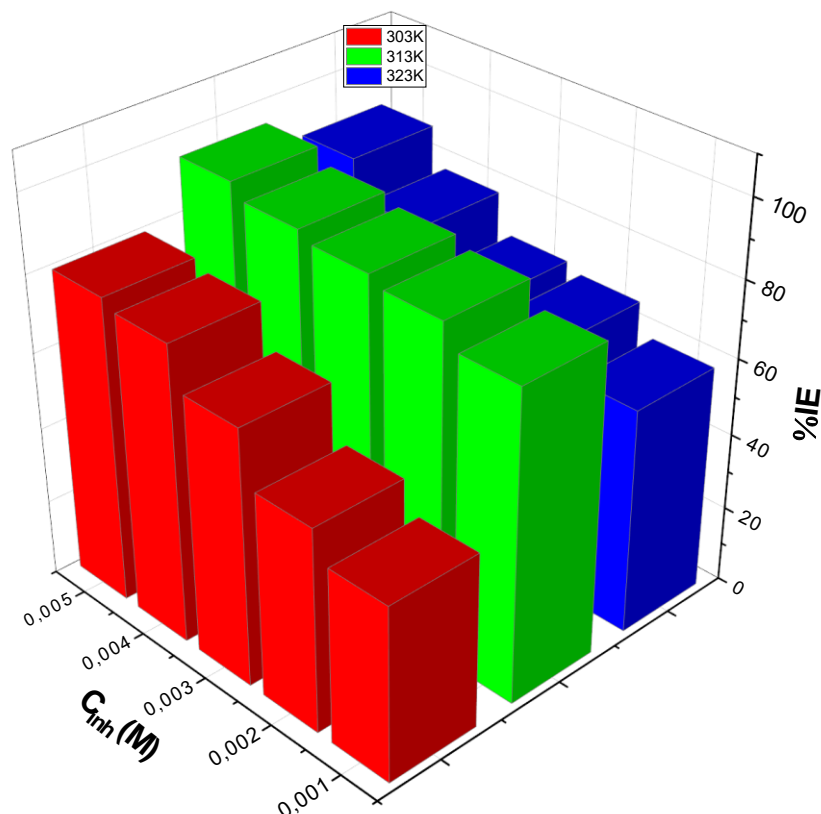


Figure 5. 6: The inhibition efficiency-DNT inhibitor concentration at different temperatures (303K, 313K, and 323K).

5.1.2. Effect of temperature on aluminium metal in uninhibited 1M HCl solution and inhibited solution.

The effect of temperature on the corrosion of Al depends on the type of corrosive environment, and the specific corrosion inhibitor used. The rate at which the uninhibited (Blank) solution corrodes simultaneously increases with temperature. The higher temperature causes aggressive species to diffuse more quickly to and from the metal surface, increasing thermal energy and giving the aggressive species more mobility and a higher chance of colliding and destroying the activation energy, which speeds up corrosion reactions[256, 284-286]. Table 5.1 indicates an increase in corrosion rate for the blank with a temperature from 0.0159g/cm²h at 303K to 0.0221g/cm²h at 313K and 0.0265g/cm²h at 323K which was the highest temperature in this study. When using inhibitors, higher temperatures can either improve or decrease their effectiveness. When it comes to DMT and DPT inhibitors, the corrosion rate of aluminum metal drops when compared to the blank and increases with temperature. This could be because increasing temperatures cause the molecules in the inhibitors to break down, making it harder

for them to form a protective layer on the metal surface, which is why the corrosion rate of DMT and DPT increases with temperature. The corrosion rate at the highest (0.005M) DMT and DPT inhibitor concentration at 303K was 0.0059g/mol.cm², 0.0028g/mol.cm² increased to 0.0048g/cm²h, 0.0052g/cm²h and 0.0103g/cm²h, 0.0089g/cm²h when the temperature increases to 313K and 323K respectively. When DNT is used as an inhibit, a higher temperature increases its effectiveness; however, the corrosion rate does not exhibit slight behavior; rather, it decreases from 0.0032g/cm²h to 0.0011g/cm²h as the temperature rises from 303K to 313K and then increases to 0.0031g/cm²h as the temperature rises to 323K. This implies that the corrosive solution's viscosity and ionic conductivity are impacted by temperature variations. These changes may impact the transport of reactants to the Al metal surface, influencing the corrosion rate[287, 288]. The effect of inhibitor concentration can also be temperature-dependent. In the presence of DMT and DPT, the inhibition efficiency decreases with the increase in temperature. However, the inhibition efficiency for DNT increases when the temperature increases. For example, at the highest concentration (0.005M), the inhibition efficiency increases from 80.10% at 303K to 95.02% at 313K and decreases when the temperature rises to 323K at 88.25%. Still, the inhibition efficiency for 323K was higher than at 303K, indicating that the DNT becomes more soluble and more effective at 313K and 323K than at lower temperatures (303K). In some cases, higher temperatures may require higher concentrations of inhibitors to maintain effective corrosion protection; this was observed in the presence of DMT and DPT at 323K; the inhibitor started to be more effective at 0.005M and 0.003M, respectively.

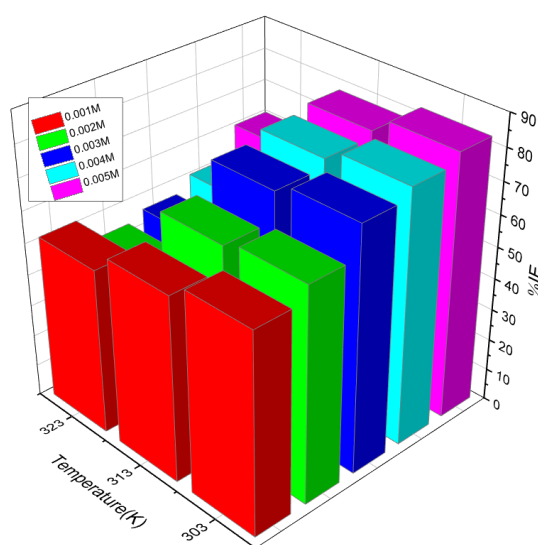


Figure 5. 7: The inhibition efficiency-temperature of the inhibitor at different DMT inhibitor concentrations.

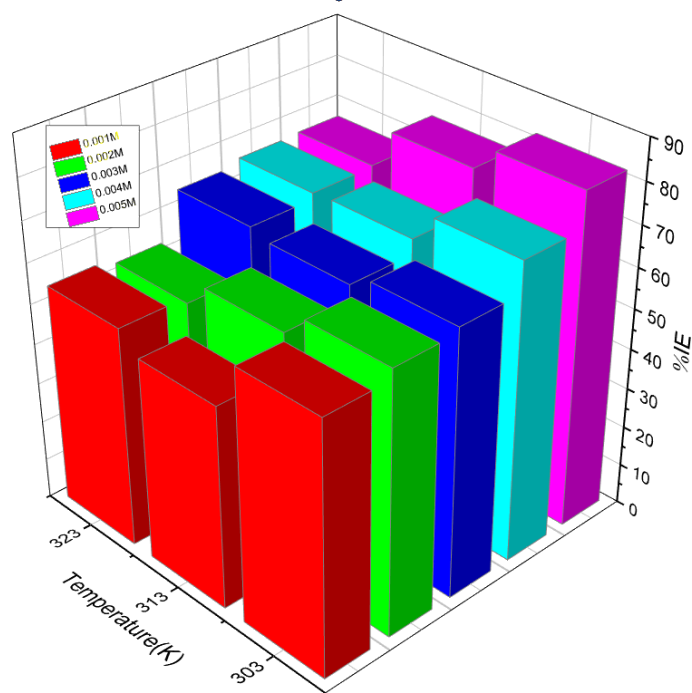


Figure 5. 8: The inhibition efficiency-temperature of the inhibitor at different DPT inhibitor concentrations.

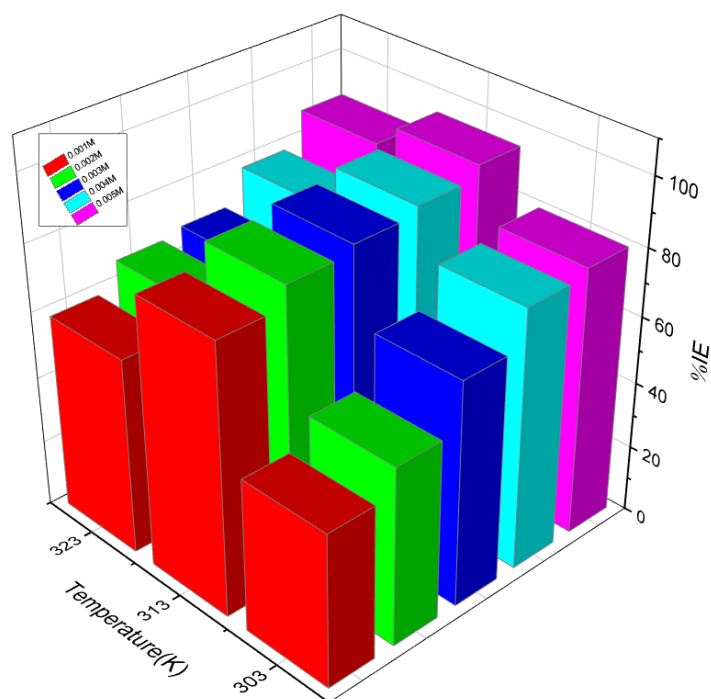


Figure 5. 9: The inhibition efficiency-temperature of the inhibitor at different DNT inhibitor concentrations.

5.1.3. Activation parameters on the inhibition process

The Arrhenius equation is the fundamental chemical kinetics equation that relates the reaction's rate constant to the activation energy, temperature, gas constant, and pre-exponential factor[289, 290]. Equation 5.1 is the general equation of the Arrhenius equation. The activation energy (E_a) for a metal in the presence of inhibitors can be calculated using the Arrhenius equation 5.2.

$$k = Ae^{-\frac{E_a}{RT}} \quad (5.1)$$

$$\log C_R = \log A - \frac{E_a}{2.303RT} \quad (5.2)$$

Where k is the rate constant, A is the pre-exponential rate constant, R gas constant (8.314J/Kmol), T temperature in kelvin, and C_R is the corrosion rate[291-293].

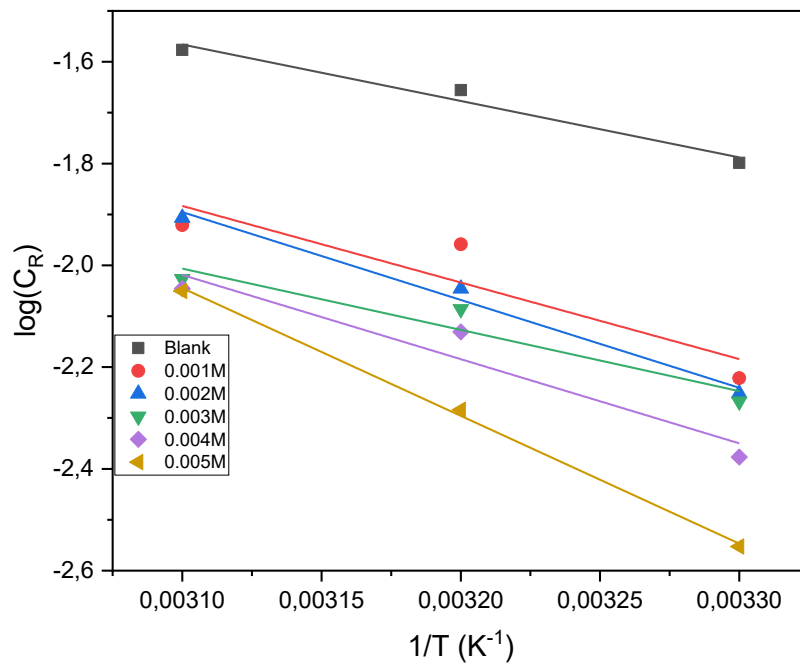


Figure 5. 10: Arrhenius plot at a different concentration for DMT inhibitor

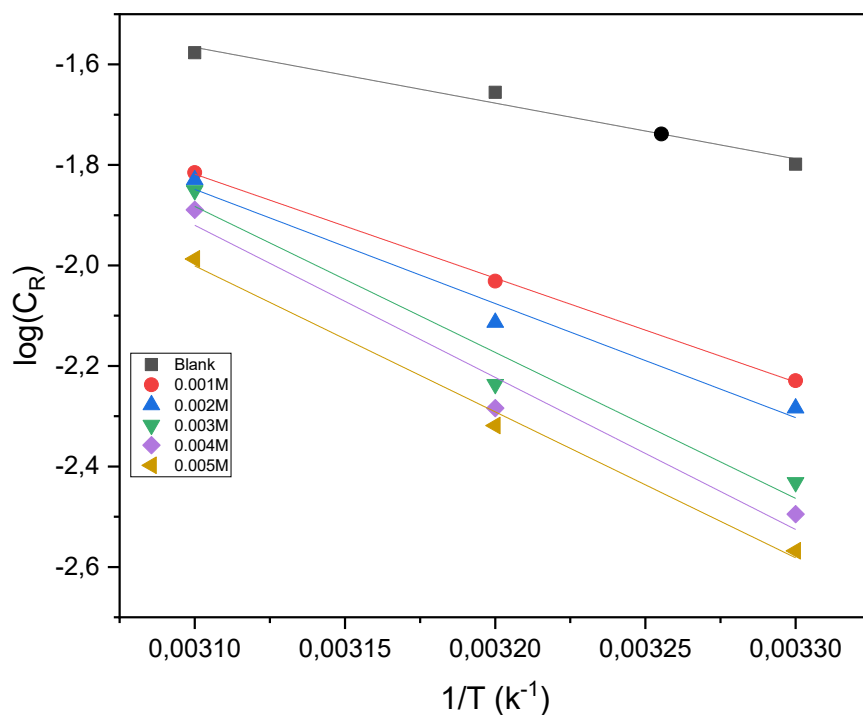


Figure 5. 11: Arrhenius plot at a different concentration for DPT inhibitor.

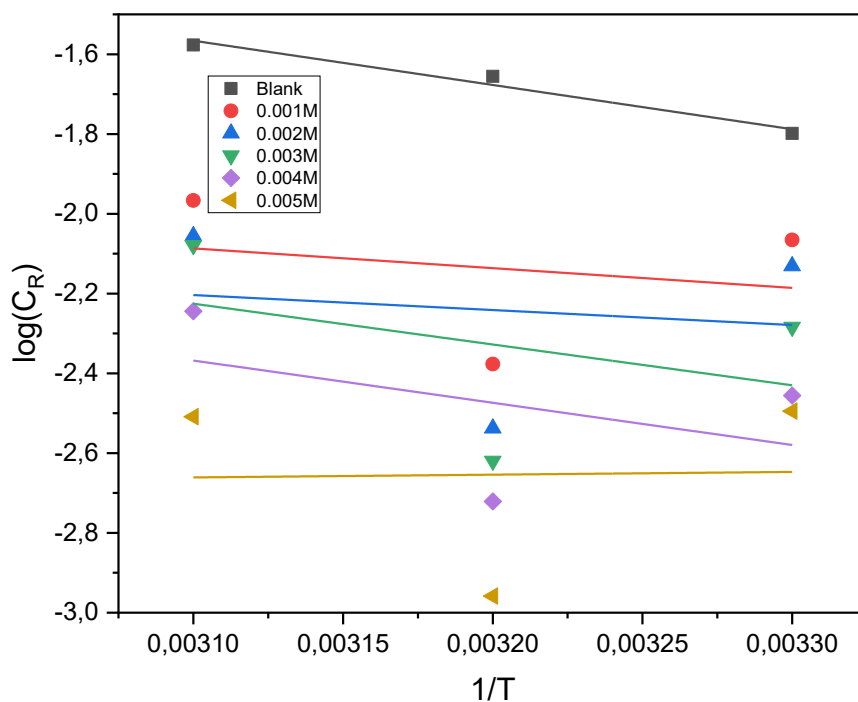


Figure 5. 12: Arrhenius plot at a different concentration for DNT inhibitor.

A plot of the log of corrosion rate obtained by weight loss measurement versus $1/T$ gave a straight line with a regression coefficient close to unity for DMT and DPT, as shown in Figures

5.10-5.11. However, DNT did not provide a regression coefficient closer to unity because the effect of temperature is unstable in Figure 5.12. The values of apparent activation energy obtained from the slope ($\frac{-E_a}{2.303R}$) of the lines and the pre-exponential factor (A) obtained from the intercept (log A) [294] are given in Table 5.2.

The presence of a corrosion inhibitor can lead to the formation of either a more stable chemisorbed layer or a more stable physisorbed layer on the metal surface, depending on the nature of the inhibitor and its interactions with the metal. According to previous studies, the activation energy for the physisorption process tends to be higher when the inhibitor is present than when it is not, attributed to forming an inhibitor–metal complex in the solution. Contrarily, in cases where chemisorption occurs, the activation energy is lower in the presence of the inhibitor than in its absence. Strong chemical bonds between the inhibitor and the metal surface are created during chemisorption. These bonds lower the activation energy, facilitating metal dissolution even in the presence of the inhibitor [295-298]. The results in Table 5.2 show that in the inhibitor DMT and DPT, physisorption occurs because the activation energy increases from blank. The DNT inhibitor activation energy is lower than blank, which is attributed to chemisorption. The value of activation energy on both inhibitors in Table 5.2 also agrees with what Bentiss *et al.* and Hegazy *et al.* stated: when the inhibition efficiency decreases with an increase in temperature, the activation energy will be higher than the blank, and when the %IE increases with temperature the E_a of inhibited solution will be lower than the blank [299, 300].

From equation (5.2), it is clear that both activation energy and pre-exponential influence the corrosion rate. Generally, a lower pre-exponential value and a higher value of activation energy lead to a lower corrosion rate [295]. It is evident from the value of activation energy and pre-exponential in Table 5.2 that the activation energy influenced the corrosion rate on aluminum corrosion when DMT and DPT were used as inhibitors due to the pre-exponential factor having a higher value than the blank. The lower pre-exponential factor observed when using DNT as a corrosion inhibitor indicates that DNT reduces the effective collision frequency between the corrosive agents and the Al surface. This reduction in collision frequency means fewer reactant molecules can successfully interact and react, thus lowering the overall corrosion rate. This finding suggests that DNT is an effective corrosion inhibitor by creating a barrier that impedes the necessary interactions for the corrosion process, highlighting its role in influencing the corrosion rate significantly [301-304]. For a better understanding of the energy change and structural rearrangement that take place during a reaction's transition state, entropy (ΔS_a) and

enthalpy (ΔH_a) of the activation energy was also calculated using the transition state equation 5.3.

$$\log\left(\frac{C_R}{T}\right) = \left[\log\left(\frac{R}{Nh}\right) + \frac{\Delta S_a}{2.303R}\right] - \frac{\Delta H_a}{2.303R} \quad (5.3)$$

Where h is plank constant ($6.626176 \times 10^{-34} \text{ Js}$) and N is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$).

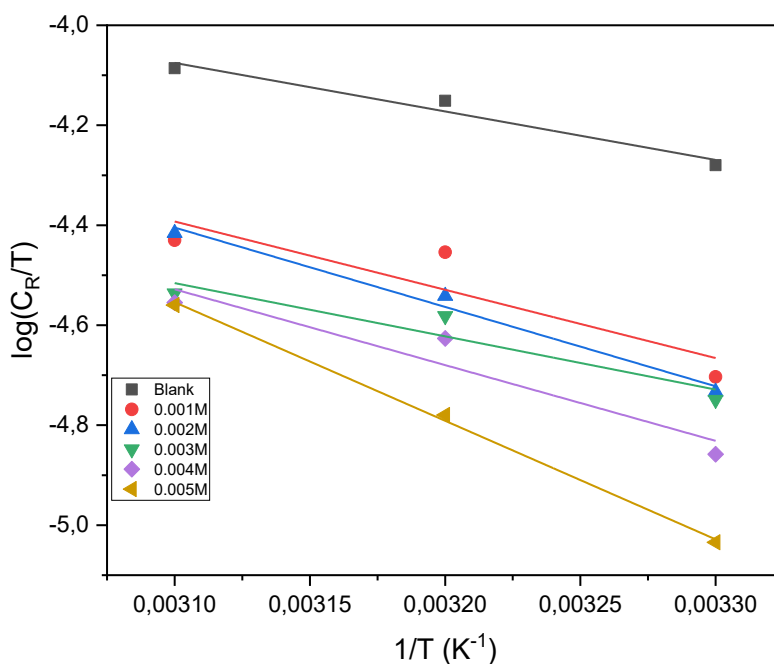


Figure 5. 13: Transition plot at different DMT inhibitor concentrations

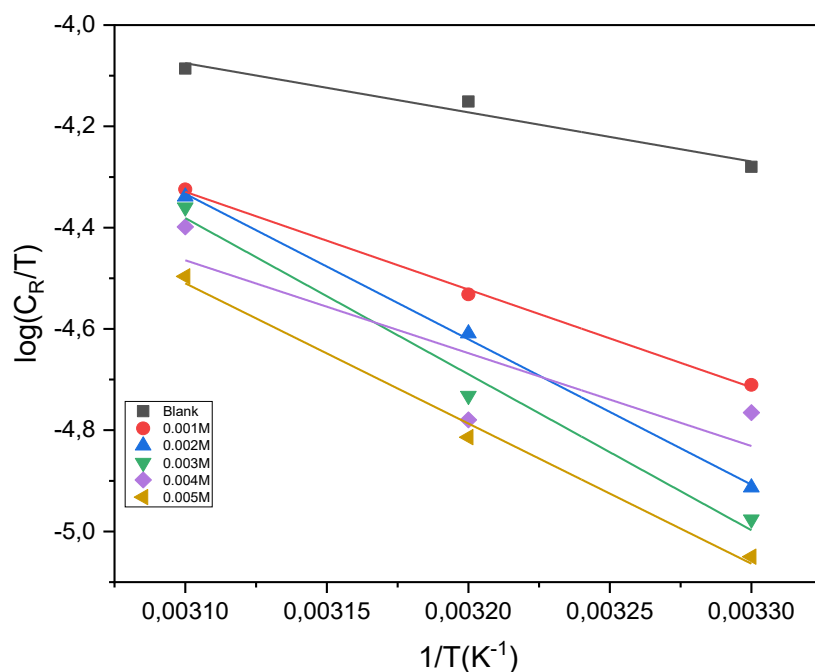


Figure 5. 14: Transition plot at different DPT inhibitor concentrations

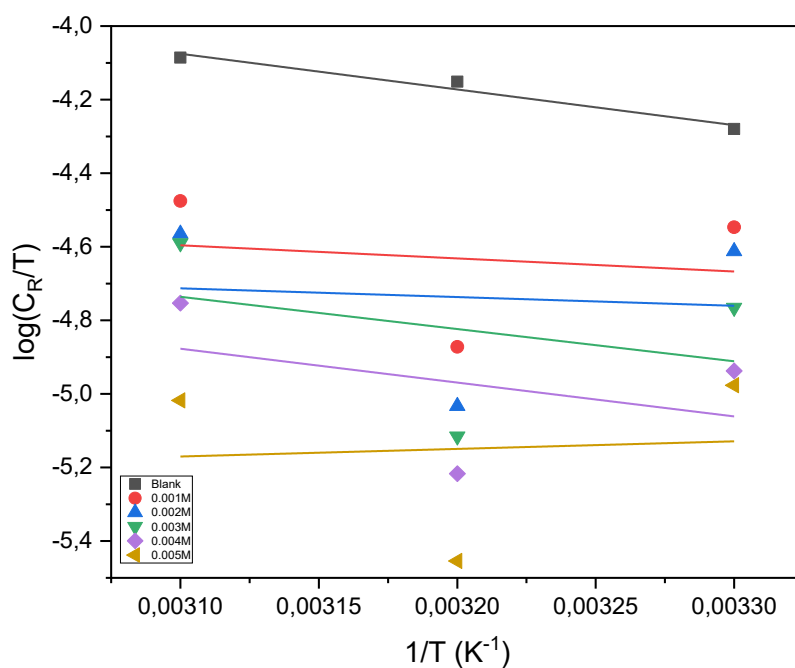


Figure 5. 15: Transition plot at different DNT inhibitor concentrations

The values of ΔH_a and ΔS_a are deduced by plotting a linear fit of $\log (C_R/T)$ against $1/T$ in Figure 5.13-5.15 with a slope of $\frac{-\Delta H_a}{2.303R}$ and intercepts of $\log \left(\frac{R}{Nh} \right) + \frac{\Delta S_a}{2.303R}$ [296, 305] and tabulated in Table 5.2. The enthalpy of activation (ΔH_a) values shows a similar trend to that observed in E_a and are positive in both cases when the inhibitor is present. The negative sign

of (ΔH_a) has been conclusively linked in the literature to an exothermic process, which may involve chemisorption, physisorption, or a combination of the two. Nevertheless, the endothermic process, which is attributed to physisorption, is linked to the positive sign[125, 277, 306, 307]. The current study shows a positive sign for the ΔH_a for all the inhibitors, indicating that the dissolution of aluminium is an endothermic process. Although the ΔH_a values for DNT are also positive, they decrease compared to blank, indicating that the Al is exothermically dissolved. The inhibited and uninhibited acid solutions had a large and negative activation value entropy (ΔS_a), implying decreased disorder, going from reactant to the activated complex. For inhibitor DMT and DPT, the ΔS_a has less negative than uninhibited, suggesting that the inhibitor stabilizes the transition state, making it more difficult for the corrosion reaction to proceed. On the other hand, the ΔS_a of DNT is more negative than blank(uninhibited), which suggests that the corrosion process involves a higher degree of disorder in the presence of the inhibitor; this may indicate that the inhibitor is disrupting the corrosion process by increasing disorder at the metal surface[140, 165, 308-312].

Table 5. 2: Activation parameters for DMT, DPT, and DNT on aluminium in 1M HCl.

Concentration (M)	E_a (kJ/mol)	A	ΔH (kJ /mol)	$-\Delta S$ (J/mol.K)
Blank	21.2342	74.44	18.57	218.02
DMT				
0.001	39.62	3.93×10^4	36.96	165.88
0.002	43.79	1.56×10^5	40.83	154.43
0.003	55.60	1.32×10^5	52.97	117.45
0.004	57.97	2.92×10^7	55.31	110.93
0.005	55.66	1.03×10^7	53.01	108.11
DPT				
0.001	28.82	6.06×10^2	26.16	200.56
0.002	33.05	2.85×10^3	30.40	187.68
0.003	23.04	5.30×10^1	20.38	174.29
0.004	31.69	3.93×10^4	29.03	194.29
0.005	48.08	1.29×10^3	45.43	143.94
DNT				
0.001	9.47	2.74×10^{-1}	6.82	264.44
0.002	7.21	9.19×10^{-2}	4.547	273.71
0.003	19.44	1.20×10^{-1}	16.78	236.22
0.004	20.28	1.22×10^{-1}	17.61	236.34
0.005	1.33	1.33×10^{-3}	3.98	308.91

5.1.4. Adsorption isotherm

Adsorption isotherm is used to understand the relationship between the concentration of a corrosion inhibitor in a solution and its adsorption onto the metal surface. The adsorption isotherm provides insights into the mechanism and behavior of the inhibitor at the metal-

solution interface. Several adsorption isotherms are commonly used in corrosion studies, including Langmuir, Freundlich, and Temkin isotherms[293, 313-317]. In this investigation, the interactions between the examined inhibitor and the metal surface during the corrosion inhibition process were ascertained by fitting the surface coverage (θ) from experimental data as a concentration (C) function to derive the Langmuir and Temkin adsorption isotherms.

Based on Figures 5.16-5.18 and Table 5.3, the Langmuir isotherm equation is the best-fit equation with the regression coefficient (R^2) values closer to unity. According to equation 5.4, Langmuir isotherm assumes that the adsorption process forms a monolayer (single layer) of adsorbate on the surface of the adsorbent, with no further adsorption occurring on the occupied sites.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5.4)$$

where K_{ads} is the equilibrium adsorption constant, which represents the strength between adsorbate and adsorbent[318], and Figure 5.14-5.16 represents C/θ against C , where the intercept is $\frac{1}{K_{ads}}$ [319].

Furthermore, the standard adsorption Gibbs free energy (ΔG_{ads}) can be assessed using equation 5.5.

$$\Delta G_{ads} = -2.303RT \log(55.5K_{ads}) \quad (5.5)$$

where, ΔG_{ads} is Gibbs free energy of adsorption, T is the temperature in Kelvin, K_{ads} is the equilibrium constant for the adsorption process, and 55.5 is the molar concentration of water in solution[313, 320]. Assuming the thermodynamic model, corrosion inhibition of aluminium in the presence of DMT, DPT, and DNT can explained better using enthalpy (ΔH_{ads}) which can be calculated from van't Hoff equation 5.6 and entropy (ΔS_{ads}) of adsorption using equation 5.7 [295, 321].

$$\log K_{ads} = \frac{-\Delta H_{ads}}{2.303RT} + C \quad (5.6)$$

$$\Delta S_{ads} = \frac{\Delta H_{ads} - \Delta G_{ads}}{T} \quad (5.7)$$

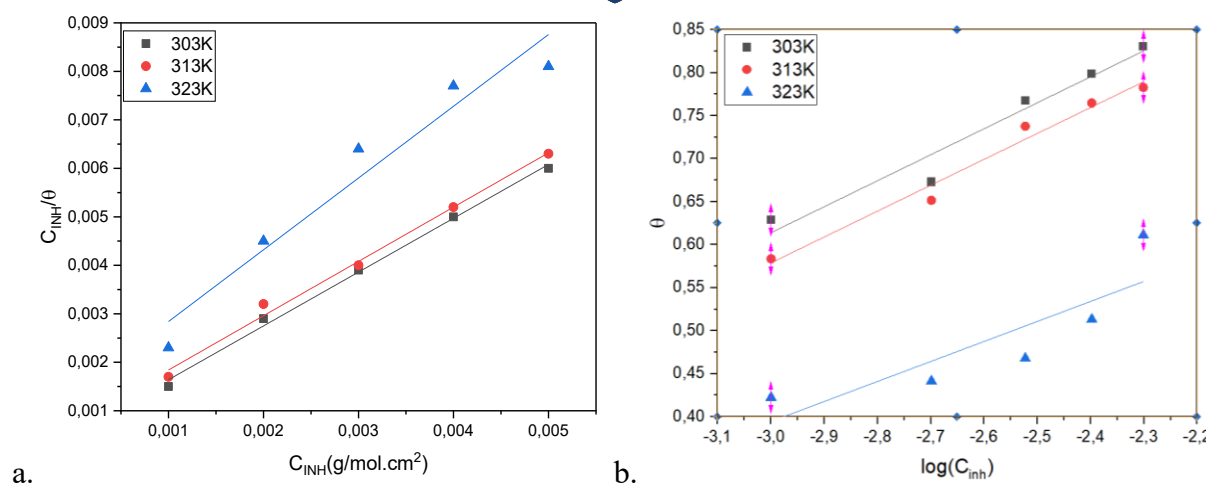


Figure 5. 16: a. Langmuir and b. Temkin adsorption isotherm plot at different temperatures for various DMT inhibitor concentrations

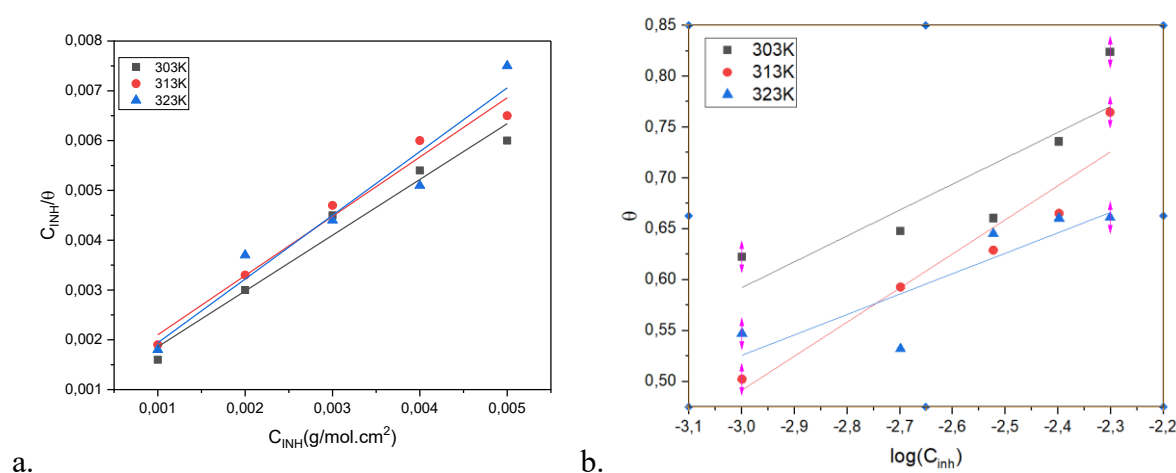


Figure 5. 17: a. Langmuir and Temkin adsorption isotherm plot at different temperatures for various DPT inhibitor concentrations

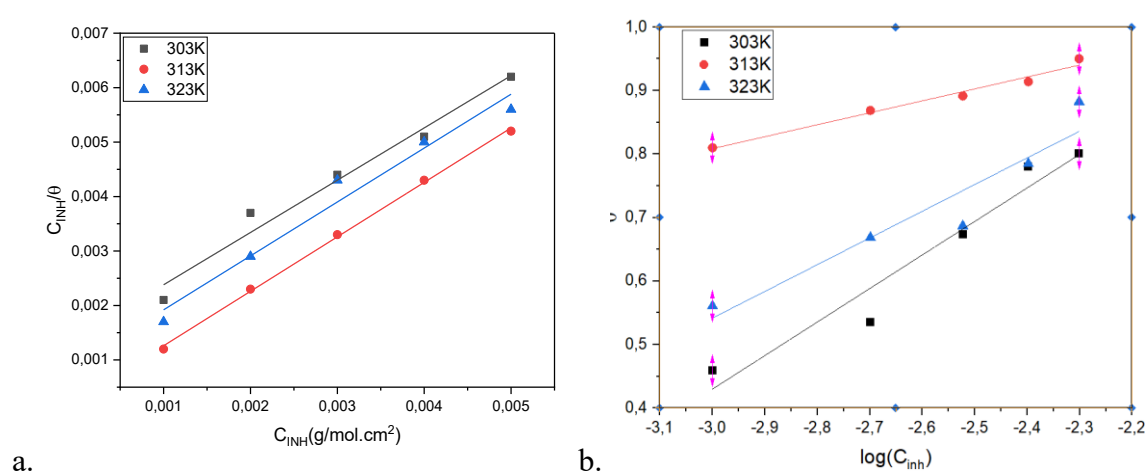


Figure 5. 18: a. Langmuir and Temkin adsorption isotherm plot at different temperatures for various DNT inhibitor concentrations

Table 5. 3: The correlation coefficients (R^2) of DMT, DPT, and DNT for Langmuir and Temkin adsorption isotherm at different temperatures.

Adsorption isotherm types	Temperature (K)	R^2
DMT		
Langmuir	303	0.9958
	313	0.9933
	323	0.9441
Temkin	303	0.9533
	313	0.9775
	323	0.7292
DPT		
Langmuir	303	0.9709
	313	0.9774
	323	0.9470
Temkin	303	0.7328
	313	0.9212
	323	0.7526
DNT		
Langmuir	303	0.9742
	313	0.9988
	323	0.9704
Temkin	303	0.9454
	313	0.9794
	323	0.8615

It is evident from Table 5.4 that the value of K_{ads} for DMT is favourable at lower temperatures (303K), which is 1886.79 L/mol; for DPT and DNT, the K_{ads} were high at 323 K and 313K with a value of 1515.15 L/mol and 3846.15 L/mol respectively, which implies that there is more efficient adsorption and better inhibition efficiency at that temperature. The values of ΔG°_{ads} are negative, indicating that the reaction process is spontaneous. From the literature, the value of ΔG°_{ads} that are closer or lower than -20kJ/mol are considered physisorption, this type of adsorption involves the attractive forces between the adsorbate and adsorbent are rather slight, mostly resulting from van der Waals interactions or dipole-dipole interactions. This adsorption phenomenon arises from the creation of many layers of adsorbate on the adsorbent surface. While the values that are closer to or higher than -40kJ/mol involve the chemisorption process. In chemical adsorption, the interaction between the adsorbate and adsorbent is governed by chemical forces of attraction, which might manifest as chemical bonds. In this form of adsorption, there is a greater affinity between the molecules that are adsorbed and the surface of the adsorbent[149, 322-328].

The result from Table 5.4 indicates that the range of ΔG°_{ads} falls between -20kJ/mol and -40kJ/mol meaning that the inhibitor molecules adsorb onto the Al metal surface through weak force (Physisorption) and chemical bond (Chemisorption) forming a protective layer that helps to reduce the corrosion rate. The negative value of ΔH°_{ads} for the DMT inhibitor (-39.1846kJ/mol) signifies that the adsorption of the inhibitor onto the metal surface is an exothermic process, releasing energy and stabilizing the system. The positive values of DPT(4.7523kJ/mol) and DNT(17.5962kJ/mol) indicate an endothermic nature, suggesting that the adsorption process of the inhibitor molecule's on to metal surface spontaneity and effectiveness depend on the temperature and entropy change[329-335]. An increase in entropy ($\Delta S_{ads} > 0$) indicates an increase in disorder, while a decrease in entropy ($\Delta S_{ads} < 0$) indicates a decrease in disorder or an increase in orderliness[295, 321, 331]. DMT inhibitors have the value of ΔS , which is less than 0, suggesting that the corrosion inhibitor molecules are effectively adsorbed onto the metal surface in an organized manner. While DPT and DNT increased disorder, this implies that the inhibitor molecules are not arranging themselves in an ordered manner on the metal surface. To find out whether it is favourable or unfavorable the K_L is calculated and tabulated in Table 5.5. The results obtained in this study indicate that the reaction is favorable and fits the Langmuir adsorption isotherm, because it falls between 0 and 1.

Table 5. 4: Langmuir adsorption isotherm calculated parameters for DMT, DPT, and DNT on the Al surface at different temperatures.

Inhibitor	Temperature (K)	K_{ads} (L/mol)	$-\Delta G^{\circ}_{ads}$ (kJ/mol)	ΔH°_{ads} (kJ/mol)	ΔS°_{ads} (J/mol K)
DMT	303	1886.79	29.12	-39.1846	-33.2165
	313	1388.88	29.29		-31.6121
	323	735.29	28.52		-33.0173
DPT	303	1351.35	28.28	4.7523	109.017
	313	1098.90	28.67		106.7805
	323	1515.15	30.41		108.8616
DNT	303	704.22	26.64	17.5962	145.9940
	313	3846.15	31.93		158.2306
	323	1075.27	29.53		145.8904

Table 5. 5: The K_L values for DMT, DPT, and DNT at varying concentrations at 303 to 323 K for MS corrosion in 1 M HCl calculated from weight loss Langmuir isotherm parameters

Inhibitors	Concentration (M)	K_L		
		303K	313K	323K
DMT	0.001	0.9671	0.9755	0.9869
	0.002	0.9363	0.9523	0.9741
	0.003	0.9074	0.9301	0.9617
	0.004	0.8802	0.9090	0.9496
	0.005	0.8547	0.8887	0.9378
Mean		0.9091	0.9311	0.9620
DPT	0.001	0.9762	0.9805	0.9734
	0.002	0.9535	0.9619	0.9482
	0.003	0.9319	0.9439	0.9242
	0.004	0.9112	0.9266	0.9015
	0.005	0.8914	0.9099	0.8798
Mean		0.9328	0.9445	0.9254
DNT	0.9874	0.7093	0.9351	0.9809
	0.9752	0.5495	0.8782	0.9626
	0.9633	0.4485	0.8278	0.9450
	0.9516	0.3788	0.7829	0.9280
	0.9403	0.3279	0.7426	0.9116
Mean		0.9635	0.8333	0.9456

5.2. Open circuit potential (OCP) with immersion period

OCP is the working electrode's potential (WE) relative to a reference electrode when no external current is applied to the system. It represents the natural potential of the electrode in the given environment, reflecting the balance between anodic (metal dissolution) and cathodic (reduction) reactions[336-338]. Upon the introduction of the inhibitor, the OCP may initially shift negatively or positively. This initial shift is due to the immediate interaction of the inhibitor molecules with the electrode surface, affecting the local electrochemical environment[339-343]. Over time, as the inhibitor adsorbs onto the electrode surface, forming a protective film, the OCP stabilizes. The direction of this stabilization (positive or negative) depends on how the inhibitor affects the anodic and cathodic reactions[114, 122, 344, 345]. The electrodes were immersed in 1 M HCl with and without different concentrations of DMT, DPT, and DNT for 1 hour. Figures 5.19-5.21 the steady-state DMT and DNT potential was more negative than the uninhibited Al, indicating that the inhibitor primarily act on the cathodic reaction. The opposing shifts in both positive and negative directions of the curves in Figure 5.20, with respect to the unconstrained Al metal, suggest that DPT provides a comprehensive

protective mechanism by inhibiting both the metal dissolution and the reduction reactions[344-348]. This indicates that DPT functions as a mixed-type inhibitor for aluminum metal. The highest inhibitor concentrations (0.004M and 0.005M) used shifted the potential values furthest in the positive direction. The OCP curves are straight lines for both uninhibited and inhibited Al systems, indicating that the equilibrium potential has been reached in both cases

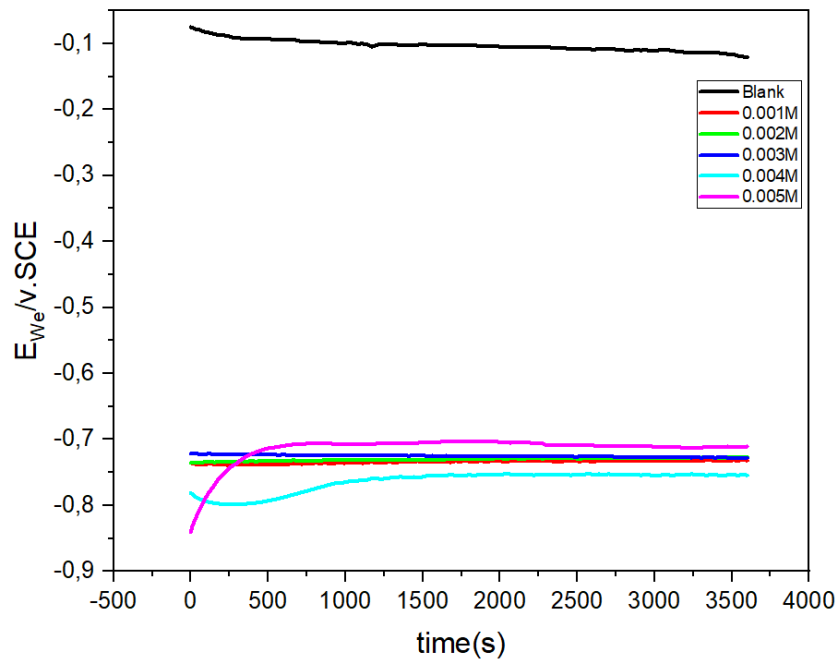


Figure 5. 19: Evolution of open-circuit potential (E_{OCP}) versus exposure time for Al with and without DMT in 1 M HCl solution.

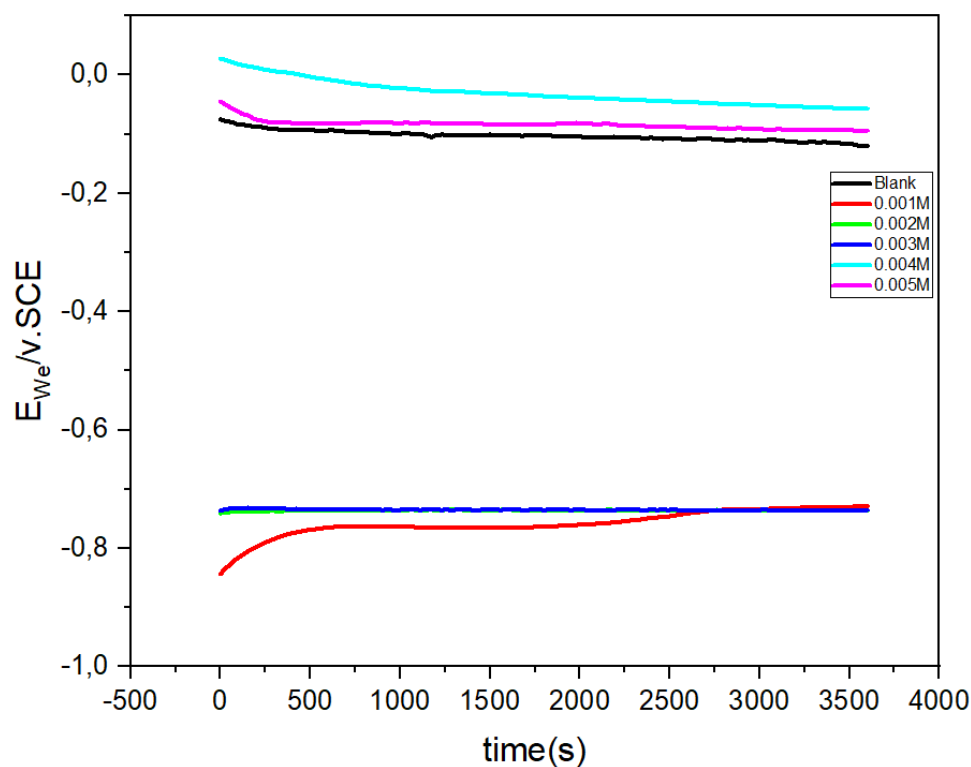


Figure 5. 20: Evolution of open-circuit potential (E_{OCP}) versus exposure time for Al with and without DPT in 1 M HCl solution.

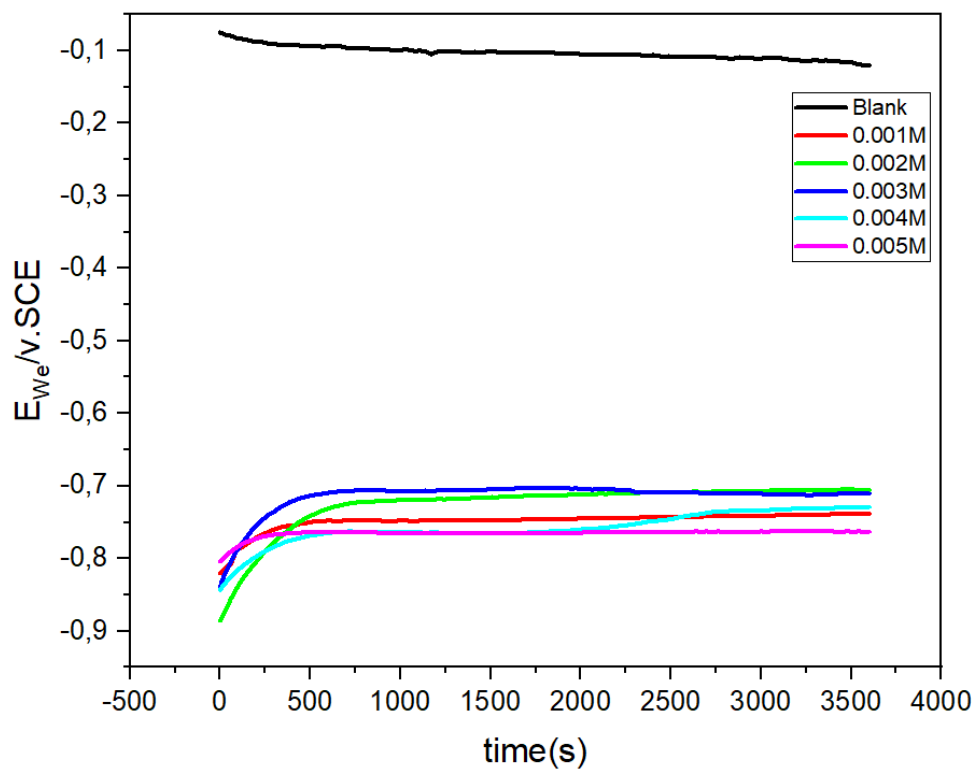


Figure 5. 21: Evolution of open-circuit potential (E_{OCP}) versus exposure time for Al with and without DNT in 1 M HCl solution.

5.3. Electrochemical impedance spectroscopy (EIS)

The Nyquist plot for aluminium in the absence (Blank) and the presence of various concentrations of DMT, DPT, and DNT are shown in Figures 5.22-5.24. The EIS fitting data for Al in 1M HCl in the absence and presence of diverse inhibitor concentrations at 303K are listed in Table 5.5. Figures 5.22-5.24 show that the inhibitor did not change how the Al corrosion proceeds because all Nyquist plots have the same curve in the blank and inhibited solutions. The impedance spectra consist of capacitive loops at a higher frequency and inductive loops at a lower frequency. The capacitive loops represent the charge transfer resistance of the corrosion process and double layer. The inductive loops are attributed to the relaxation process in the oxide film covered on the metal surface[349, 350]. When the concentration of DPT and DMT inhibitors was raised, the Nyquist plot shifted; from the literature, this behavior is attributed to forming the binding film layer on the metal surface[351, 352].

Furthermore, the diameter of the semi-circle (capacitive loop) increases with the increase in inhibitor concentration, indicating that more molecules can provide higher coverage of the Al surface. The phase angle in Figures 5.26-5.28 observing two maxima in the phase angle versus frequency plot suggests the presence of two distinct time constants or processes. The introduction of DMT, DPT, DNT inhibitor increases the size Phase angle $|\theta|$. The maximum $|\theta|$ values of DMT, DPT, DNT is around -60° , -60° , -50° . Higher slope values in the medium-frequency region of the Bode modulus plot in the presence of an inhibitor indicate that the inhibitor is effectively enhancing the protective properties of the aluminum surface. This is achieved by increasing the capacitive behavior, forming a more uniform and robust protective layer, and reducing the diffusion of corrosive species[353-355]. Figure 5.25 shows the electrical circuit structure used to fit the impedance spectra; the electrical circuit has the electrolyte resistance (R_s) represented by R_1 , constant phase (CPE) represented by Q_1 , inductive elements represented by R_3 and L_3 [356, 357]. The inhibition efficiency(%IE_{EIS}) and polarisation resistance at different inhibitor concentrations were calculated using equations 3.4 and 3.6.

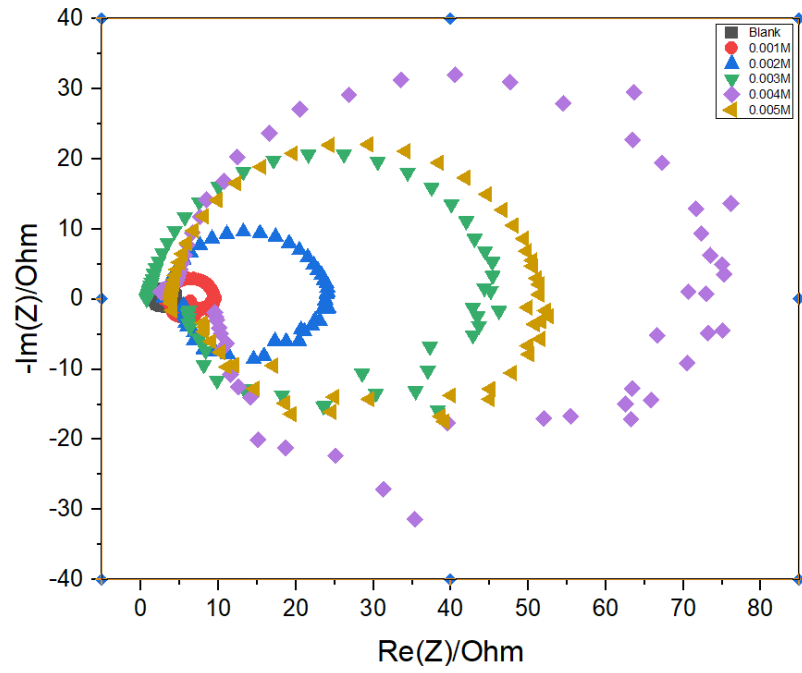


Figure 5. 22: Nyquist plot for DMT

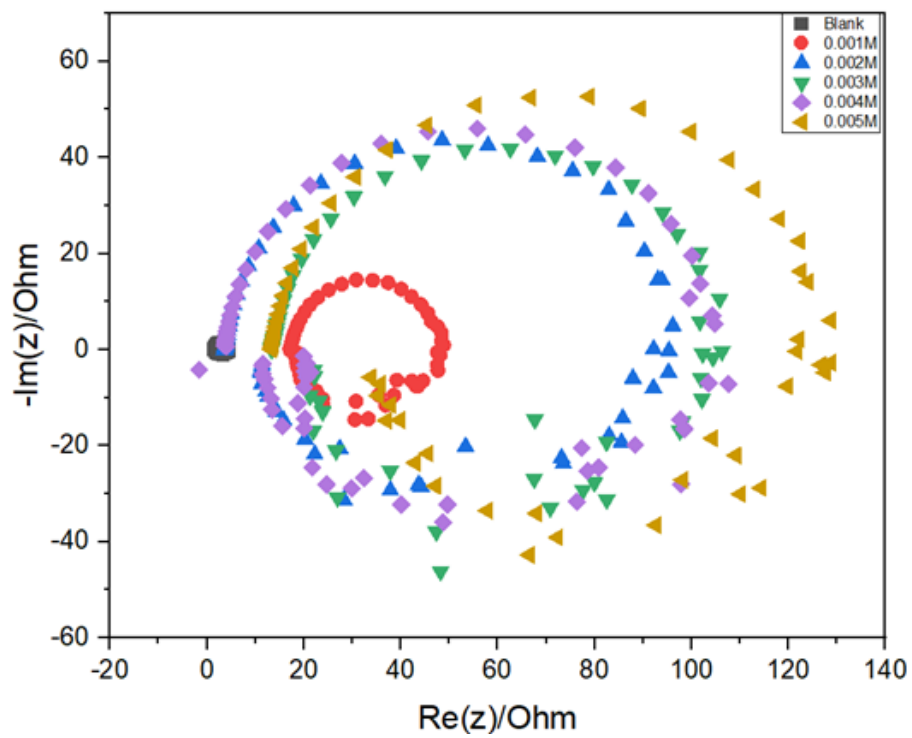


Figure 5. 23: Nyquist plot for DPT

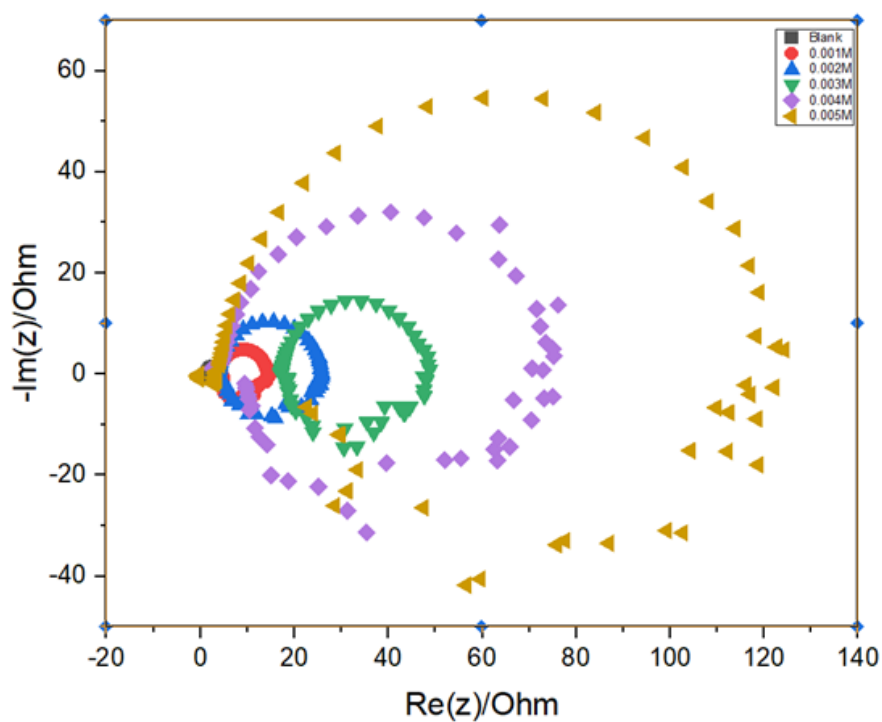


Figure 5. 24: Nyquist plot for DNT.

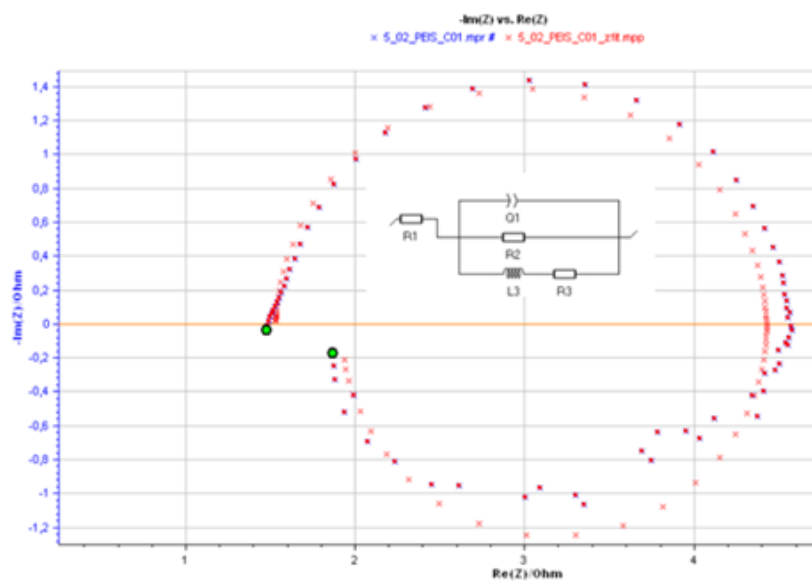
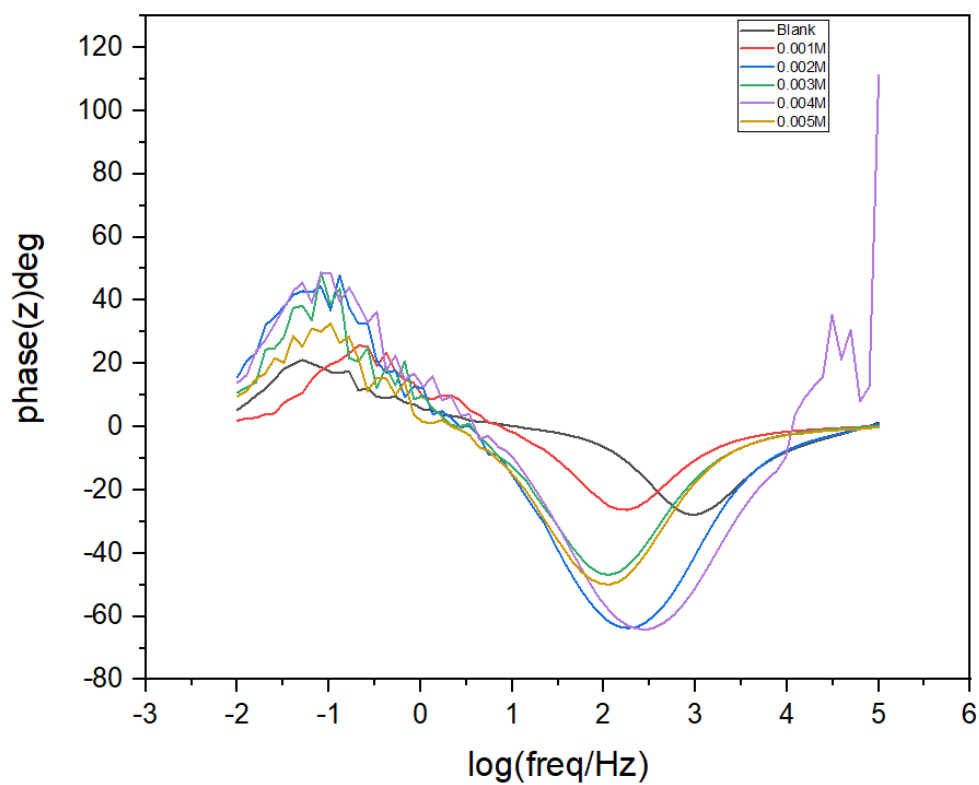
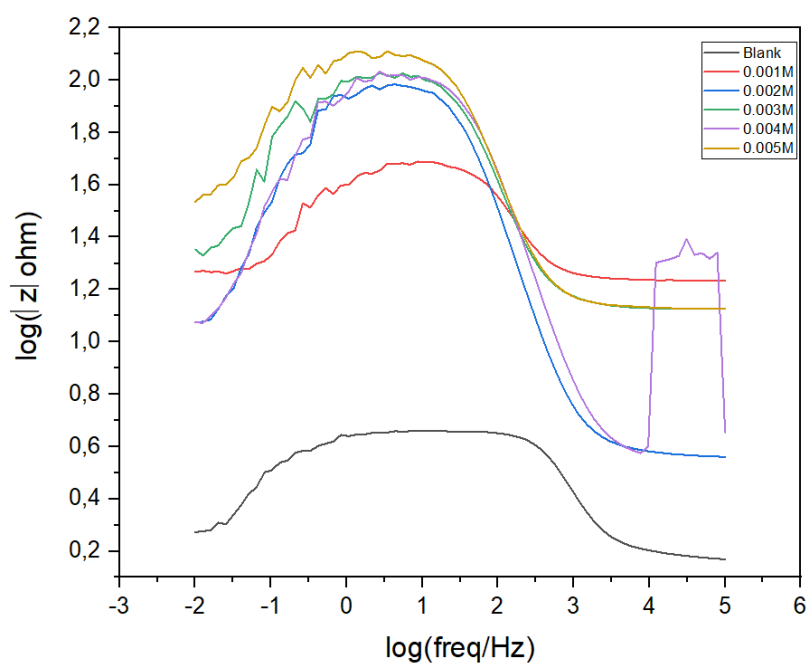


Figure 5. 25: Nyquist plot for a blank and electrical circuit structure used to fit all inhibitor concentrations.

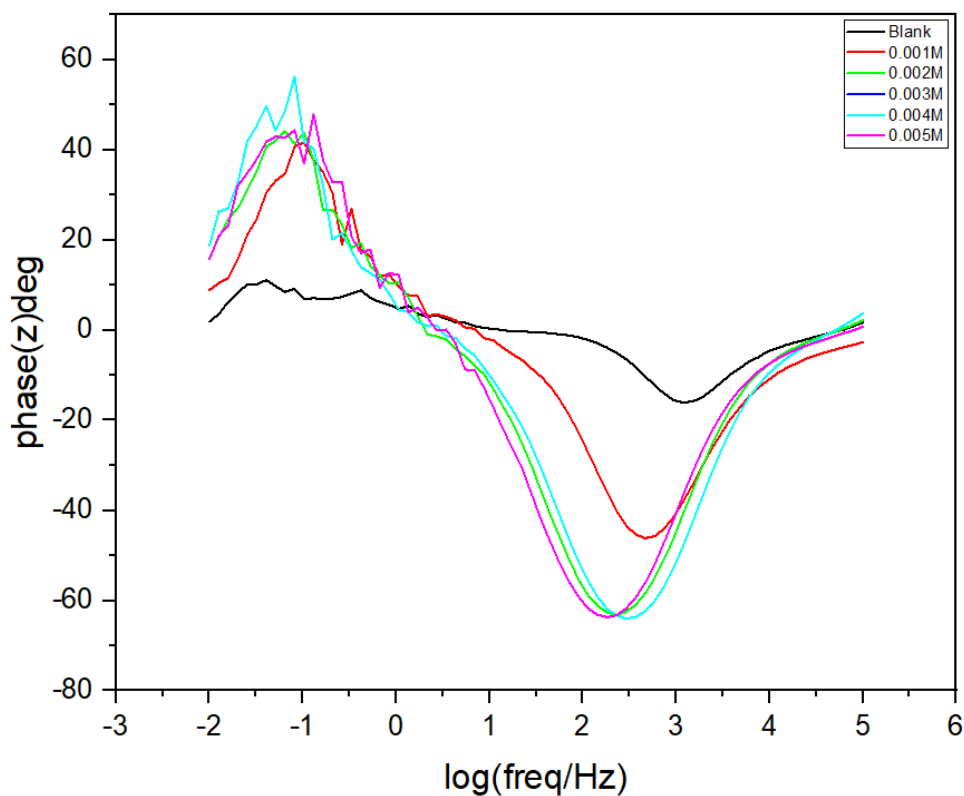


a.

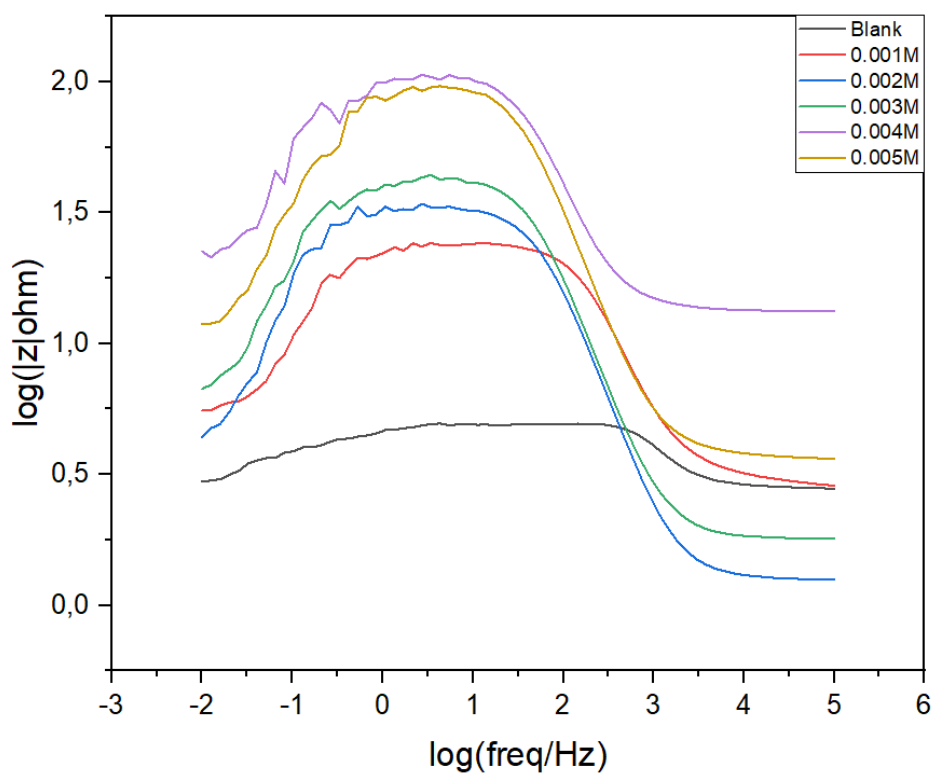


b.

Figure 5. 26: a. phase angle b. Bode modulus plot in 1 M HCl solution with and without DMT at various concentrations at 303 K

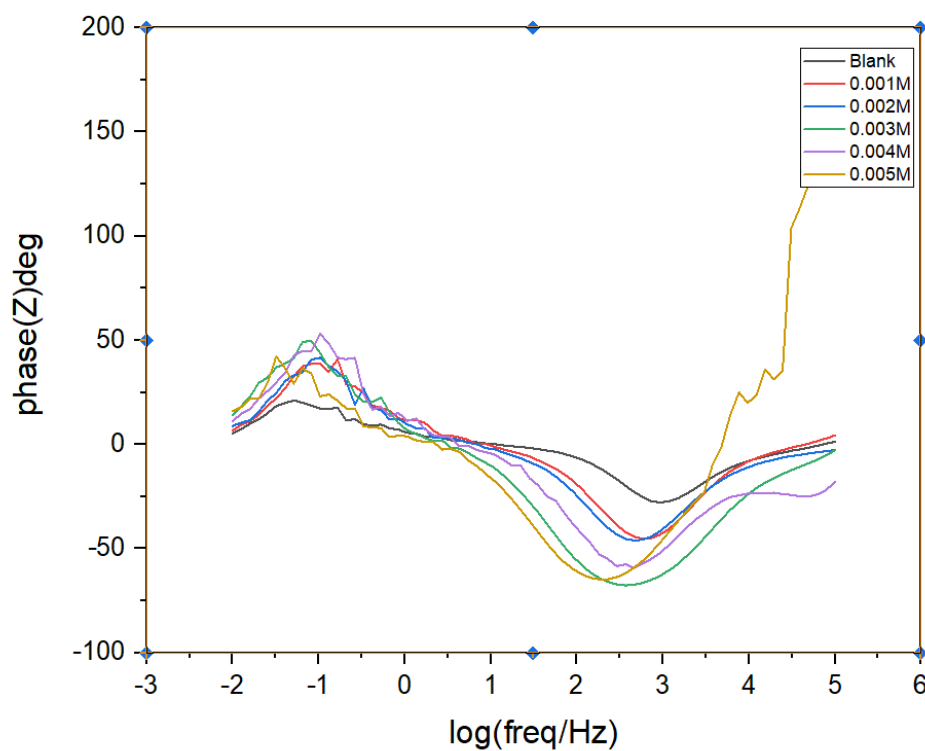


a.

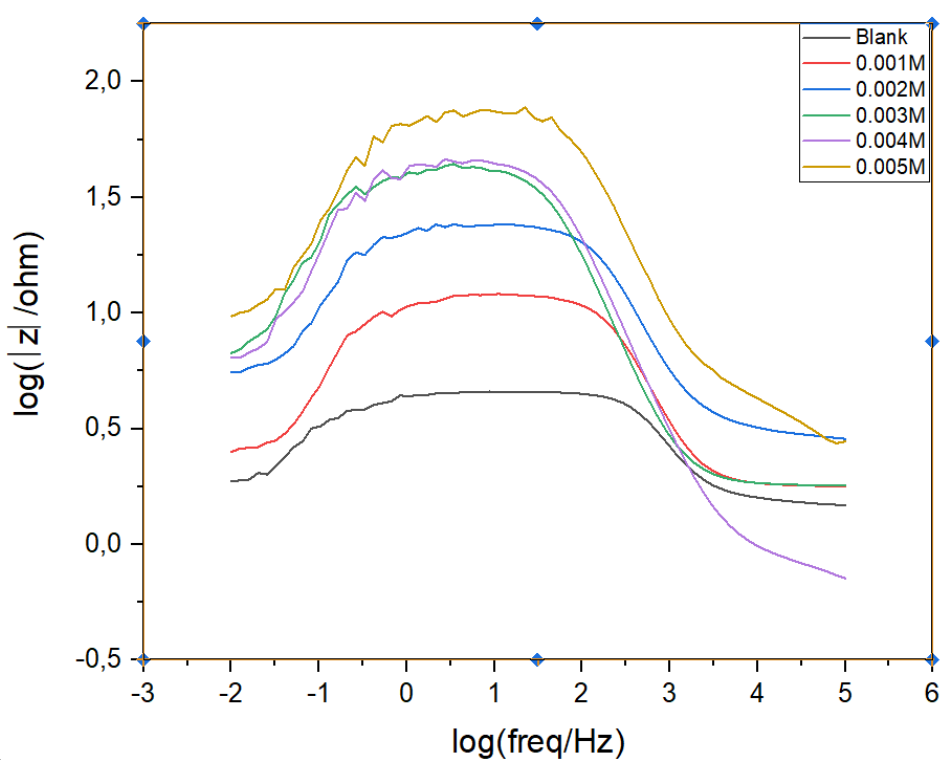


b.

Figure 5. 27: a. phase angle b. Bode modulus plot in 1 M HCl solution with and without DPT at various concentrations at 303 K



a.



b.

Figure 5. 28: a. phase angle b. Bode modulus plot in 1 M HCl solution with and without DNT at various concentrations at 303 K.

The introduction of the inhibitor into 1M HCl solution resulted in notable changes in the electrochemical parameters as evidenced in Table 5.6. These changes included an elevation in electrolyte resistance (R_s), a rise in inductive elements (L), and a reduction in CPE impedance (Q). The increase in R_s can be attributed to the adsorption of inhibitor molecules onto the metal surface. This adsorption forms a protective film, which reduces the number of free ions in the solution, thereby increasing resistance. The inhibitor may also interact with hydrogen ions in the HCl solution, reducing their concentration and further contributing to the increased resistance. Moreover, the interaction between the inhibitor and ions in the solution might result in the creation of complexes, which in turn can hinder the movement of ions and hence raise the resistance[160, 358, 359]. Because the inhibitor forms a protective layer on the metal surface, which may reduce the mobility of ions in the solution, an increase in inhibitor concentration for each inhibitor causes an increase in R_p , which raises inhibition efficiency. The trend observed in the gravimetric studies is also demonstrated in EIS; the rise in inhibitor concentration increases the inhibition efficiency. When the concentration was 0.001M the %IE was 66.72%, 50.22%, 73.25% and increased to 98.52%, 91.61%, 98.23% for 0.005M DMT, DPT, and DNT, respectively.

The increase in L , suggests the presence of adsorption kinetics and delayed electrochemical responses. The inhibitor's adsorption on the metal surface can introduce a time delay in the system's response, manifesting as inductive behavior. This is likely due to the formation of a protective film that temporarily stores and releases charge. Changes in reaction mechanisms induced by the inhibitor can also lead to inductive behavior, as the system adjusts to the altered electrochemical environment. The decrease in CPE impedance Q indicates a reduction in pseudo-capacitance, likely due to the inhibitor forming a more homogeneous protective layer on the metal surface. This layer reduces surface roughness and heterogeneity, leading to a decrease in effective capacitance. The inhibitor's blocking effect on active sites reduces the double-layer capacitance, contributing to the lower Q . These changes reflect the improved uniformity of the surface and the inhibitor's effectiveness in protecting the metal[360-364].

Table 5. 6: EIS data of Al corrosion in 1M HCl without and with different molarities of inhibitor at 303K

Inhibitor	Conc. (M)	R_s (Ω)	R_{ct} (Ω)	R_p (Ω)	n	Cdl ($\mu F/cm^2$)	L H	CPE ($\mu.F\hat{S}$)	%IE
Blank	000	1.53	2.898	0.388	0.972	366.1	4.51	113.00	-
DMT	0.001	17.67	28.34	1.166	1.000	189.71	12.21	51.43	66.72
	0.002	3.75	84.59	7.5872	0.962	195.10	60.2	60.51	94.88
	0.003	13.83	87.84	8.349	0.998	87.950	71.43	41.15	95.35
	0.004	3.82	93.13	8.189	0.966	117.05	55.79	39.62	95.26
	0.005	13.53	109.0	22.34	0.957	45.487	136.3	52.58	98.52
DPT	0.001	3.867	10.16	0.779	0.964	204.37	10.65	77.82	50.22
	0.002	4.057	24.26	0.912	0.991	170.25	24.09	46.32	57.45
	0.003	17.35	28.79	1.131	0.999	132.88	12.42	50.31	65.69
	0.004	3.01	20.59	2.399	0.92	144.50	0.0032	74.02	83.82
	0.005	4.03	45.37	4.629	0.98	64.60	0.0227	26.12	91.61
DNT	0.001	3.20	50.918	1.451	1.00	324.24	0.0023	56.30	73.25
	0.002	1.80	42.92	5.439	0.91	253.98	0.0026	0.116	92.86
	0.003	4.028	50.37	5.446	0.989	142.97	54.89	25.12	92.87
	0.004	2.98	69.94	6.922	0.85	52.31	0.0059	73.39	94.39
	0.005	13.74	106.9	21.967	0.999	27.41	137.5	39.88	98.23

5.4. Potentiodynamic polarization (PDP)

Typically, the polarisation curve changes that occur when an inhibitor is present are utilized to categorize inhibitors as either anodic, cathodic, or mixed. A shift in corrosion potential can provide insights into the mode of action of corrosion inhibitors. When comparing the inhibited solutions to the free acid solution(Blank), a shift in E_{corr} values towards less negative values was seen in Figures 5.26-5.28 of Tafel curves, suggesting that the metal is less likely to experience anodic reactions such as oxidation or dissolution by raising the potential at which metal tends to corrode[365]. When inhibitor concentration is increased, the Tafel curves for both inhibitors move towards lower i_{corr} values, indicating that aluminium corrosion is being inhibited or slowed down[366]. All the potentiodynamic parameters like anodic (β_a) and cathodic(β_c) tafel constant, corrosion current density(i_{corr}), and corrosion potential(E_{corr}) values are summarised in Table 5.6

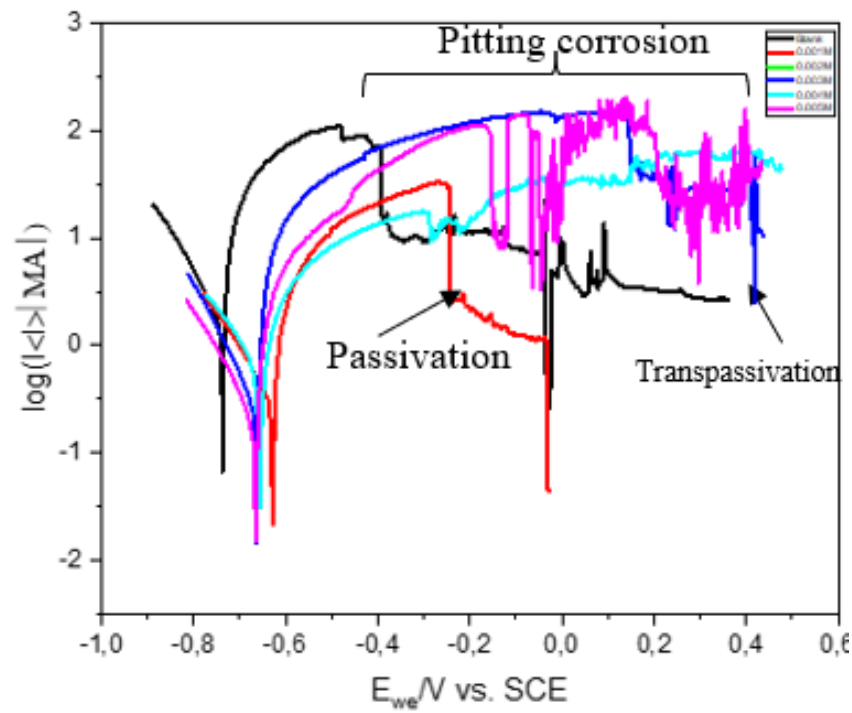


Figure 5. 29: The polarization curves of Al without and with DMT inhibitor

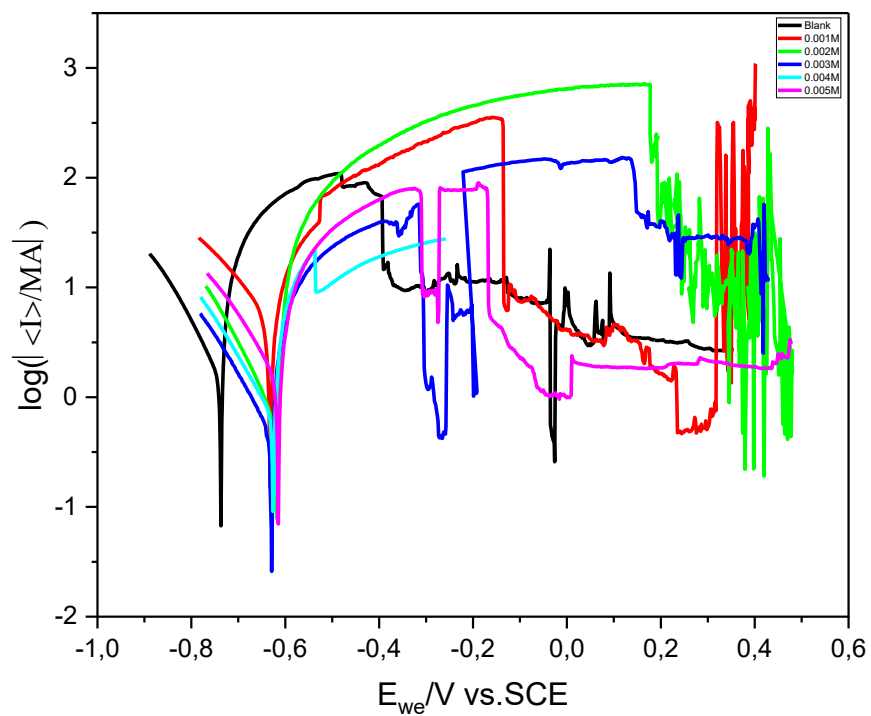


Figure 5. 30: The polarization curves of Al without and with DPT inhibitor

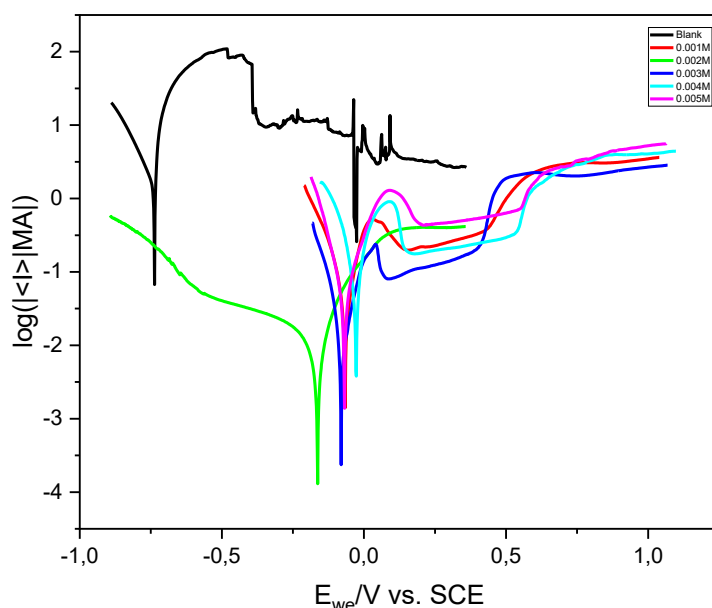


Figure 5. 31: The polarization curves of Al without and with DNT inhibitor

It is clear in Table 5.6 that the corrosion current density (i_{corr}) of Al decreases when the DMT, DPT, and DNT inhibitors are introduced. Considering the corrosion potential (E_{corr}) values, an increase in E_{corr} (a less negative value) was observed with a sustained rise in the DMT, DPT, and DNT concentration. In this study, all inhibitors are either anodic or cathodic inhibitors; according to the literature, if E_{corr} is less than -85mV, the inhibitor is considered as a mixed type corrosion inhibitor, but if the shift in E_{corr} in the presence of inhibitor is greater than 85mV for that of blank it is classified as a cathodic or anodic inhibitor[254, 367, 368]. As the concentration of DMT, DPT, and DNT increases, there is a change in the values of β_c and β_a , but no clear trend. Less β_a change value was seen in the presence of a DNT inhibitor, and greater β_a value changes were seen in the presence of DMT and DPT compared to β_c value changes. In line with the weight loss and EIS findings, the calculated inhibition efficiency of PDP also increased as the inhibitor's concentration increased. To ascertain the specific type of corrosion inhibition displayed by the DMT, DPT, and DNT. Equations 3.10 and 3.11 were utilized to calculate the anodic interaction coefficient (f_a) and cathodic interaction coefficient (f_c), respectively, based on the parameters of the polarisation curve[254], as indicated in Table 5.6. The fact that the DMT and DPT values of f_a and f_c in Table 5.6 are less than 1 suggests that the inhibitor molecules that were adsorbed had an effect on both the cathodic and anodic reactions. However, DNT values of f_a less than 1 show that inhibitor molecules adsorbed had an impact on the cathodic reaction. All inhibitors, however, have f_a values that are less than f_c .

If f_a is considerably less than f_c ($f_a < f_c$), it indicates that the inhibitor is more effective in slowing down the anodic reactions [254, 367].

Table 5. 7: Electrochemical parameters obtained from the polarisation curve.

Con. (M)	$-E_{corr}$ (mV)	i_{corr} ($\mu A.cm^{-2}$)	β_a (mV.dec $^{-1}$)	$-\beta_c$ (mV.dec $^{-1}$)	f_a	f_c	$\frac{f_a}{f_c}$	% IE _{PDP}
B lank	780.35	3718.91	111.50	137.50	-	-	-	-
DMT								
0.001	750.00	1438.48	51.50	77.20	0.2946	0.4823	0.6108	61.31
0.002	625.60	1175.32	55.60	204.9	0.0788	0.9736	0.0809	68.39
0.003	640.09	932.95	53.50	146.7	0.0713	0.6957	0.1024	74.90
0.004	657.72	570.66	80.10	154.4	0.0510	0.3744	0.1362	84.65
0.005	643.95	457.73	68.90	164.20	0.0362	0.3319	0.1090	87.69
DPT								
0.001	639.16	412.05	55.30	160.0	0.0312	0.3093	0.1008	88.91
0.002	635.43	366.24	51.8	164.3	0.0268	0.2825	0.0948	90.15
0.003	676.23	285.15	27.9	119.3	0.0301	0.1635	0.1840	92.33
0.004	694.97	207.05	28.4	117.4	0.0258	0.1035	0.2492	94.43
0.005	691.18	163.17	21.2	109.7	0.0197	0.0839	0.2348	95.61
DNT								
0.001	92.15	391.72	161.5	103.70	2.2×10^{-4}	15.712	1.4×10^{-5}	89.47
0.002	86.03	299.36	111.8	96.50	1.6×10^{-4}	12.554	1.2×10^{-5}	91.95
0.003	130.83	97.74	143.3	154.1	7.8×10^{-5}	2.9591	2.6×10^{-5}	97.37
0.004	77.06	79.25	94.60	75.10	3.9×10^{-5}	3.5475	1.1×10^{-5}	97.86
0.005	75.24	47.97	95.30	62.30	2.3×10^{-5}	2.1759	1.0×10^{-5}	98.71

5.5. Scanning electron microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX)

The purpose of using Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX) in studying aluminum corrosion inhibitors is to understand the inhibitor's effectiveness at a microstructural and elemental level. SEM and EDX are complementary techniques that provide a comprehensive understanding of how corrosion inhibitors interact with aluminum surfaces. SEM offers high-resolution surface morphology images, revealing the physical effects of corrosion and inhibition, while EDX provides crucial elemental

composition data, elucidating the chemical interactions at play. The SEM images of untreated aluminum (Figures 5.31a-5.33a) show a relatively smooth surface with minor imperfections. After exposure to HCl (Figure 5.31b-5.33b), the aluminum surface exhibits significant pitting and roughness, indicating severe corrosion.

In contrast, the aluminum treated with the corrosion inhibitor (Figures 5.31c -5.33c) shows a much smoother surface with fewer pits, suggesting that the inhibitor forms a protective layer that mitigates the corrosive effects of HCl. The EDX spectrum of untreated aluminum (Figures 5.31a-5.33a) primarily shows the presence of aluminum. After HCl exposure (Figures 5.31b-5.33b), oxygen significantly increases, indicating the formation of aluminum oxides. In the inhibitor-treated sample (Figures 5.31c-5.33c), the EDX spectrum reveals the presence of elements from the inhibitor, along with a reduced oxygen signal, suggesting that the inhibitor prevents the formation of corrosion products by forming a protective layer.

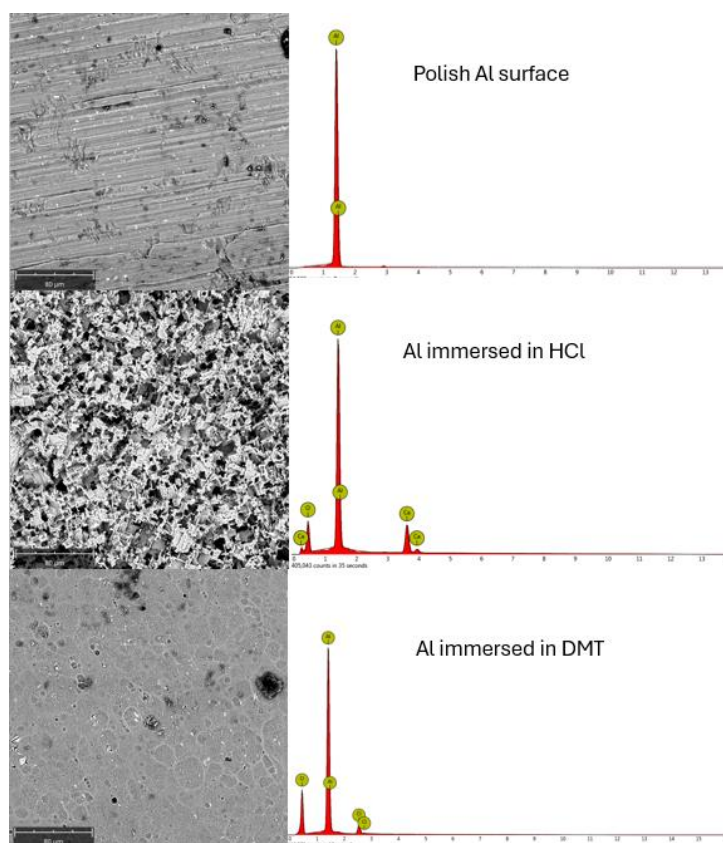


Figure 5. 32: SEM images and EDS spectra of unexposed-polished Al surface, Al immersed in uninhibited 1 M HCl, and Al immersed in DMT-inhibited 1 M HCl solution

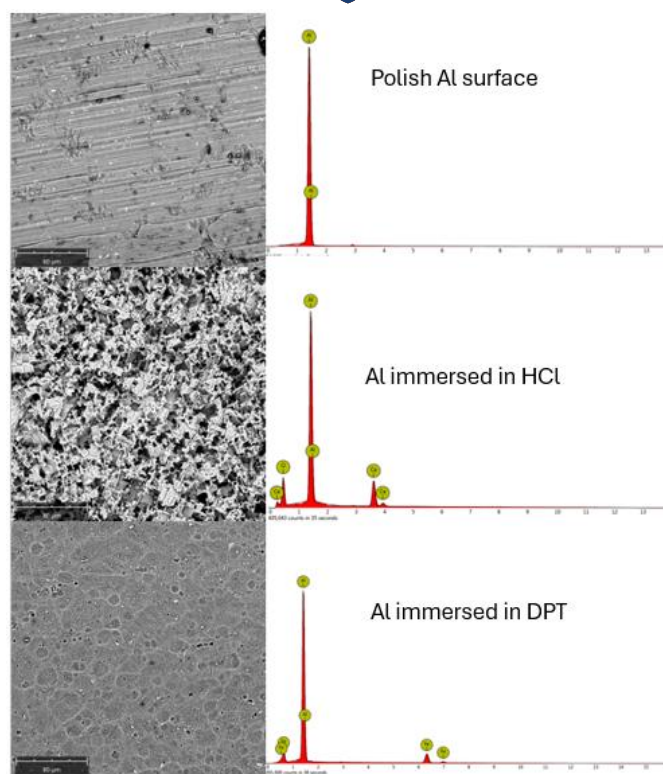


Figure 5. 33: SEM images and EDX spectra of unexposed-polished Al surface, Al immersed in uninhibited 1 M HCl, and Al immersed in DPT-inhibited 1 M HCl solution

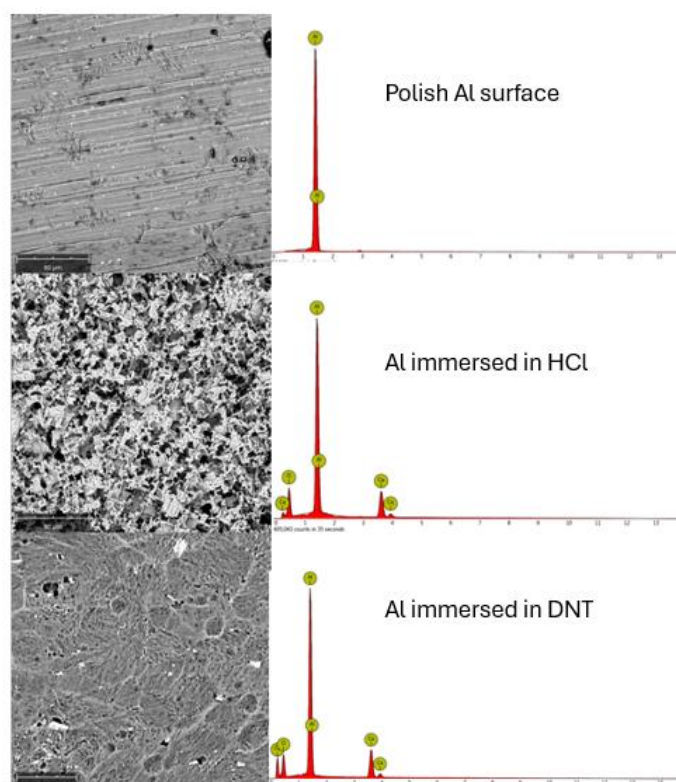


Figure 5. 34: SEM images and EDX spectra of unexposed-polished Al surface, Al immersed in uninhibited 1 M HCl, and Al immersed in DNT-inhibited 1 M HCl solution

5.6. Water contact angle measurement

Contact angle measurements are crucial in assessing the effectiveness of corrosion inhibitors on metal surfaces. They provide insights into changes in surface wettability, indicating how water interacts with a solid surface[369, 370]. The contact angle measurements for untreated Al sample, Al sample immersed in a 1 M HCl medium without inhibitor, and metal substrates immersed in the presence of 0.005M DMT, DPT, and DNT inhibitor for 6 hours at 303 K are displayed in Figure 5.31a-e respectively. According to Figure 5.31b, the contact angle of Al minimized from 90.000° to 47.386° when the metal was submerged in a solution of 1 M HCl, in comparison to the untreated Al sample. The decrease in contact angle of Al that is immersed in a solution of 1 M HCl is because when Al is exposed to 1M HCl, the acidic environment promotes the oxidation and dissolution of the Al surface. This forms aluminum chloride and hydrogen gas, forming a rough, pitted surface[371-373]. The decrease in contact angle of 47.386° creates hydrophilic sites. These sites increase the surface's affinity for water, lowering the contact angle. When the DMT, DPT, and DNT inhibitor is introduced the contact angle increases to 96.151° , 112.805° , and 144.666° , respectively. This is because when the inhibitor is introduced into the HCl solution its molecules adsorb onto the Al surface, forming a protective layer. This layer can block active sites, reducing corrosion. This increase in contact angle creates a hydrophobic barrier on the metal surface[374-380].

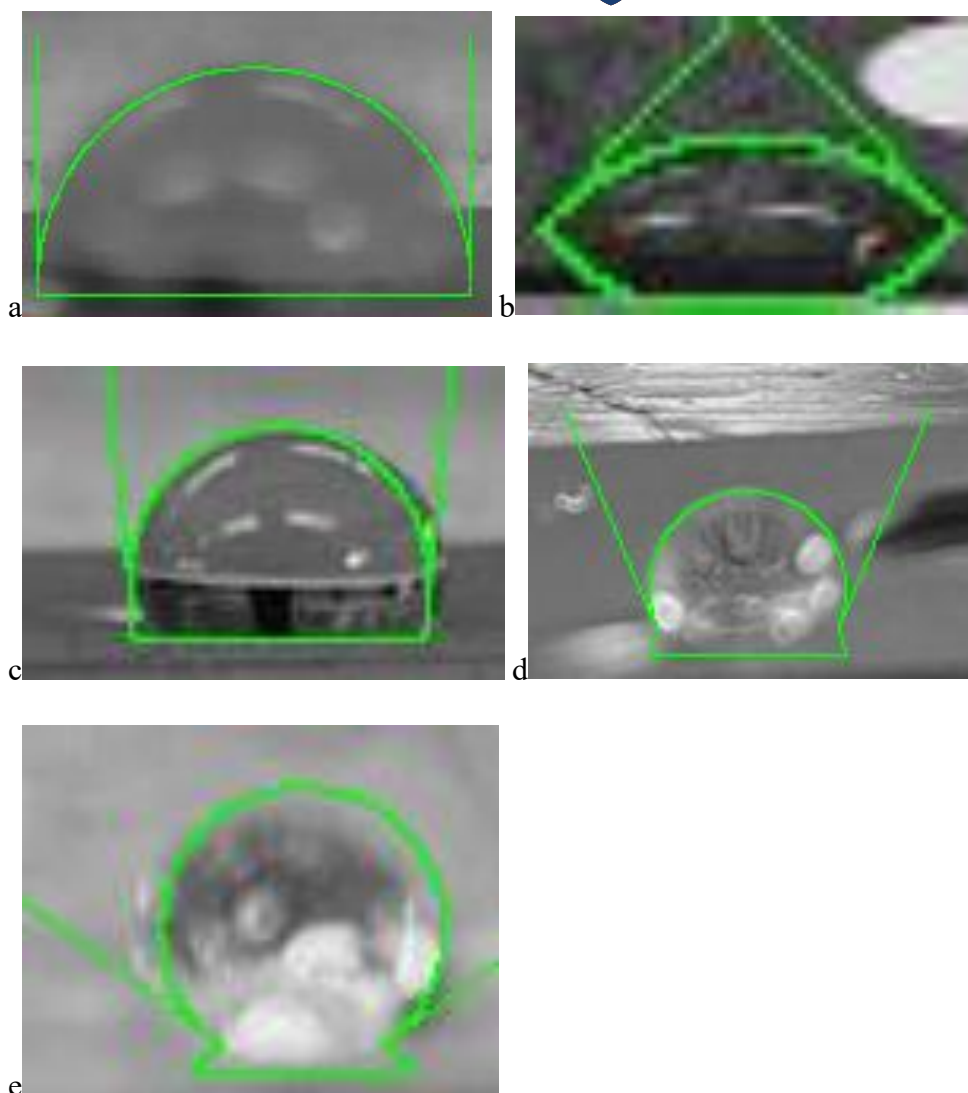


Figure 5. 35: Surface wettability behavior of (a) untreated Al sample 90.00° , (b) Al sample after 6 hours of immersion in 1 M HCl medium with no inhibitor 47.386° , and (c) in the presence of 0.005M of DMT 96.151° , (d) DPT 112.805° , and (e) DNT 144.666° .

5.7. Fourier transform infrared Spectroscopy (FTIR) analysis of corrosion products on the Al surfaces

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful analytical technique widely used in the study of corrosion inhibitors. FTIR helps identify the specific functional groups present in the corrosion inhibitors. Analyzing the inhibitor's FTIR spectra before and after interaction with the metal surface can infer the adsorption mechanism. Shifts in the peaks or changes in intensity can indicate the formation of bonds between the inhibitor molecules and the metal surface. In the spectrum of aluminum without inhibitor, characteristic peaks at approximately 3400 cm^{-1} (O-H stretching), approximately 1800 cm^{-1} (O-H bending), and approximately $950\text{-}900\text{ cm}^{-1}$ (Al-O stretching) were observed (Figure 5.36-5.38). In Figure

5.36-5.37, the spectrum of Al with DMT and DPT, these peaks are significantly reduced or absent, and the spectrum appears relatively flat, suggesting that DMT and DPT have formed a passivating layer on the aluminum surface, preventing the detection of characteristic aluminum and hydroxyl group peaks. When the DNT inhibitor is introduced (Figure 5.38), new peaks at approximately 1500 cm^{-1} and 1300 cm^{-1} indicate DNT forming complexes with Al, likely involving coordination with nitrogen atoms from DNT. Another peak was formed at 3000 cm^{-1} , indicating the presence of a new chemical group, which could be attributed to C-H stretching vibrations, suggesting the presence of new alkyl groups from the DNT inhibitor due to its interaction with a metal surface.

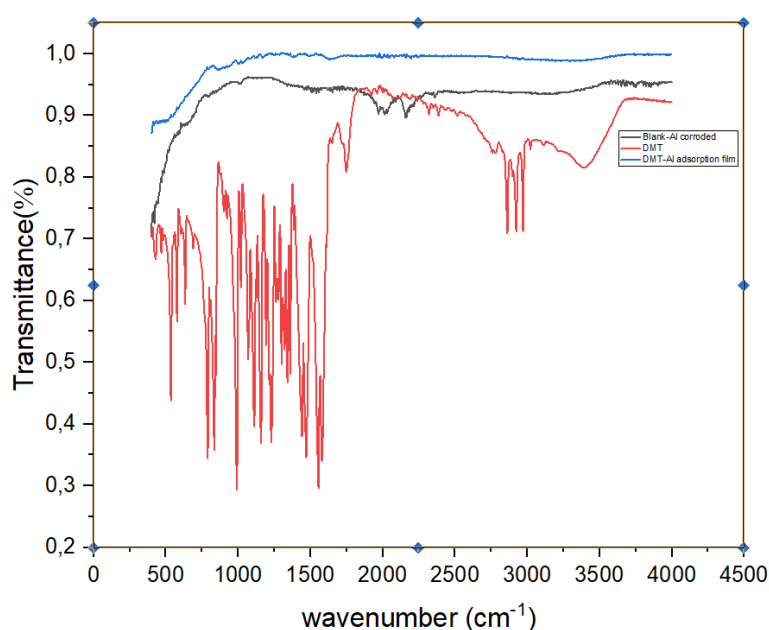


Figure 5. 36: The FTIR spectrum of the adsorption film formed on the Al surface compared to the crude DMT and corrosion products formed on Al (Blank Al corrosion products).

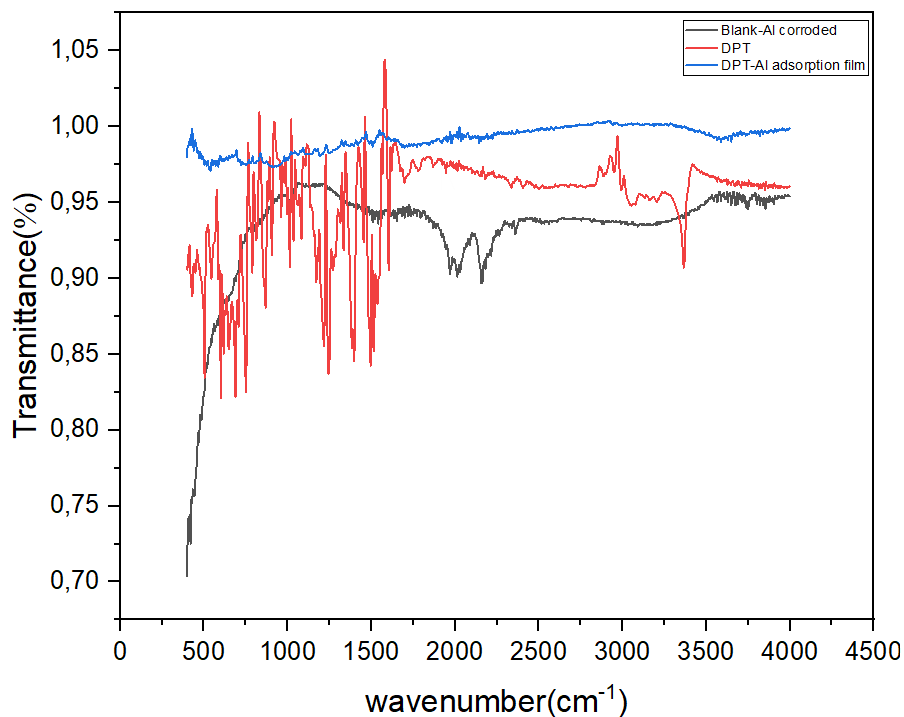


Figure 5. 37: The FTIR spectrum of the adsorption film formed on the Al surface compared to the crude DPT and corrosion products formed on Al (Blank Al corrosion products).

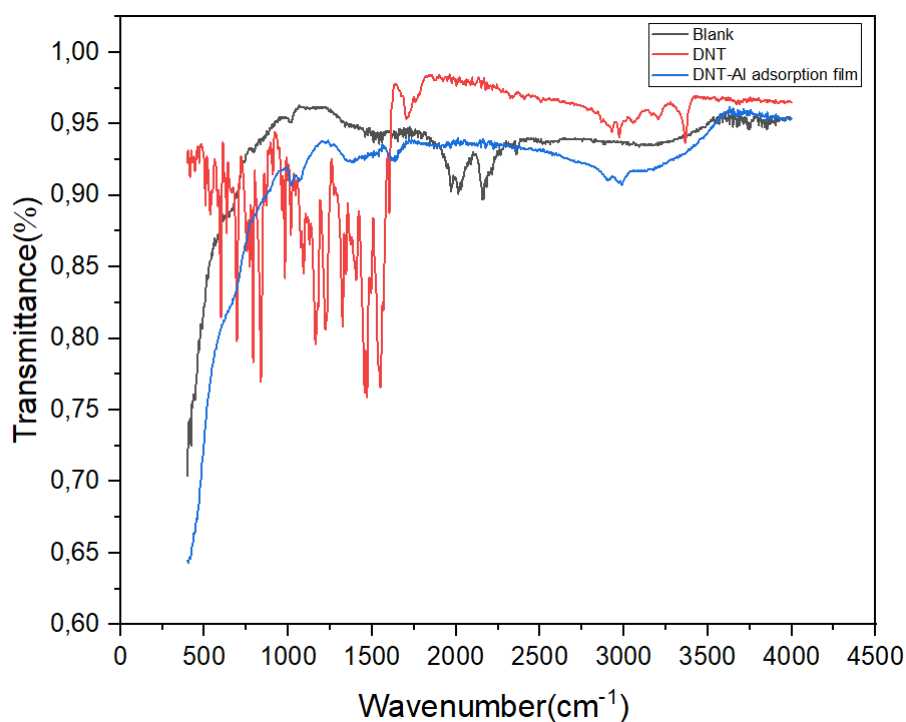


Figure 5. 38: The FTIR spectrum of the adsorption film formed on the Al surface compared to the crude DNT and corrosion products formed on Al (Blank Al corrosion products).

5.8. Structures and binding energies for the inhibitor...Al interacting species

Adsorption energy represents the amount of energy released or absorbed when one mole of adsorbate molecules is adsorbed onto the surface of the adsorbent material. As indicated by the literature, the inhibitor may adsorb on the metal surface in perpendicular orientations, which is classified as chemisorption, and horizontal orientations, which is classified as physisorption, or a mix (chemisorption and physisorption)[381-383]. When adsorbing molecules on metal surfaces, care must be taken to select suitable model surface plates for such metals. This is achieved by choosing the lowest energy, most stable surfaces, which are most likely to be the predominantly exposed crystal faces in a realistic system. The face-centered cubic (FCC) surface plane chosen for the study on the Al surface was Al(111), as it is believed to be one of the most stable planes for this metal. The optimized inhibitor...Al structures are shown in Figures 5.39-5.41 along with selected bond distances; the relative energies (ΔE , kcal/mol), binding energies (ΔE_{bind} , kcal/mol), and bond distances ($\text{\AA}$) between the Al surface and the inhibitor molecule are reported in Table 5.8. Among the DMT...Al structures, all structures have relative energies below 3 kcal/mol relative to the lowest energy structure. This means that all structures obtained are stable and significant. In other words, the molecule may choose to align itself in any of the six arrangements obtained. DMT inhibitors tend to have either horizontal or perpendicular orientations to adsorb on the Al surface; perpendicular orientation is due to the interaction of the Al surface with the O atoms present on DMT, forming Al...O bonds. The interaction between the DMT inhibitor and Al (111) surface involves two heteroatoms, oxygen, and nitrogen, having a distance less, greater, and around $3\text{\AA}$. The lowest distance between oxygen and metal surface is $2.499\text{\AA}$ for DMT-f, and the highest is $3.943\text{\AA}$ for DMT-d orientation. The lowest and highest distance between nitrogen and Al(111) surface are $3.805\text{\AA}$ and $5.007\text{\AA}$ for DMT-d and DMT-b, respectively. A distance less than $3\text{\AA}$ indicates a closer interaction between the atom and the aluminium surface, effectively inhibiting corrosion [229, 384-386].

Among the DPT...Al structures out of 3 arrangements, inhibitor molecules many choose to align themselves in arrangements having relative energies ranging around two and 3kcal/mol because their various configurations of the inhibitor on the metal surface are energetically competitive and stable. For DNT...Al structures, all structures have relative energies that are less than 1 kcal/mol. The most stable arrangements are those in which the inhibitors are

arranged horizontally on the Al(111) surface, giving rise to physisorption or mixed adsorption. DPT and DNT inhibitors interact with the Al surface through the use of the nitrogen atom. DPT involves a distance greater and higher than $3\text{\AA}$ between the inhibitor and metal surface; the highest distance is $4.312\text{\AA}$ for DPT-c, and the lowest is $3.872\text{\AA}$ for DPT-a. The interaction distance for the DNT inhibitor between the nearest nitrogen atom and Al(111) surface involved is greater than $3\text{\AA}$, with the lowest distance, $3.961\text{\AA}$ for DNT-a, and the highest distance, $4.511\text{\AA}$ for DNT-b orientation.

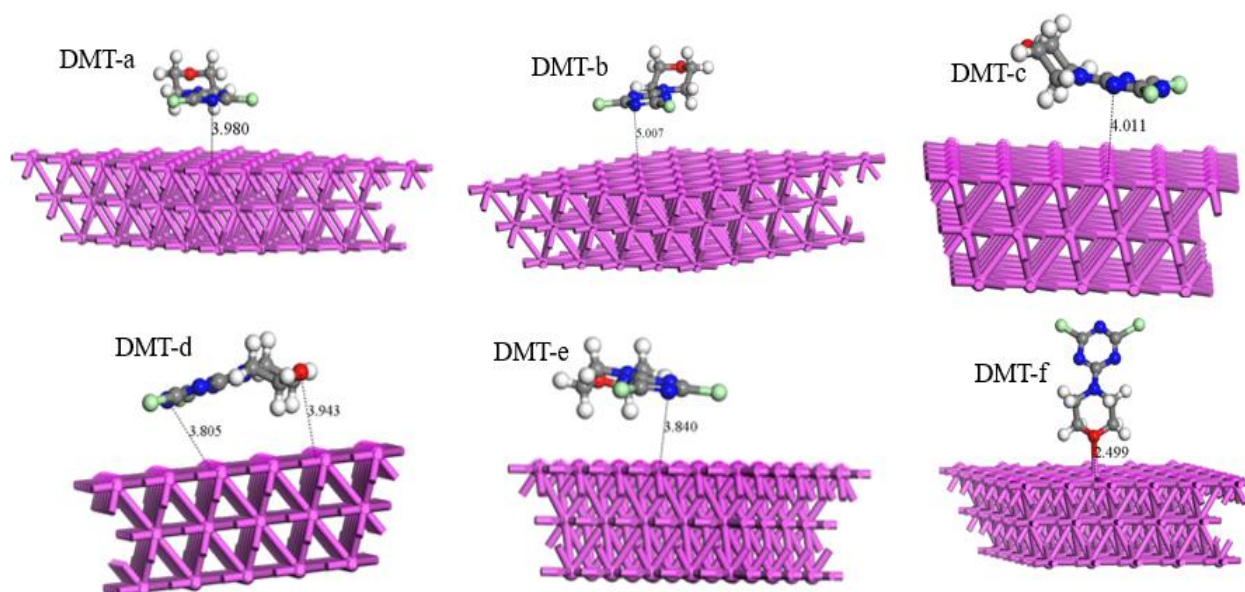


Figure 5. 39: Different adsorption geometries of DMT molecules on the Al(111) surface and the distance between the nearest oxygen and nitrogen atom to the Al surface.

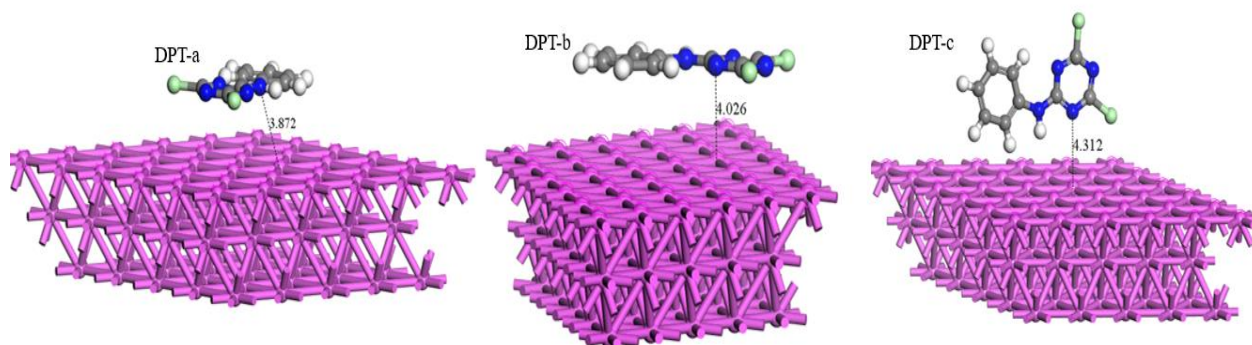


Figure 5. 40: Different adsorption geometries of DPT molecules on the Al(111) surface and the distance between the nearest nitrogen atom to the Al surface.

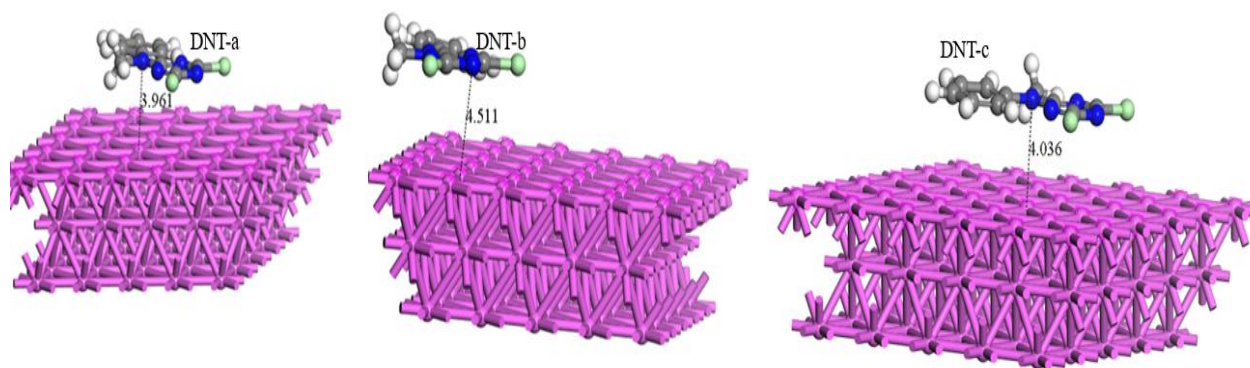


Figure 5. 41: Different adsorption geometries of DNT molecules on the Al(111) surface and the distance between the nearest nitrogen atom to the Al surface.

Table 5. 8: Optimised energies calculated for DMT(-1485.423062Ha), DPT(-1485.40897Ha), and DNT(-1256.371923Ha) adsorption sites on the Al(111) surface(-18176.58391) and the distance between the nearest heteroatom to the metal surface.

Configuration	-E _{ads} (kcal/mol)	E _{binding} (kcal/mol)	ΔE (kcal/mol)	Bond distance (Å)
DMT				
(DMT...Al)-a	8.6971	8.6971	0	Al...N(3.980)
(DMT...Al)-b	8.5980	8.5980	0.0991	Al...N(5.007)
(DMT...Al)-c	8.5402	8.5402	0.1569	Al...N(4.011)
(DMT...Al)-d	8.5114	8.5114	0.1857	Al...O(3.943) Al...N(3.805)
(DMT...Al)-e	8.4957	8.4957	0.2014	Al...N(3.840)
(DMT...Al)-f	7.3003	7.3003	1.3968	Al...O(2.499)
DPT				
(DPT...Al)-a	9.2744	9.2744	0	Al...N(3.872)
(DPT...Al)-b	9.2681	9.2681	0.0063	Al...N(4.026)
(DPT...Al)-c	7.0970	7.0970	2.1774	Al...N(4.312)
DNT				
(DNT...Al)-a	17.2688	17.2688	0	Al...N(3.961)
(DNT...Al)-b	17.0993	17.0993	0.1694	Al...N(4.511)
(DNT...Al)-c	17.0366	17.0366	0.2321	Al...N(4.036)

The adsorption energy values of the DMT, DPT, and DNT inhibitors on the Al surface indicate that they are negative values suggesting that the interaction between inhibitor molecules and the Al (1 1 1) surface is spontaneous but weak. Chemical adsorption is characterized by binding energies greater than 100 kcal/mol, whereas values below that indicate physical adsorption[269, 382, 387-390]. Table 5.8 shows that all of the inhibitors' adsorption energies on the Al(111) surface are less than 100 kcal/mol. The closest distance between the heteroatom

and the Al(111) agrees with this, indicating that all of the compounds physically adsorb on the Al(111) metal surface. The highest adsorption energy and binding inhibitor was observed at 17.2688kcal/mol for the DNT inhibitor, and the lowest was at 7.0970kcal/mol for the DPT inhibitor.

Chapter 6: Mild steel (MS) results and discussion

This chapter discusses and summarises the findings for MS metal. Using weight loss analysis, the synthesised inhibitors were tested for their anticorrosive properties on mild steel in 1M HCl. The effects of adsorption isotherms, temperature, inhibitor concentration, and thermodynamic parameters were all investigated. The inhibitors' mechanisms for corrosion resistance, inhibition, and degradation were assessed using electrochemical techniques. The synthesized DMT, DPT, and DNT modified with graphene oxide inhibitors were examined for their ability to prevent corrosion on MS in a solution of 1M HCl in this chapter using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) techniques. The mild steel surface and the synthetic substitute triazine were examined for surface morphology. The structures and binding energies for inhibitor -Fe(100) were explored through computational methods.

6.1. Weight loss measurement

The MS sample was immersed in a 1 M HCl solution for six hours at different temperatures. Weight loss analysis was conducted to evaluate the effects of DMT, DPT, and DNT concentration and temperatures on the corrosion of MS in the 1 M HCl solution.

6.1.2. Effect of temperature on mild steel metal in uninhibited 1M HCl and inhibited solutions.

Temperature plays a significant role in the corrosion behavior of mild steel in both inhibited and uninhibited conditions. As temperature increases, the corrosion rate of mild steel in the absence and presence of inhibitors tends to increase. This is because higher temperatures provide more energy to the chemical reactions at the metal surface, leading to faster dissolution of the metal and more aggressive corrosion[24, 54, 77, 391, 392]. According to Table 6.1, when the temperature rises from 303K to 323K, the corrosion rate for an uninhibited (blank) solution increases from 0.0049 to 0.0210g/cm²h. Figures 6.7-6.9 demonstrate how temperature negatively affects the inhibition efficiency, with the inhibitor's effectiveness decreasing as the temperature rises. The inhibitor molecules' ability to protect the metal surface is reduced when the temperature increases because higher temperatures increase the aggressiveness of the corrosive environment. For instance, in aqueous systems, elevated temperatures can increase the corrosiveness of dissolved oxygen or other oxidizing species, making it more challenging for inhibitors to maintain their protective role[393, 394]. For instance, the DMT%IE decreased from 93.87% to 83.83% when the temperature increased from 303K to 323K with the highest concentration inhibitor (0.005M) for this study. Similarly, the DPT %IE decreased from 90.20% to 76.66%, and the DNT %IE decreased from 87.95% to 80.47%. Among the three, DMT exhibited the highest %IE of 93.87% at 303 K using 0.005 M, this because DMT is attributed to the presence of nitrogen and oxygen heteroatoms, which facilitate strong interaction with the vacant d-orbitals of the Fe surface, enhancing its adsorption and corrosion protection.

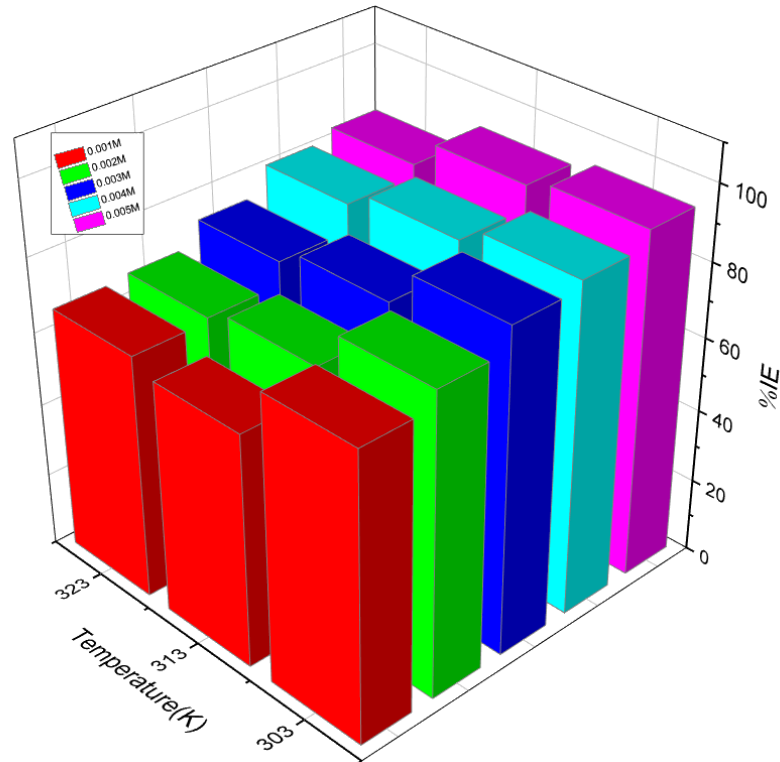


Figure 6. 1: The inhibition efficiency temperature of the inhibitor at different DMT inhibitor concentrations.

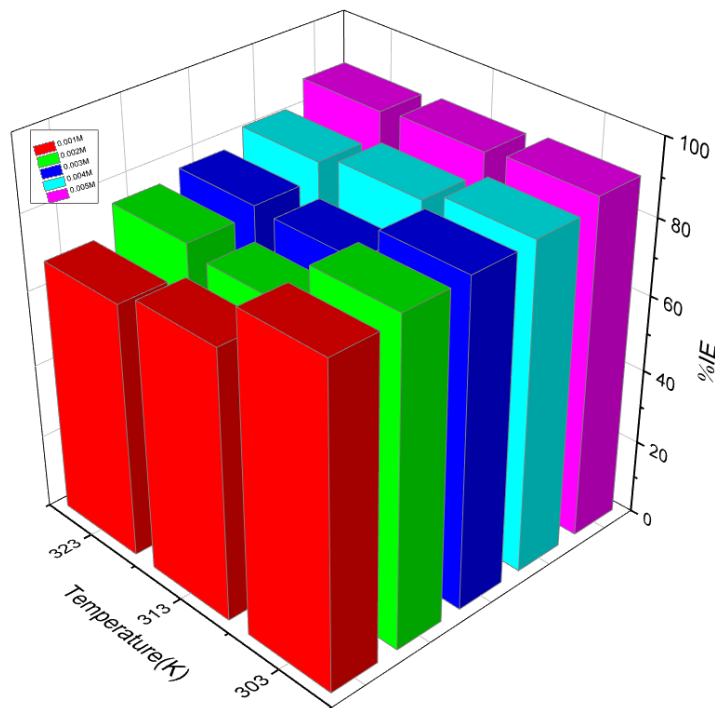


Figure 6. 2: The inhibition efficiency-temperature of the inhibitor at different DPT inhibitor concentrations.

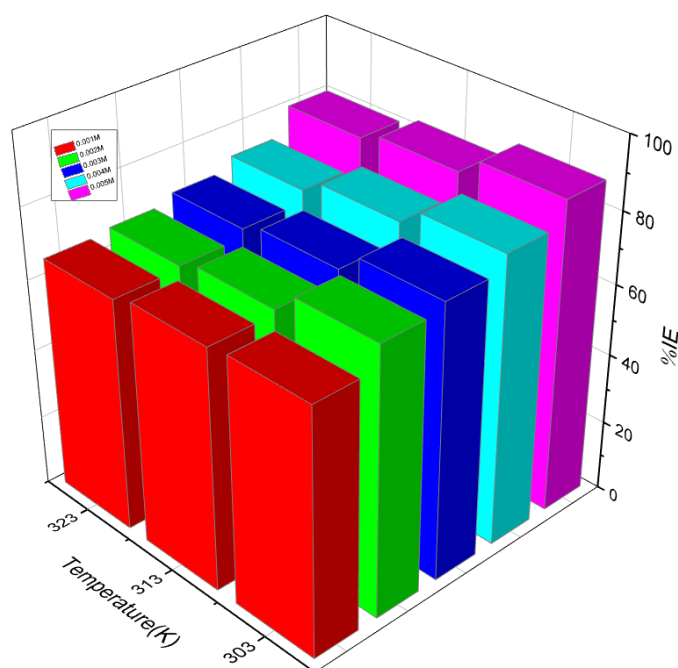


Figure 6. 3: The inhibition efficiency-temperature of the inhibitor at different DPT inhibitor concentrations.

6.1.1. Effect of inhibitor (DMT, DPT, and DNT) concentrations on Ms metal in 1M HCl solution.

The corrosion of mild steel in hydrochloric acid (HCl) solution is affected by multiple factors, such as the concentration of inhibitors. Table 6.1 displays the calculated CR, θ , and %IE based on the weight loss measurements. The corrosion rate of mild steel in an uninhibited (blank) solution is greater at all temperatures of 303K, 313K, and 323K, with values of 0.0049g/h.cm^2 , 0.0082g/h.cm^2 , and 0.0210g/h.cm^2 , respectively. When dimethyltryptamine (DMT), dipropyltryptamine (DPT), and diethyltryptamine (DNT) are added to a hydrochloric acid (HCl) solution, the rate at which mild steel (MS) corrodes is decreased at all temperatures. At a temperature of 303K, the corrosion rate was initially measured at 0.0049g/h.cm^2 . However, with the introduction of DMT, DPT, and DNT, the corrosion rate dropped to 0.0011g/h.cm^2 , 0.00076g/h.cm^2 , and 0.0015g/h.cm^2 , respectively. As the concentration of the inhibitor increases, the corrosion rate reduces at all temperatures. When DMT is utilized, the corrosion rate decreases to 0.0011, 0.0009, 0.006, 0.005, 0.0003 g/h.cm^2 as the inhibitor concentration increases to 0.001, 0.002, 0.003, 0.004, 0.005M correspondingly. When exposed to concentrations of 0.001, 0.002, 0.003, 0.004, and 0.005M of DPT inhibitor, the corrosion rate reduces to 0.00076, 0.00068, 0.00065, 0.00062, and 0.00048 g/h.cm^2 correspondingly. When exposed to DNT inhibitor concentrations of 0.001, 0.002, 0.003, 0.004, and 0.005M, the

corrosion rate reduces to 0.0015, 0.0012, 0.0011, 0.0009, and 0.00059g/h.cm², respectively. The correlation between DMT, DPT, and DNT concentrations and corrosion rate, as shown in Figures 6.1-6.3 indicates that higher inhibitor concentrations led to decreased corrosion rates. Figures 6.4-6.6 demonstrate a positive correlation between the concentration of DMT, DPT, and DNT and the inhibitory efficiency. The highest level of protection is achieved at 0.005M. The reason for the low corrosion rate and high inhibition efficiency values obtained at 0.005M is the increased availability of inhibitor molecules compared to 0.001M. This leads to a stronger probability for the inhibitor to adsorb at the metal/solution interface of the MS surfaces. The three inhibitors provide a protective effect on the MS by adsorbing inhibitor molecules onto their surfaces [327, 395-397].

Table 6. 1: Weight loss parameters of DMT, DPT, and DNT inhibitor on the corrosion of MS at various temperatures for 6 hours immersion.

Temperature (K)	Inhibitor concentration (M)	Weight loss (g)	Corrosion rate (g/h.cm ²)	Surface coverage (θ)	%IE
DMT					
303	Blank	0.1741	0.0049	-	-
	0.001	0.0396	0.0011	0.7755	77.55
	0.002	0.0318	0.0009	0.8163	81.63
	0.003	0.0213	0.0006	0.8775	87.75
	0.004	0.0179	0.0005	0.8979	89.79
	0.005	0.0113	0.0003	0.9387	93.87
31	Blank	0.2959	0.0082	-	-
	0.001	0.1067	0.0030	0.6341	63.41
	0.002	0.0879	0.0024	0.7073	70.73
	0.003	0.0630	0.0018	0.7804	78.04
	0.004	0.0430	0.0012	0.8536	85.36
	0.005	0.0253	0.0007	0.9146	91.46
323	Blank	0.7569	0.0210	-	-
	0.001	0.2554	0.0070	0.6666	66.66
	0.002	0.2449	0.0068	0.6761	67.61
	0.003	0.1995	0.0055	0.7380	73.80
	0.004	0.1443	0.0040	0.8095	80.95
	0.005	0.1248	0.0034	0.8380	83.80
DPT					
303	Blank	0.1741	0.0049	-	-
	0.001	0.0273	0.00076	0.8448	84.48
	0.002	0.0248	0.00068	0.8612	86.12
	0.003	0.0234	0.00065	0.8673	86.73
	0.004	0.0225	0.00062	0.8734	87.34
	0.005	0.0172	0.00048	0.9020	90.20
	Blank	0.2959	0.0082	-	-

313	0.001	0.0838	0.0023	0.7195	71.95
	0.002	0.0813	0.0022	0.7317	73.17
	0.003	0.0690	0.0019	0.7682	76.82
	0.004	0.0467	0.0013	0.8414	84.14
	0.005	0.0333	0.0009	0.8902	89.02
323	Blank	0.7569	0.0210	-	-
	0.001	0.2421	0.0067	0.6809	68.09
	0.002	0.2393	0.0066	0.6857	68.57
	0.003	0.2074	0.0057	0.7285	72.85
	0.004	0.1908	0.0053	0.7476	74.76
	0.005	0.1790	0.0049	0.7666	76.66
DNT					
303	Blank	0.1741	0.0049	-	
	0.001	0.0544	0.0015	0.6938	69.38
	0.002	0.0404	0.0012	0.7551	75.51
	0.003	0.0410	0.0011	0.7755	77.55
	0.004	0.0326	0.0009	0.8163	81.63
	0.005	0.0215	0.00059	0.8795	87.95
313	Blank	0.2959	0.0082	-	-
	0.001	0.0936	0.0026	0.6829	68.29
	0.002	0.0925	0.0025	0.6951	69.51
	0.003	0.0814	0.0023	0.7195	71.95
	0.004	0.0666	0.0019	0.7683	76.83
	0.005	0.0504	0.0014	0.8292	82.93
323	Blank	0.7569	0.0210	-	-
	0.001	0.2591	0.0071	0.6619	66.19
	0.002	0.2501	0.0069	0.6714	67.14
	0.003	0.2293	0.0064	0.6952	69.52
	0.004	0.2069	0.0057	0.7285	72.85
	0.005	0.1467	0.0041	0.8047	80.47

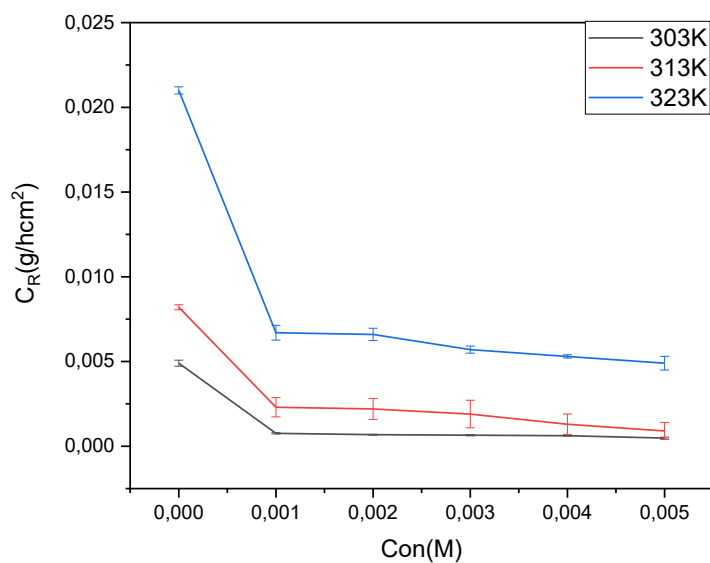


Figure 6. 4: Corrosion rate variation as a function of different DMT inhibitor concentrations for MS metal sample at 303 to 323K

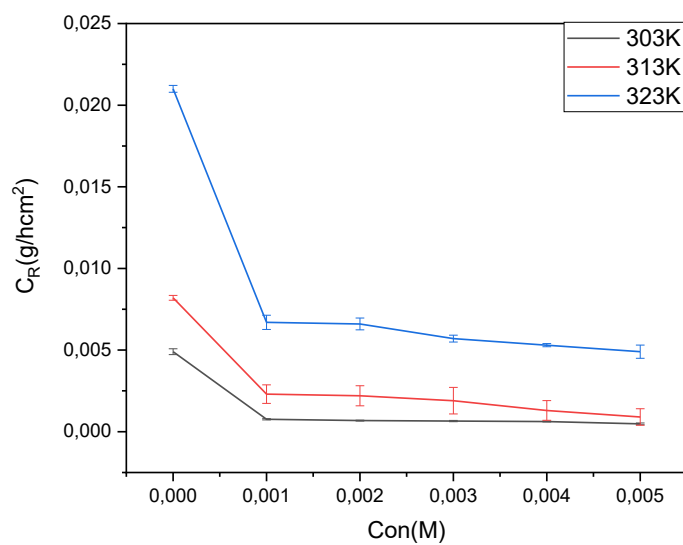


Figure 6. 5: Corrosion rate variation as a function of different DPT inhibitor concentrations for Al metal sample at 303 to 323 K

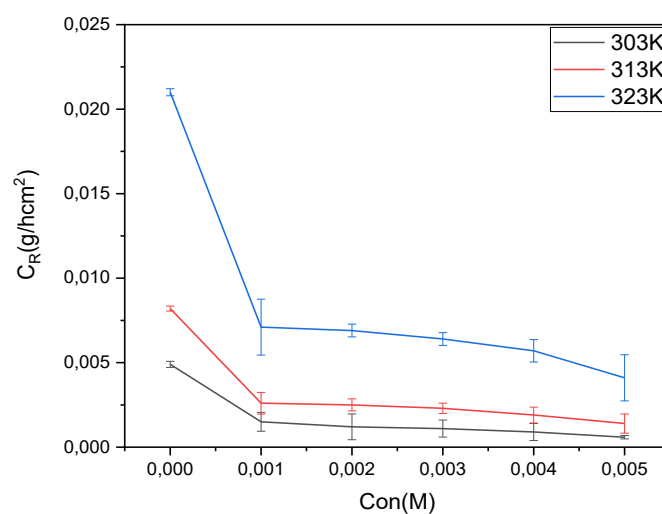


Figure 6. 6: Corrosion rate variation as a function of different DNT inhibitor concentrations for MS metal sample at 303 to 323 K

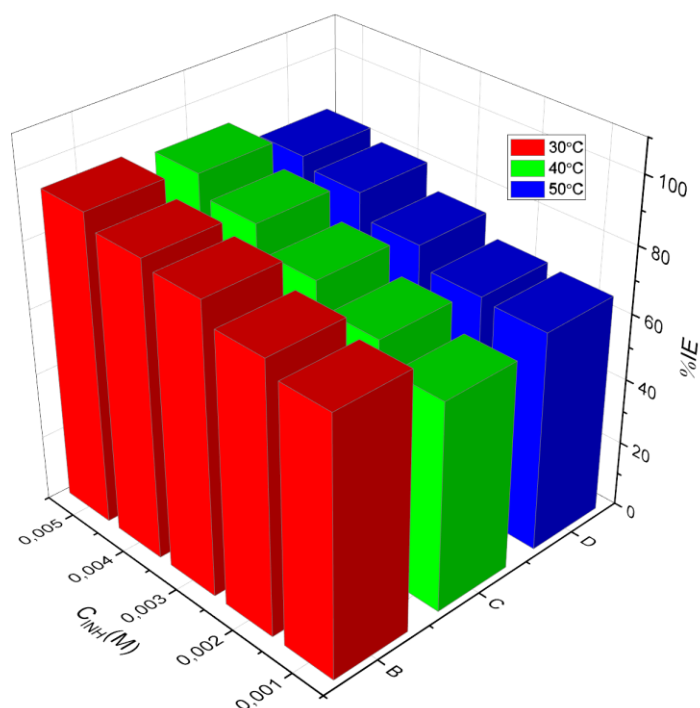


Figure 6. 7: The inhibition efficiency- DMT inhibitor concentration at different temperatures (303K, 313K, and 323K).

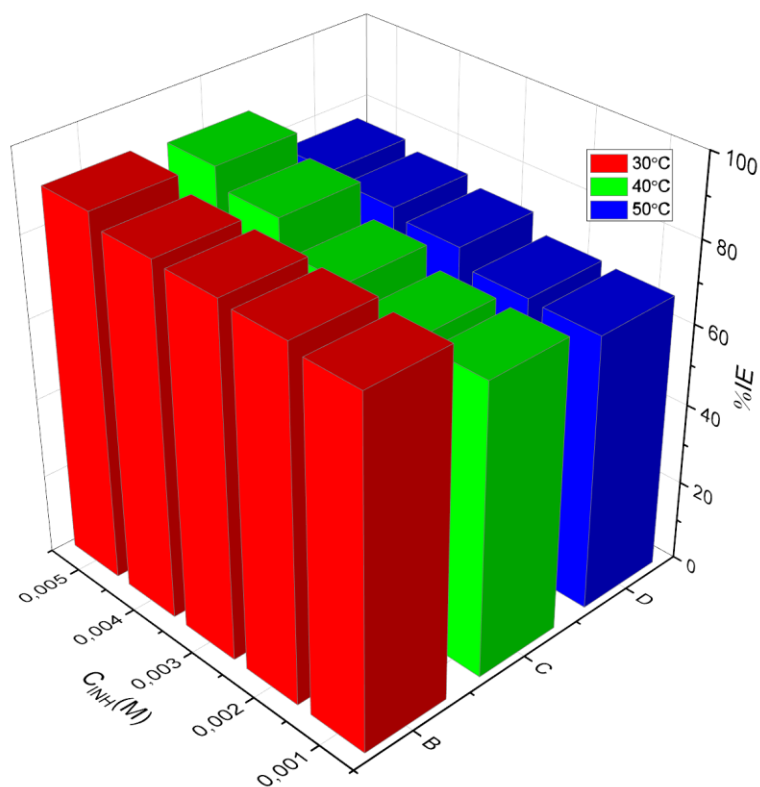


Figure 6. 8: The inhibition efficiency- DPT inhibitor concentration at different temperatures (303K, 313K, and 323K).

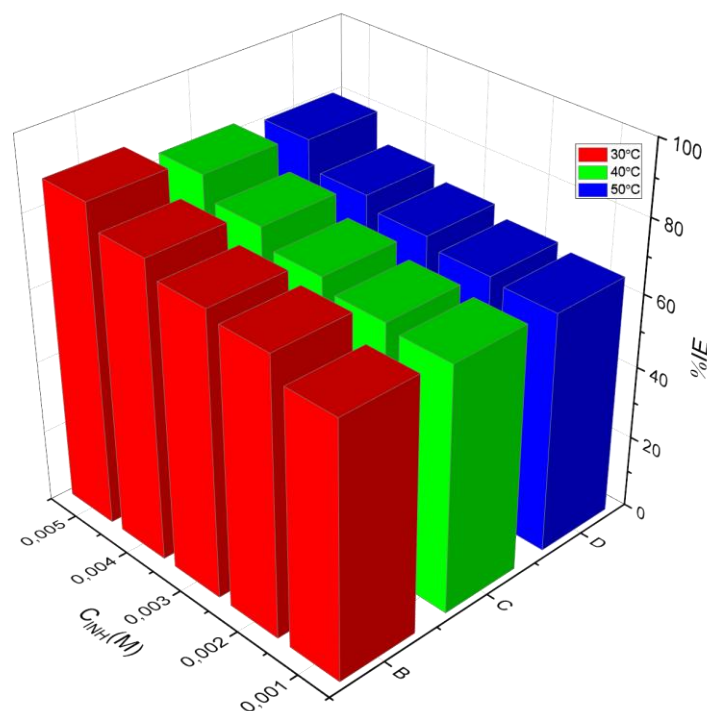


Figure 6. 9: The inhibition efficiency- DNT inhibitor concentration at different temperatures (303K, 313K, and 323K).

6.1.3. Activation parameters on mild steel for the inhibition process

The temperature dependency of inhibition efficiency is often expressed through Arrhenius, which relates the rate constant of a reaction to temperature and activation energy. Activation energy is a measure of the energy barrier that must be overcome for a chemical reaction to occur. The activation energy (E_a) has been calculated by applying the Arrhenius equation 5.1. and 5.2. E_a was calculated from the slope ($\frac{-E_a}{2.303R}$) of the straight lines obtained by plotting the log of corrosion rate obtained by weight loss measurement versus $1/T$ Figure 6.4[294]. Entropy (ΔS_a) and enthalpy (ΔH_a) of the activation energy were also computed using the transition state equation 5.3 to gain a better understanding of the energy change and structural rearrangement that occur during a reaction transition state. The values of ΔH_a and ΔS_a are deduced by plotting a linear fit of $\log(C_R/T)$ against $1/T$ in Figures 6.11-6.15 with a slope of $\frac{-\Delta H_a}{2.303R}$ and intercepts of $\log\left(\frac{R}{Nh}\right) + \frac{\Delta S_a}{2.303R}$ [296, 305]. The E_a , ΔS_a , and ΔH_a are tabulated in Table 6.1.

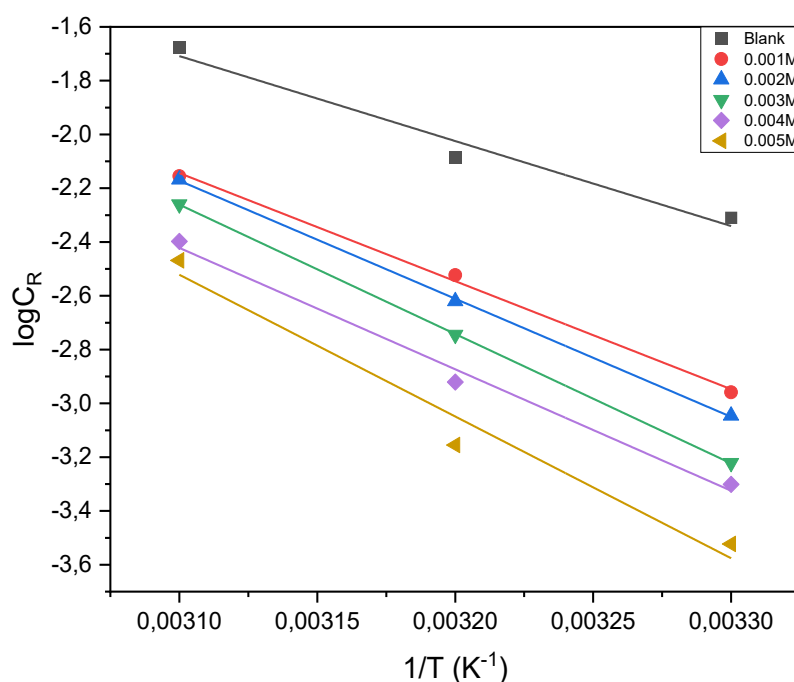


Figure 6. 10: Arrhenius plot at a different concentration of DMT

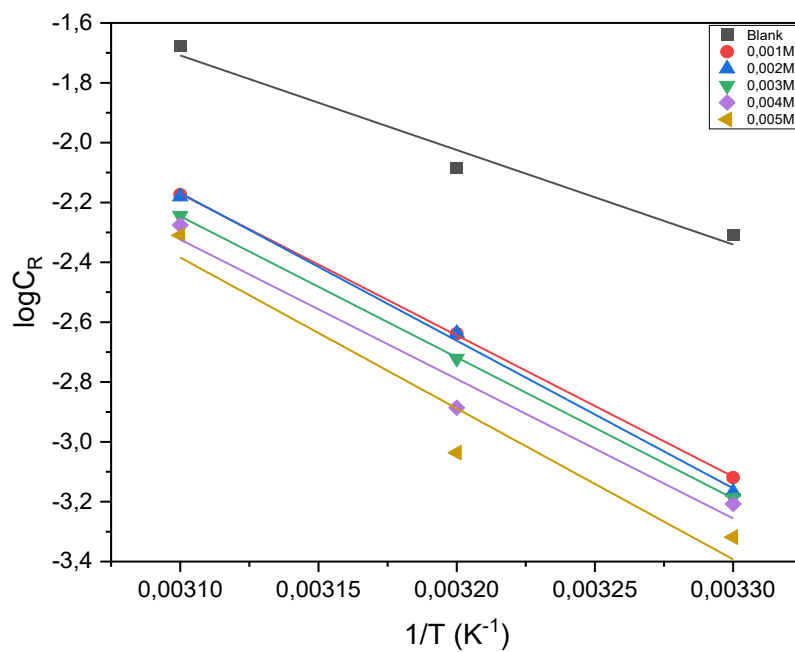


Figure 6. 11: Arrhenius plot at a different concentration of DPT

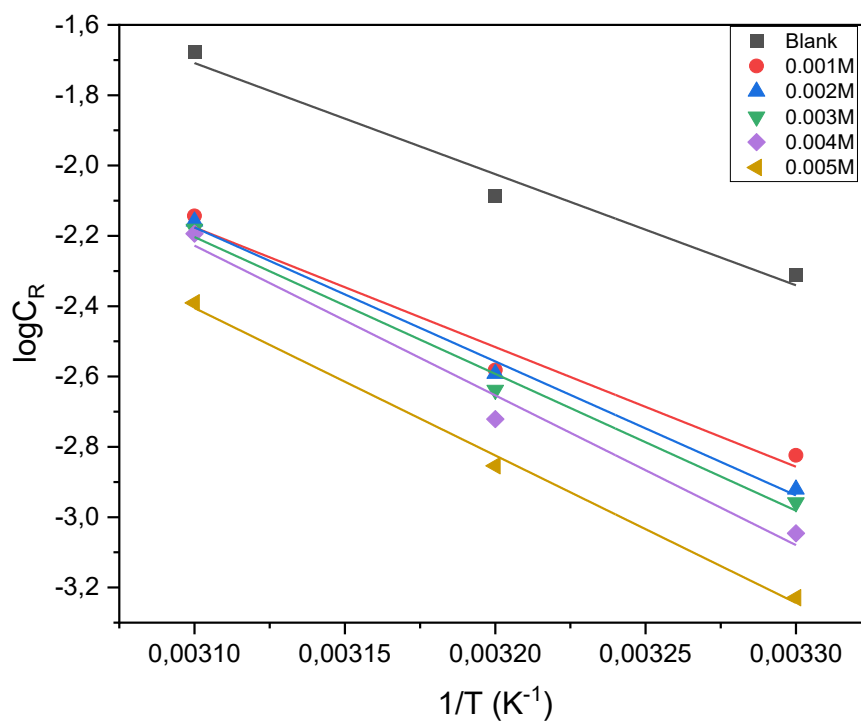


Figure 6. 12: Arrhenius plot at a different concentration of DNT

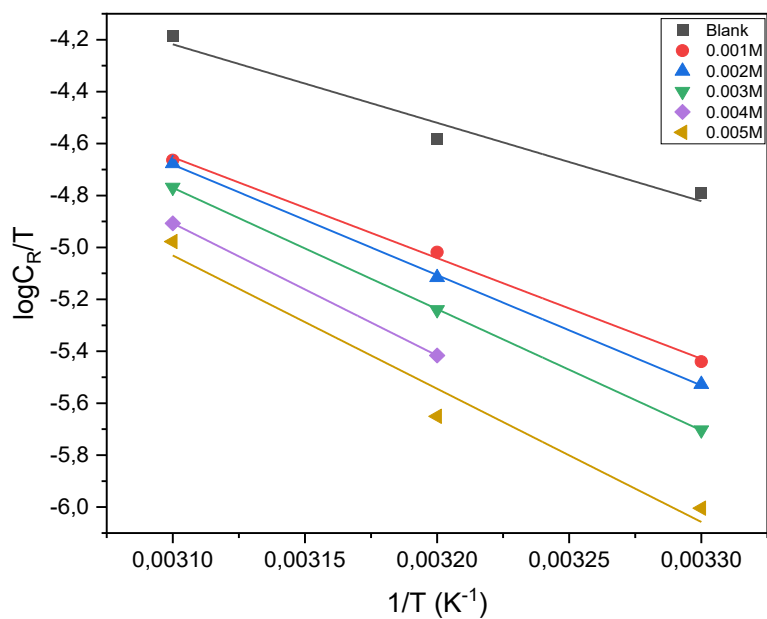


Figure 6. 13: Transition plot at different DPT inhibitor concentrations

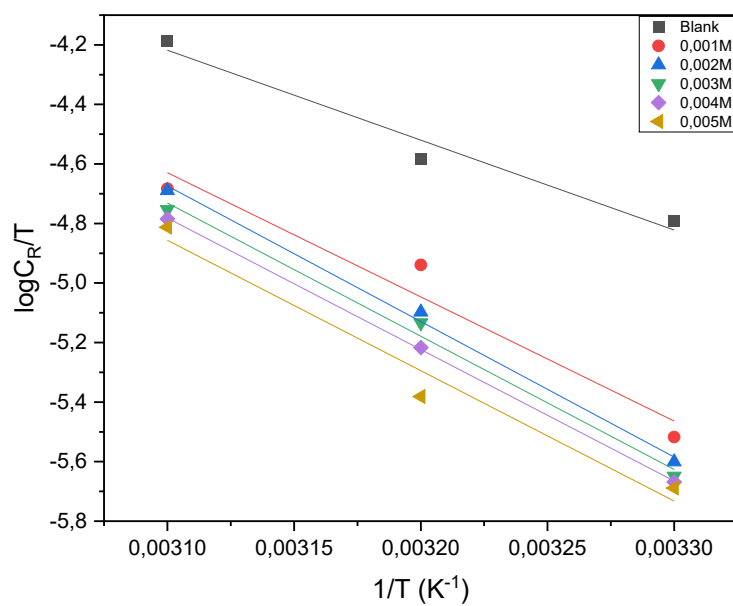


Figure 6. 14: Transition plot at different DMT inhibitor concentrations

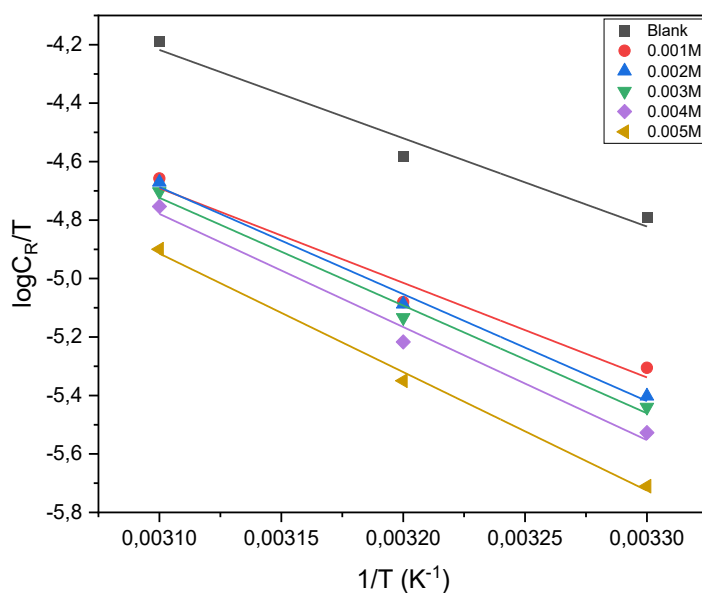


Figure 6. 15: Transition plot at different DNT inhibitor concentrations

Table 6.2 shows that the acid-metal reaction inhibitor's E_a is higher than that of the acid-meal reaction. This demonstrates that the formation of an inhibitor-metal-activated complex, which slowed down MS dissolution, was achieved by substituting water molecules on the metal surface. For MS, the activated complex is defined as $\text{Fe-H}_2\text{O}$ in the absence of an inhibitor from the corrosive solution. During corrosion, this complex breaks down to produce Fe^{2+} , H_2 , and OH^- .

Table 6.2. of corrosion inhibition for DMT, DPT, and DNT inhibitors shows positive values of the enthalpy change (ΔH), referring to an endothermic behaviour related to the interaction between inhibitor compounds and the Ms surface. The presence of an energy barrier to the corrosion process is thought to be the cause of endothermic behaviour, which indicates that energy is absorbed during the adsorption process. In contrast to the uninhibited solution, the inhibited solution's ΔS values are in Table 6.2. indicate a reduction in disorder during the activation process. This could be attributed to a more ordered or structured adsorption of the inhibitor molecules on the metal surface. The inhibitor may cause molecules to arrange themselves more orderly, which could reduce disorder during the activation process.

Table 6. 2: Activation parameters for DMT, DPT, and DNT on Ms in 1M HCl.

Concentration	Ea (KJ/mol)	ΔH (kJ /mol)	$-\Delta S$ (J/mol.K)
Blank	60.5145	57.8530	98.9833
DMT			
0.001	76.9332	74.2813	56.3880
0.002	84.0847	81.4327	34.7574
0.003	92.1169	89.4554	11.5932
0.004	86.4589	97.4972	-10.7131
0.005	100.9441	98.2822	-10.7795
DPT			
0.001	90.4893	91.2552	4.1814
0.002	94.4911	91.8392	2.5577
0.003	90.2692	87.6747	17.0048
0.004	89.2161	86.5546	21.7910
0.005	96.5875	94.5294	-1.8824
DNT			
0.001	65.1672	61.9792	95.2509
0.002	72.9697	70.0689	70.1050
0.003	74.5015	70.5572	69.2893
0.004	81.5572	74.0898	59.3922
0.005	80.2935	77.6320	51.0076

6.1.4. Adsorption isotherm

The mechanism of corrosion inhibition can be explained based on the adsorption behavior of inhibitors on the metal surface. Adsorption is dependent on the inhibitor's structure, the metal type and surface characteristics, and nature of the corrosion media, temperature, and the electrochemical potential of the metal-solution interface. Additionally, the adsorption offers details on the interactions that take place between the adsorbed molecules and the metal surface. To fit the experimental data of the current work, two mathematical relationships for the Langmuir adsorption isotherms, such as Langmuir and Temkin, have been proposed. The best results were obtained fitted Langmuir and Temkin adsorption isotherm according to equation 3.4 with the regression coefficient(R^2) values closer to unity. The important data such as the correlation coefficients (R^2) of DMT, DPT, and DNT for Langmuir and Temkin adsorption isotherm at different temperatures are recorded in Table 6.3.

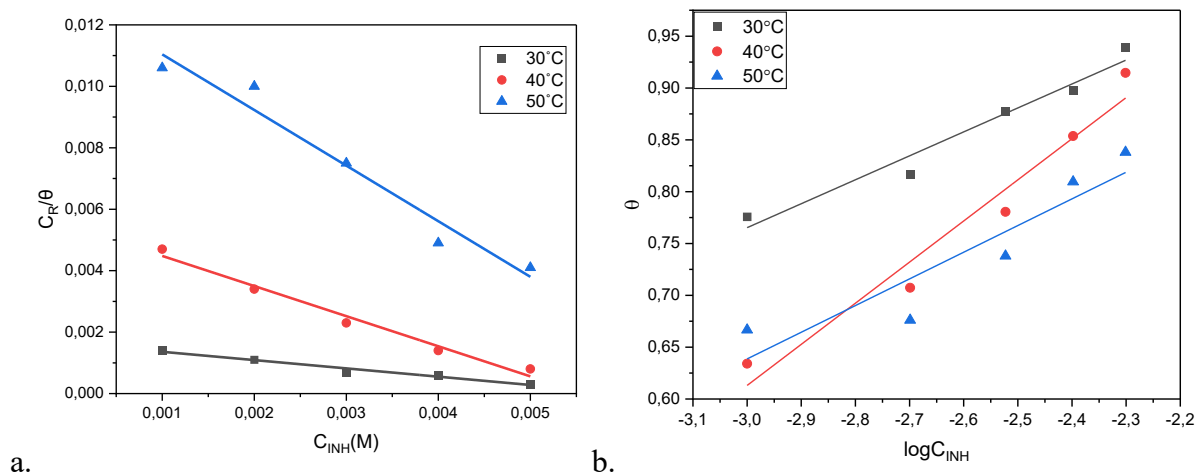


Figure 6. 16: Adsorption isotherm parameters (a. Langmuir and b. Temkin adsorption isotherm) for DMT on the MS surface at different temperatures.

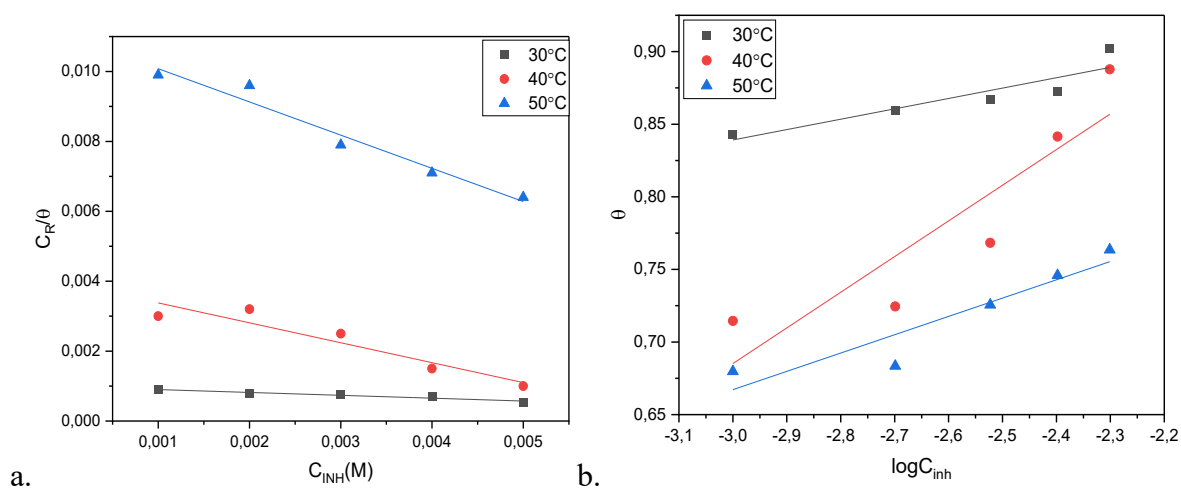


Figure 6. 17: Adsorption isotherm parameters (a. Langmuir and b. Temkin adsorption isotherm) for DPT on the MS surface at different temperatures.

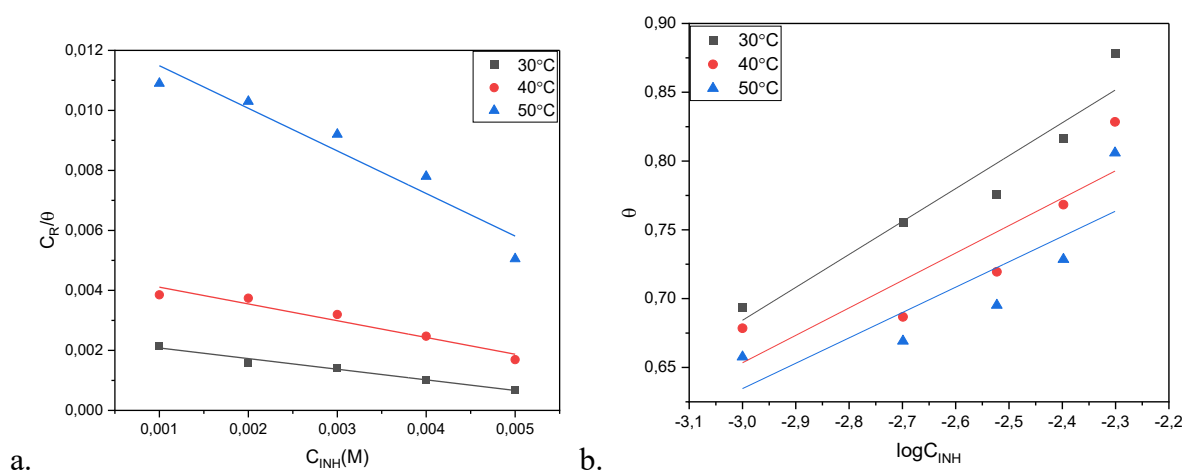


Figure 6. 18: Adsorption isotherm parameters (a. Langmuir and b. Temkin adsorption isotherm) for DNT on the MS surface at different temperatures.

Table 6. 3: The correlation coefficients (R^2) of DMT, DPT, and DNT for Langmuir and Temkin adsorption isotherm at different temperatures.

Adsorption isotherm types	Temperature (K)	R^2
DMT		
Langmuir	303	0.9682
	313	0.9828
	323	0.9516
Temkin	303	0.9630
	313	0.9571
	323	0.8495
DPT		
Langmuir	303	0.9196
	313	0.8897
	323	0.9613
Temkin	303	0.83223
	313	0.81233
	323	0.87331
DNT		
Langmuir	303	0.9786
	313	0.9453
	323	0.9262
Temkin	303	0.9222
	313	0.7763
	323	0.7308

Table 6. 4: Langmuir adsorption isotherm calculated parameters for DMT, DPT, and DNT on the MS surface at different temperatures.

Inhibitor	Temperature (K)	K_{ads} (L/mol)	$-\Delta G^{\circ}_{ads}$ (kJ/mol)	$-\Delta H^{\circ}_{ads}$ (kJ/mol)	ΔS°_{ads} (J/mol.K)
DMT	303	609.756	26.27	23.79	0.0081
	313	182.815	24.01		0.0007
	323	78.003	22.49		-0.0040
DPT	303	1018.3299	27.5652	27.85	-0.0009
	313	253.1645	24.8529		-0.0095
	323	90.6618	22.8892		-0.0153
DNT	303	409.8360	24.5117	19.28	-0.1445
	313	214.1327	22.2373		-0.1326
	323	77.4593	21.4334		-0.1260

Table 6. 5: The K_L values for DMT, DPT, and DNT at varying concentrations at 303 to 323 K for MS corrosion in 1 M HCl calculated from weight loss Langmuir isotherm parameters.

Inhibitors	Concentration (M)	K_L		
		303K	313K	323K
DMT	0.001	0.6212	0.8454	0.9276
	0.002	0.4505	0.7322	0.8650
	0.003	0.3534	0.6458	0.8103
	0.004	0.2907	0.5776	0.7621
	0.005	0.2469	0.5224	0.7194
Mean		0.3925	0.6646	0.8168
DPT	0.001	0.4954	0.7979	0.9168
	0.002	0.3293	0.6638	0.8465
	0.003	0.2466	0.5683	0.7861
	0.004	0.1971	0.4968	0.7338
	0.005	0.1641	0.4413	0.6880
Mean		0.2865	0.5936	0.7942
DNT	0.001	0.7093	0.8236	0.9281
	0.002	0.5495	0.7001	0.8658
	0.003	0.4485	0.6088	0.8114
	0.004	0.3788	0.5385	0.7634
	0.005	0.3279	0.4828	0.7208
Mean		0.4828	0.6307	0.8179

A greater value of K_{ads} shows significant adsorption of the inhibitor molecules onto the metal surface. This leads to a reduction in the corrosion rate since the inhibitor covers the metal surface, preventing the corrosive agent from accessing it. Furthermore, the thermodynamics of this process are favorable. A low K_{ads} indicates a less thermodynamically favorable situation with lower adsorption of the inhibitor onto the metal surface, leading to low inhibition effectiveness. Table 6.4 data reveals that the K_{ads} values exhibit both high and low values, indicating the presence of both strong and weak interactions between DMT, DPT, and DNT inhibitors on mild steel via physical electrostatic attraction and chemical adsorption. The interaction between the metal's surface and the extracts during corrosion inhibition can be characterized using the ΔG°_{ads} obtained from K_{ads} via the expression in equation 5.5. The negative value of ΔG°_{ads} indicates the adsorption of the inhibitor onto the metal surface is spontaneous and thermodynamically favorable. This leads to the formation of a stable protective layer, enhancing the inhibitor's effectiveness in preventing corrosion. The magnitude of the negative ΔG°_{ads} also helps determine whether the adsorption is primarily physical or chemical. If the value of ΔG°_{ads} falls within the range of -20 kJ/mol, it often indicates the occurrence of physical adsorption (physisorption). The inhibitor is adsorbed onto the surface

through weak van der Waals forces or electrostatic interactions during this process. Chemical adsorption, also known as chemisorption, occurs when chemical bonds are created between the inhibitor molecules and the metal surface. This type of adsorption is indicated by energy values of more than -40 kJ/mol. Chemisorption often denotes a stronger and long-lasting form of adsorption.

The data obtained in Table 6.4 for Langmuir isotherm adsorption indicate mixed-type adsorption with a value between -20 kJ/mol. This suggests that the interaction of DMT, DPT, and DNT inhibitors on mild steel occurs through electrostatic and chemical bonding. The $\Delta H^{\circ}_{\text{ads}}$ values indicate that the adsorption of the DMT, DPT, and DNT inhibitor onto the metal surface is an exothermic process, releasing energy stabilizing the system, and effectively adsorbing onto the MS surface in an organized manner through the entropy values. The K_L values provide insight into the adsorption process, specifically indicating whether it is favorable or unfavorable. The K_L values for the inhibitors DMT, DPT, and DNT are in Table 6.5. vary between 0 to 1, indicating a favorable adsorption process. This is crucial for achieving efficient corrosion inhibition. The effectiveness of the inhibitors decreases as the temperature rises. This is evident from the K_L values obtained for different inhibitors at temperatures of 303K, 313K, and 323K. At a higher concentration of 0.005M, the K_L values for DMT increase from 0.3925, 0.6646, and 0.8168, respectively. The K_L value for DPT increases sequentially with temperature, with values of 0.2865, 0.5936, and 0.7942. The K_L values for DNT exhibit an incremental trend of 0.4828, 0.6307, and 0.8179, respectively, as the temperature rises. Additionally, it can be noted that the inhibitors exhibit greater favorability at lower temperatures compared to higher temperatures[398-402].

6.2. Open circuit potential (OCP) with immersion period

The Open Circuit Potential (OCP) measurements provide a critical reference for PDP and EIS techniques, enabling accurate and meaningful analysis of corrosion processes and inhibitor performance. By establishing the system's resting potential, OCP ensures that subsequent electrochemical tests reflect the true behavior of the metal in its natural state, thereby enhancing the reliability and interpretability of the results[403-406]. The OCP measurement in a 1M HCl solution with and without the DMT, DPT, and DNT inhibitors is represented in Figures 6.19-6.21. The OCP tends to stabilize without the inhibitor at a more negative potential, indicating a higher rate of metal dissolution and corrosion. In the presence of DMT, DPT, and DNT inhibitors the OCP for MS gradually moved positive and negative during the first 250 seconds

of immersion until it reached stable values in the blank solution at around 1000 seconds. The drop in MS potential could be due to the dissolution of the native oxide that had previously formed on the MS surface due to exposure to the atmosphere. Figure 6.19 shows the OCP of the DMT inhibitor for MS, 0.002M, 0.003M, 0.004M, and 0.005M show a similar trend except for 0.002M which showed movement in a negative direction from the start. The negative direction in the presence of DMT suggests the gradual formation of a protective film on the MS electrode surface. Figure 6.20 shows OCP for DPT, in which 0.00M moves to the negative direction initially. The stable values in DPT inhibitor for 0.001M and 0.002M start at the 2000s, 0.003M, 0.004M, and 0.005M the stable movement starts at 500s. Figure 6.21. when the DNT is introduced the OCP moves toward a positive with an increase in inhibitor concentration.

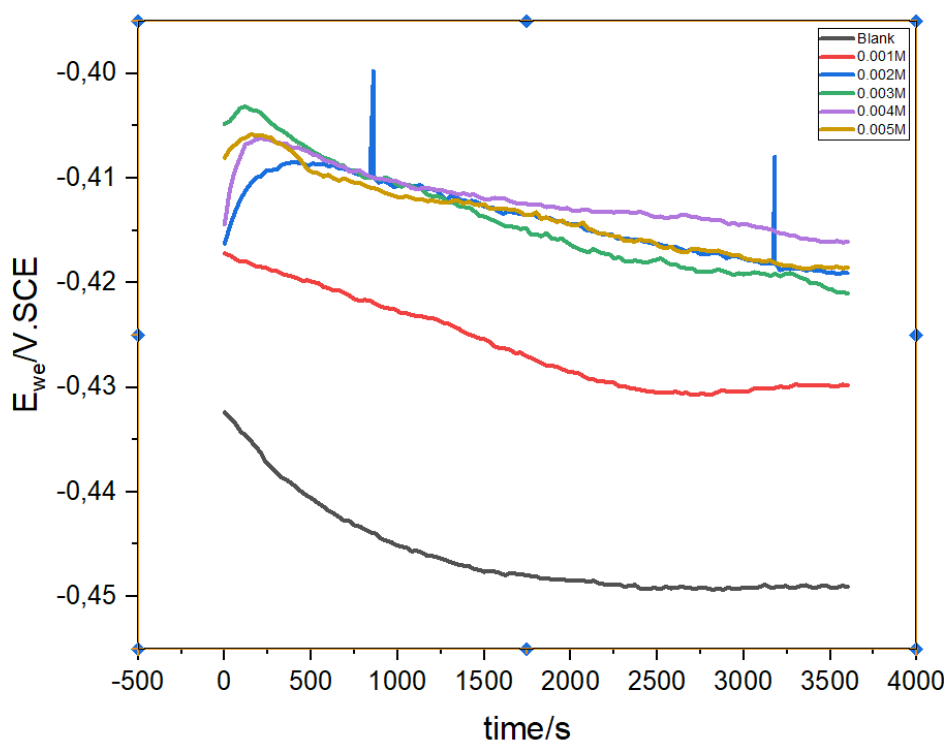


Figure 6. 19: Evolution of open-circuit potential (E_{OCP}) versus exposure time for MS with and without DMT in 1 M HCl solution.

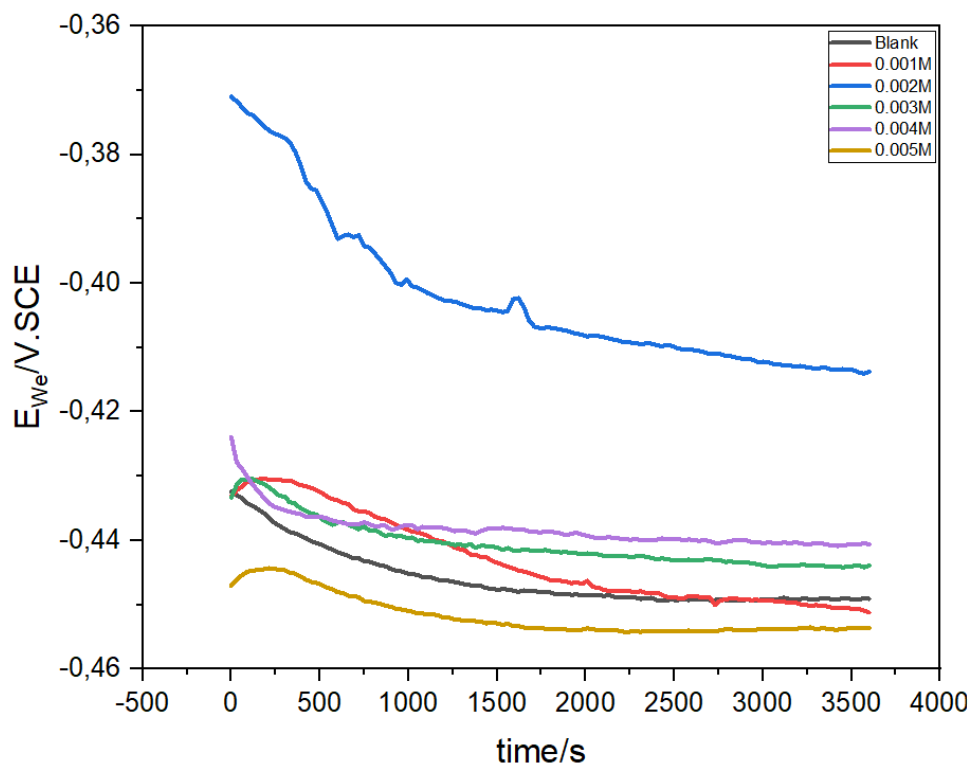


Figure 6. 20: Evolution of open-circuit potential (E_{OCP}) versus exposure time for MS with and without DPT in 1 M HCl solution.

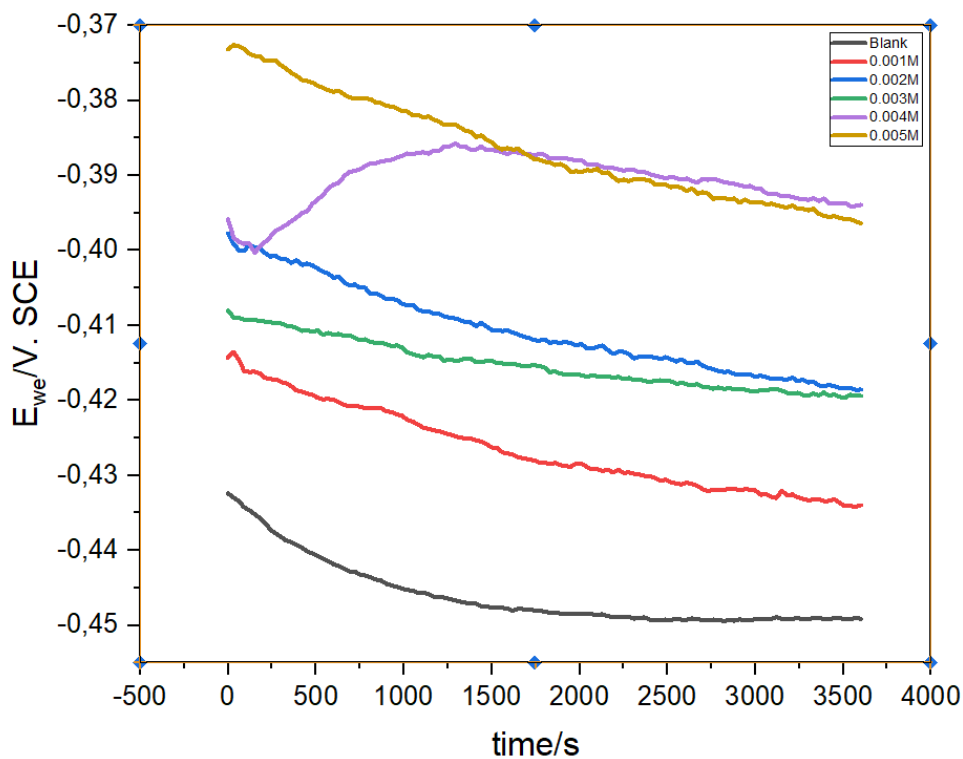


Figure 6. 21: Evolution of open-circuit potential (E_{OCP}) versus exposure time for MS with and without DNT in 1 M HCl solution.

6.3. Electrochemical impedance spectroscopy (EIS)

6.3.1. Electrochemical impedance spectroscopy of DMT, DPT, and DNT

The Nyquist plots are represented in Figures 6.22-6.24 and Bode plot in Figures 6.27-6.29 for mild steel in corrosive solution after 1 hour of immersion. A single charge transfer mechanism is involved in the acid dissolution of steel, as shown by the capacitive loop seen in the Nyquist plots for the inhibited and uninhibited cases. The diameter of the semi-circle of the Nyquist plot increases with the DMT, DPT, and DNT concentration. This finding implies that the tested inhibitors form protective films on the metal surface, hindering the charge transfer processes associated with corrosion. As the inhibitor concentration increases, more inhibitor molecules adsorb onto the metal surface, resulting in thicker and more effective inhibitor films. These thicker films lead to higher resistance to charge transfer, which is reflected in the Nyquist plot as an increase in the diameter of the semicircle. Furthermore, the Nyquist plots of the inhibited and uninhibited systems have comparable shapes. Bode modulus plot in the presence of an DMT, DPT, and DNT inhibitor increases the impedance at low frequencies. This is because the inhibitor forms a protective layer on the electrode surface, increasing the charge transfer resistance (R_{ct}). As a result, the impedance modulus $|Z|$ increases. The phase angle plot shifts to more negative values at intermediate frequencies, when the inhibitor is introduced indicating an increased capacitive behavior due to the formation of a protective layer or adsorption of the DMT, DPT, and DNT inhibitor molecules on the MS surface.

A simple equivalent circuit model, shown in Figure 3, including the solution resistance R_s and the double layer capacitance C_{dl} , positioned in parallel to the charge transfer resistance R_{ct} , was fitted to the experimental data to analyse the impedance spectra of the Nyquist plots. The results from electrochemical parameters are tabulated in Table 6.5.

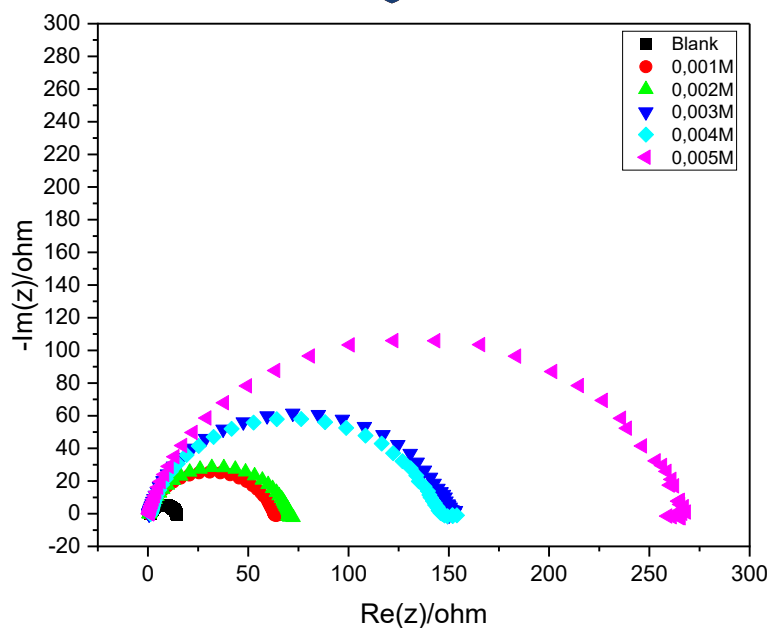


Figure 6. 22: Nyquist plot for MS in 1M HCl in the absence and presence of different concentrations of DMT

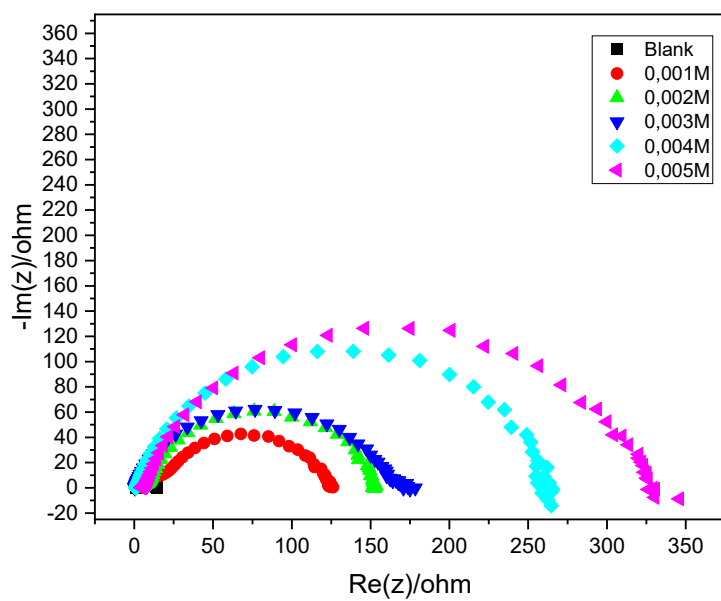


Figure 6. 23: Nyquist plot for MS in 1M HCl in the absence and presence of different concentrations of DPT

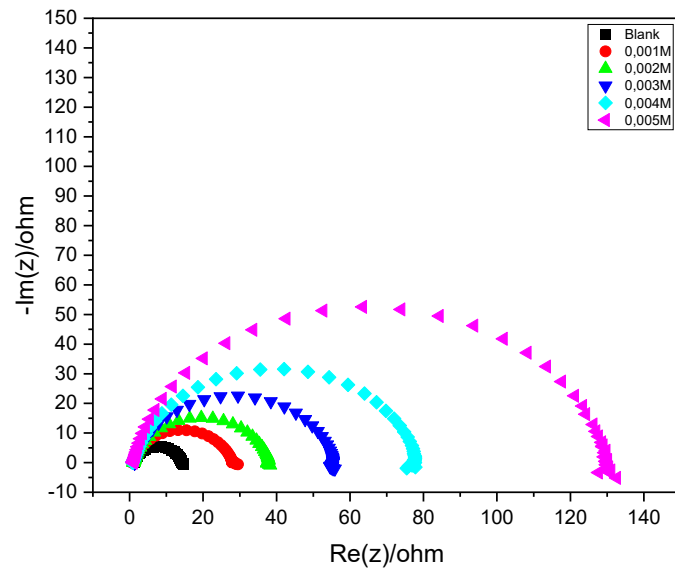


Figure 6. 24: Nyquist plot for MS in 1M HCl in the absence and presence of different concentrations of DNT

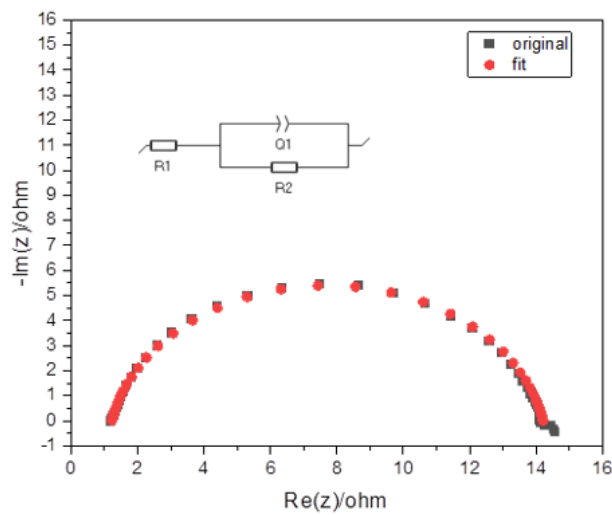


Figure 6. 25: Fitting circuit of blank and inhibitors(DMT, DPT, and DNT)

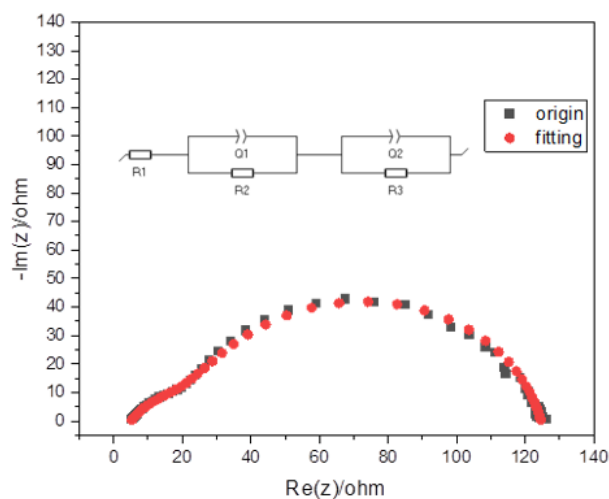
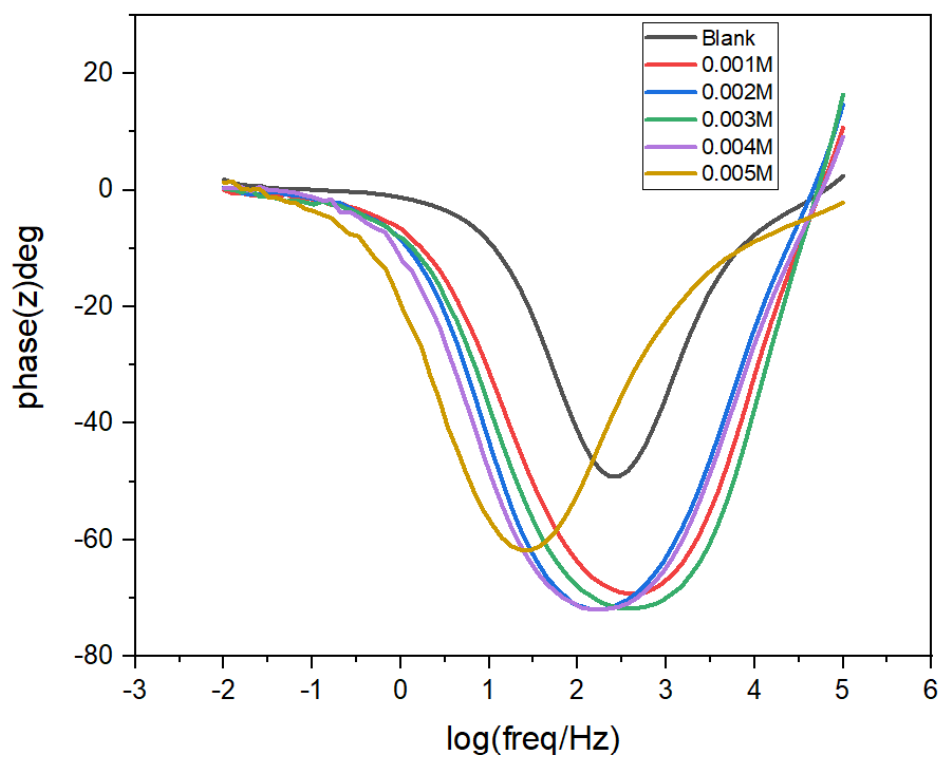
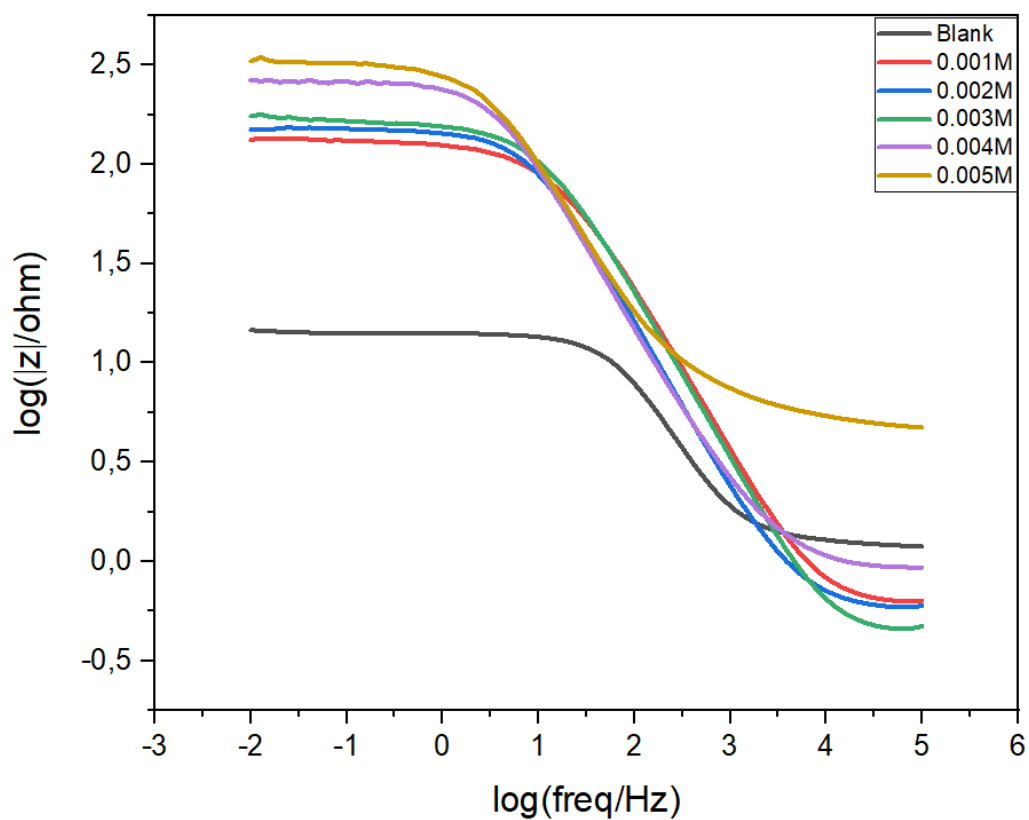


Figure 6. 26: fitting circuit for DPT inhibitor concentration (0.001M and 0.002M)

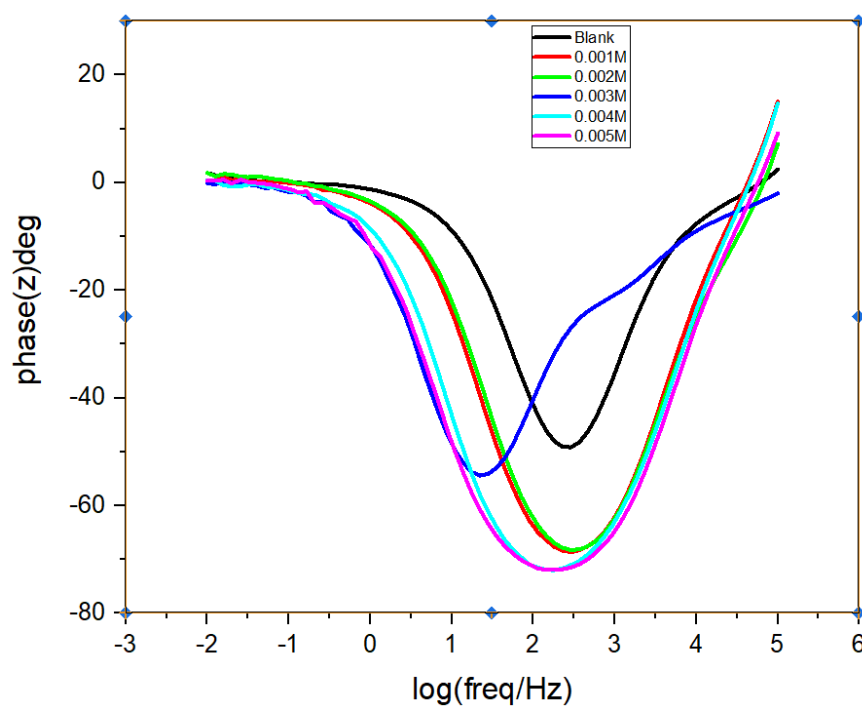


a.

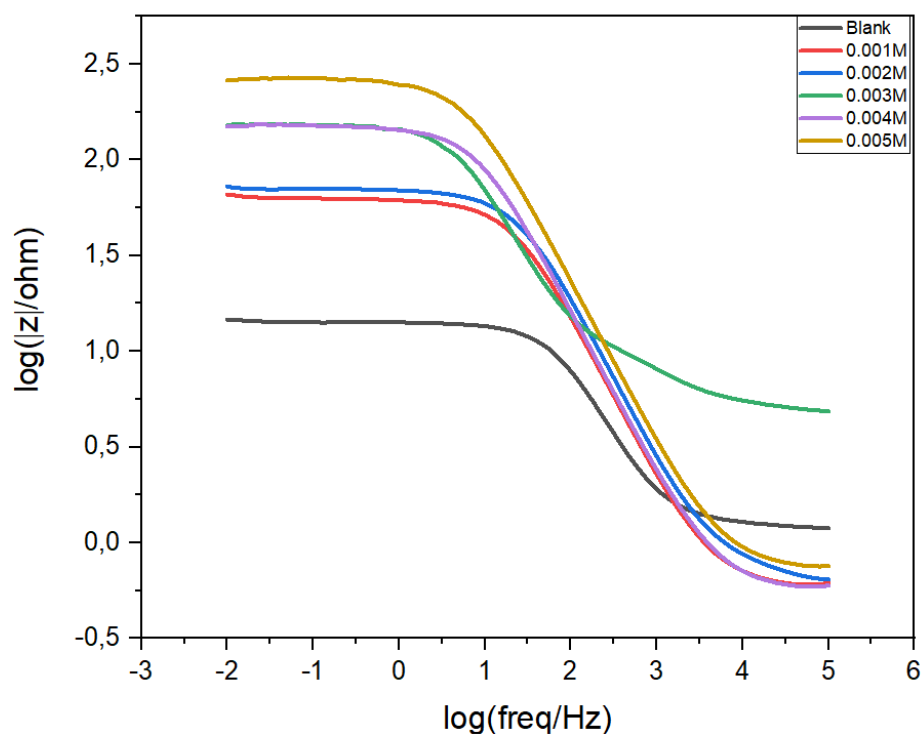


b.

Figure 6. 27: (a. phase angle and b.Bode modulus) plot in 1 M HCl solution with and without DMT at various concentrations at 303 K

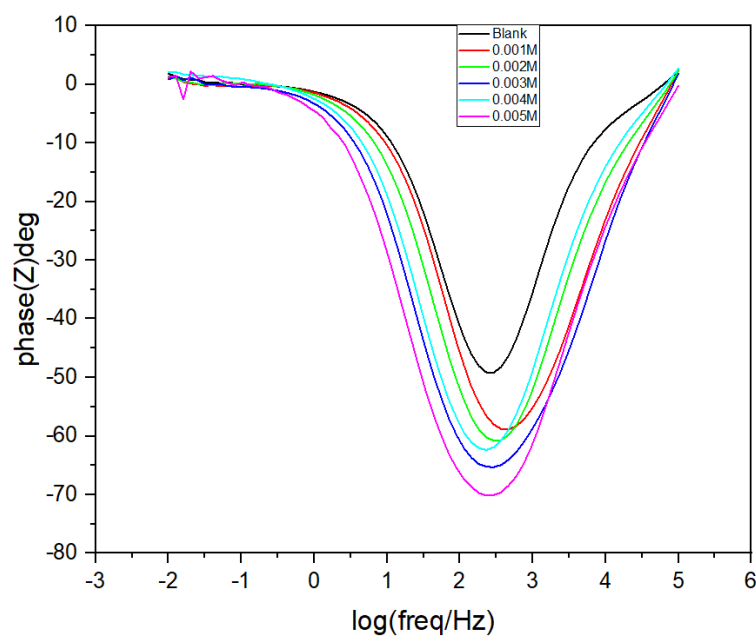


a.



b.

Figure 6. 28: a. phase angle b. Bode modulus plot in 1 M HCl solution with and without DPT at various concentrations at 303 K



a.

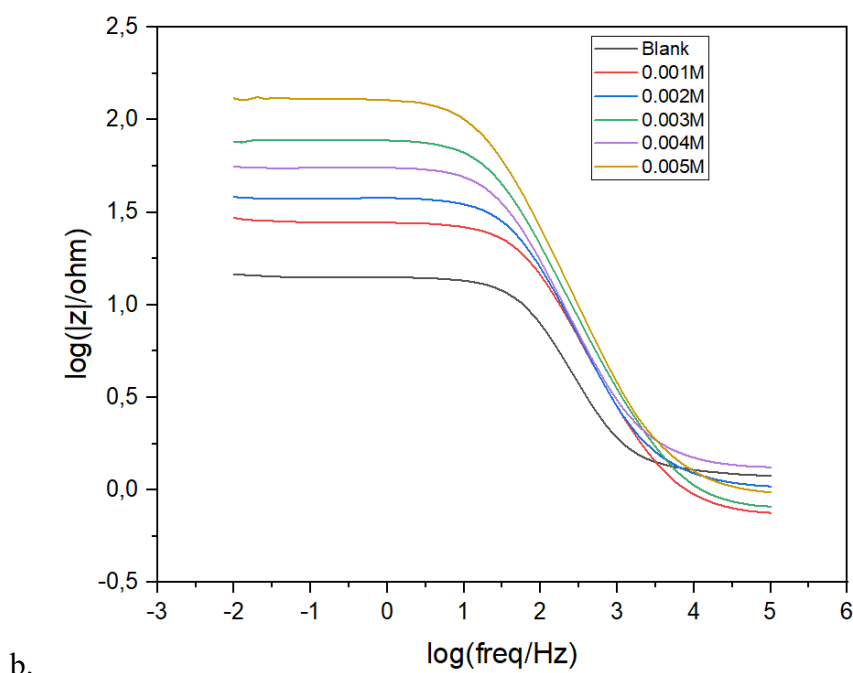


Figure 6. 29: Bode modulus and phase angle plot in 1 M HCl solution with and without DNT at various concentrations at 303 K

After examining Table 6.6, it can be concluded that the formation of a protective film on the metal-solution interface is indicated by the R_{ct} values increasing as the inhibitors' concentration increases. The formation of a protective film increases the coverage and leads to a thicker and more continuous inhibitor film, which impedes the movement of ions and electrons across the metal-electrolyte interface[407, 408]; that's why the R_{ct} increases. As more inhibitor molecules occupy the available adsorption sites, the effective surface area for ion accumulation decreases, leading to a reduction in double-layer capacitance[409, 410]. The value of double-layer capacitance (C_{dl}) decreases with the presence of the inhibitor, increasing the inhibition efficiency(%IE). Furthermore, the addition of the inhibitor increases the value of the relaxation time constant, indicating the influence of inhibitors on the dynamics of charge transfer processes and relaxation phenomena at the metal-electrolyte interface. These effects can be attributed to various mechanisms, including slower kinetics, increased diffusion limitations, inhibitor film formation, or surface morphology modifications [411, 412].

Table 6. 6: Electrochemical parameters of mild steel in 1M HCl solution in the presence of DMT. DPT. DNT inhibitor at 303K.

Inhibitors	Concentration (M)	R_s (Ω /cm ²)	R_{ct}/R_p (Ω /cm ²)	N	C_{dl} ($\mu F/cm^2$)	$\tau(s)$	%IE _{EIS}
Blank	000	1.23	12.99	0.8844	171.11	0.0022	-
DMT	0.001	0.6160	62.04	0.8869	115.03	0.0071	79.06
	0.002	0.6879	69.67	0.8739	102.43	0.0071	81.35
	0.003	1.3240	144.30	0.8750	99.36	0.0143	90.99
	0.004	0.6010	149.80	0.8791	121.28	0.0182	91.33
	0.005	0.7595	264.40	0.8690	109.64	0.0289	95.09
DPT	0.001	5.13	118.40	0.8872	203.37	0.0230	88.96
	0.002	4.823	147.37	0.9063	87.803	0.0125	91.18
	0.003	0.4551	163.30	0.8720	220.05	0.0359	92.04
	0.004	0.9486	265.90	0.8458	177.09	0.0471	95.17
	0.005	5.392	330.40	0.8031	160.39	0.0529	96.07
DNT	0.001	0.7681	27.49	0.8477	80.91	0.0022	52.75
	0.002	1.0900	36.85	0.8702	96.19	0.0035	64.75
	0.003	1.3740	54.21	0.8745	104.48	0.0057	76.04
	0.004	0.8270	77.70	0.8467	91.85	0.0071	83.28
	0.005	1.0200	129.40	0.8736	69.88	0.0090	89.96

6.3.2. Electrochemical impedance spectroscopy of DMT, DPT, and DNT grafted with graphene oxide

The diameter of the semi-circle in the Nyquist plot expands when graphene oxide is applied to modify DMT, DPT, and DNT. The diameter increases observed when graphene oxide (GO) is combined with DMT, DPT, and DNT is attributed to the exceptional barrier qualities of GO, which is impervious to the majority of gases and liquids. When utilized as an inhibitor, graphene oxide (GO) can create a highly efficient physical barrier on the surface of the metal, thereby impeding the access of corrosive substances to the metal. The enhanced barrier property leads to an overall improvement in corrosion resistance, as seen by the enlarged diameter of the Nyquist plot. Graphene oxide (GO) possesses a significant surface area and contains functional groups, including hydroxyl, epoxy, and carboxyl groups, which can strongly interact with the metal surface. This enhances the adsorption of the inhibitor onto the metal surface, resulting in a more homogeneous and resilient protective layer [407, 408]. A

higher level of adsorption increases charge transfer resistance, resulting in a bigger diameter of the Nyquist plot. Figure 6.30 For DMT inhibitor when GO is added the lowest concentration charge transfer increases from 120Ω to 179Ω and the highest concentration for this study increases from 329Ω to 397.43Ω . For DPT in Figure 6.31 the lowest and highest concentration for this study increases from 79.9Ω and 326Ω to 350Ω and 574Ω respectively. Figure 6.32, DNT increases from 28Ω and 130Ω to 250Ω and 550Ω at the lowest and highest concentrations respectively. A larger diameter in the Nyquist plot typically indicates higher R_{ct} . The %IE when the corrosive solution contains inhibitor + GO is higher than when the corrosive solution only contains DMT, DPT, and DNT inhibitors. This is because the combination of the inhibitor with GO can lead to synergistic effects where the combined properties of both materials result in superior corrosion protection compared to the inhibitor alone [180, 409]. These effects can include better film-forming abilities, improved mechanical strength, and enhanced electrical properties, all contributing to increased charge transfer resistance which then increase %IE.

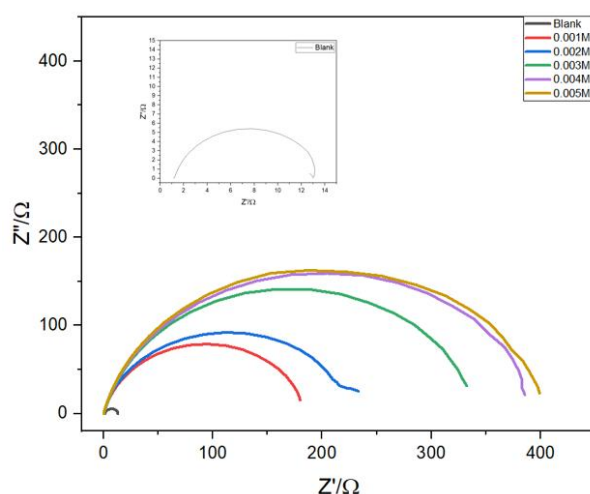


Figure 6. 30: Nyquist plot for DMT and DMT-GO on MS surface in 1M HCl at 303K

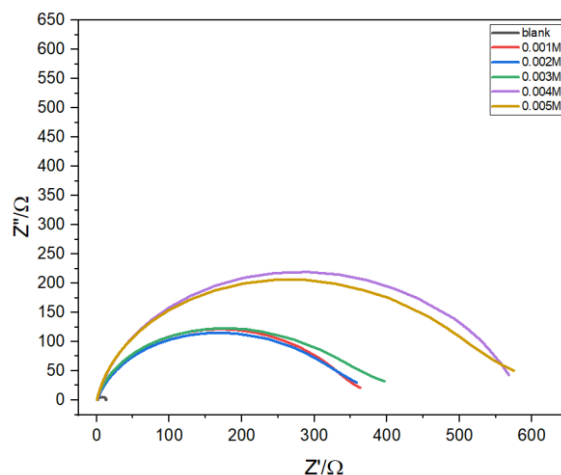


Figure 6. 31: Nyquist plot for DPT-GO on MS surface in 1M HCl at 303K

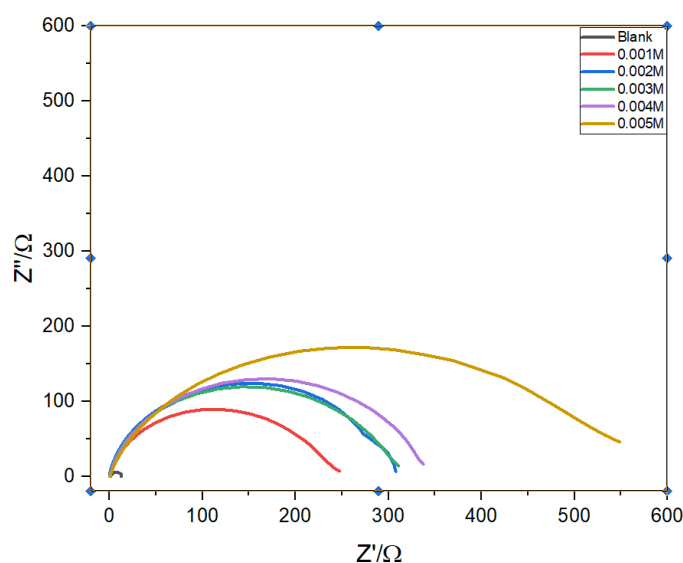


Figure 6. 32: Nyquist plot for DNT-GO on MS surface in 1M HCl at 303K

A larger diameter in the Nyquist plot typically indicates higher charge transfer resistance (R_{ct}), this was observed in Table 6.7. It is clear that when a drop of GO is added into DMT, DPT, and DNT inhibitor solution the charge transfer resistance increases, increasing the %IE. This is because the combination of the DMT, DPT, and DNT with GO can lead to synergistic effects where the combined properties of both materials result in superior corrosion protection compared to the inhibitor alone[180, 413]. For a high concentration (0.005M) the R_{ct} was $264.40 \Omega/\text{cm}^2$, $330.40 \Omega/\text{cm}^2$, and $129.40 \Omega/\text{cm}^2$ for DMT, DPT, and DNT respectively, and increased to $388.2815 \Omega/\text{cm}^2$, $534.1445 \Omega/\text{cm}^2$, $282.41 \Omega/\text{cm}^2$ for DMT-GO, DPT-GO, and DNT-GO respectively. These effects can include better film-forming abilities, improve mechanical strength, and enhance electrical properties, all contributing to increased charge transfer resistance which then increases %IE.

Table 6. 7: EIS data of MS corrosion in 1M HCl without and with different concentrations of DMT, DPT, and DNT inhibitor with GO at 303K.

Inhibitors	Concentration(M)	$R_s (\Omega/\text{cm}^2)$	$R_{ct}(\Omega/\text{cm}^2)$	$R_p (\Omega/\text{cm}^2)$	Θ	%IE _{EIS}
Blank	0	1.23	12.99	-	-	-
DMT-GO	0.001	0.3736	184.9164	185.29	0.9297	92.97
	0.002	0.2120	215.748	215.96	0.9398	93.98
	0.003	0.3860	341.754	342.14	0.9620	96.20

	0.004	0.2272	381.7528	381.98	0.9660	96.60
	0.005	0.2485	388.2815	388.53	0.9666	96.66
DPT-GO	0.001	1.4859	327.9741	329.46	0.9604	96.04
	0.002	0.6060	336.144	336.75	0.9614	96.14
	0.003	0.5056	344.6344	345.14	0.9623	96.23
	0.004	0.6525	558.0975	558.75	0.9767	97.67
	0.005	0.4055	534.1445	534.55	0.9757	97.57
DNT-GO	0.001	0.2936	114.17	113.8764	0.8862	88.62
	0.002	1.3069	137.71	136.4031	0.9056	90.56
	0.003	0.7654	193.06	192.2946	0.9327	93.27
	0.004	0.4583	209.37	208.9117	0.9380	93.80
	0.5580	282.41	281.8520	0.9540	95.40	0.005

6.3.3. Adsorption isotherm

The surface coverage degree (θ) data obtained from the EIS were utilized to ascertain the adsorption isotherm. The experimental data were analyzed and shown to obey Langmuir adsorption isotherm. Figure 6.33a-c shows the straight lines of $\frac{C_{inh}}{\theta}$ versus C_{inh} with the best linear relationship. Table 6.8, reveals that when the DMT, DPT, and DNT are modified with the GO the K_{ads} values become higher than unmodified ones, this indicates that the GO increases the effectiveness of the organic inhibitor. The ΔG_{ads} of the process was determined to be negative for all inhibitors employed, with values of -29.0124, -31.1518, and -27.1942 kJ/mol for DMT, DPT, and DNT respectively. The presence of a negative ΔG_{ads} value implies that the adsorption of the inhibitor onto the MS substrates is a spontaneous process. When the DMT, DPT, and DNT are grafted with GO the ΔG_{ads} increases to 34.5921, 36.5333, and 33.063 kJ/mol respectively. Typically, ΔG_{ads} values that are around -20 kJ/mol indicate reliable interactions between inhibitor molecules and charged steel substrate, known as physisorption. On the other hand, values higher than -40 kJ/mol suggest a chemical bonding, called chemisorption, where electrons are shared between the inhibitor molecules and the metal surface[414-420]. The ΔG_{ads} values of the examined inhibitor are closer to -20kJ/mol and -40kJ/mol indicating that this can be a physisorption or chemisorption (mixed-type) process.

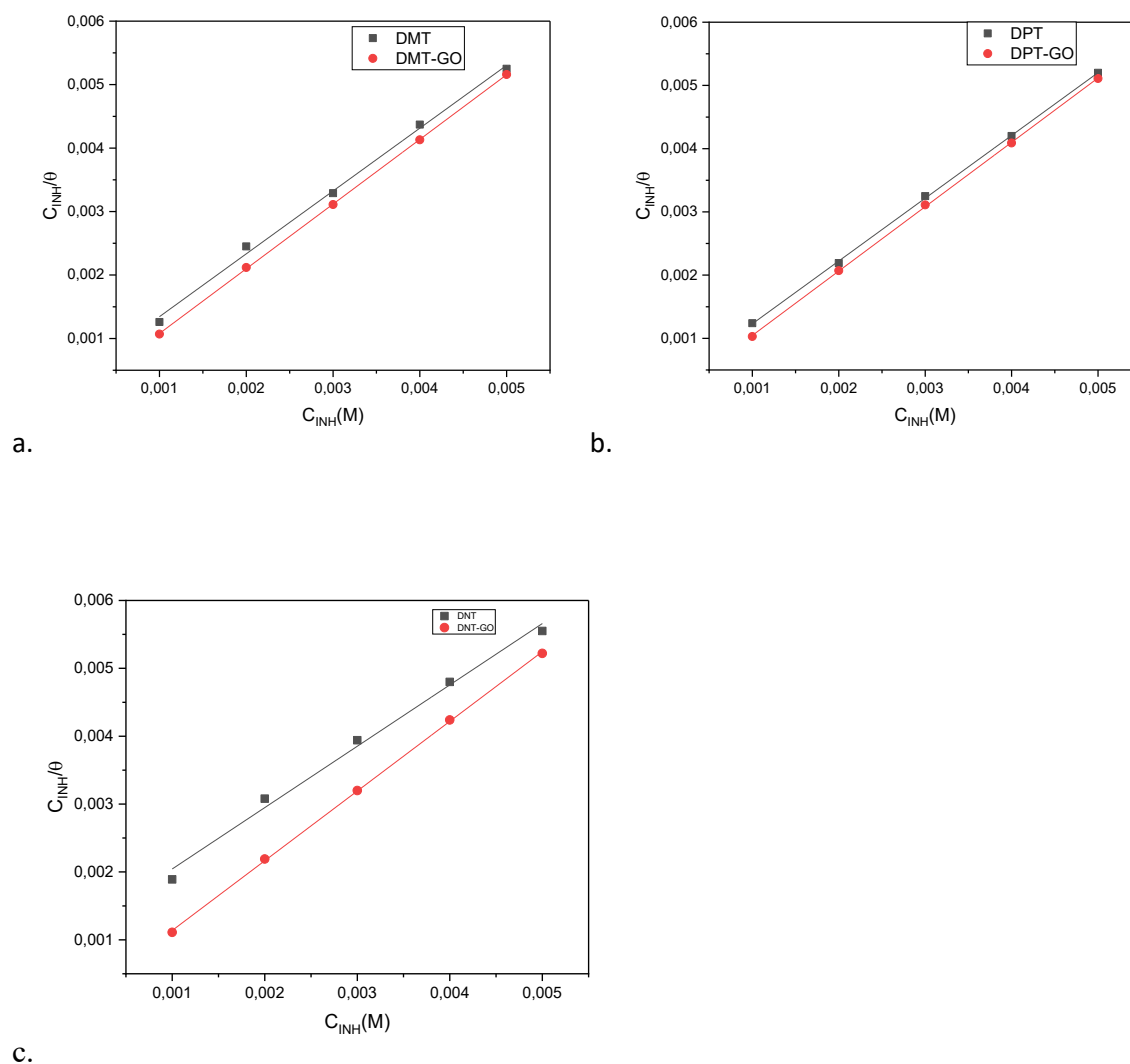


Figure 6. 33: Langmuir adsorption isotherm plot at 303K for various (a.DMT, b.DPT, and c. DNT) inhibitor concentrations.

Table 6. 8: adsorption isotherm parameters for DMT, DPT, and DNT and when it grafted with GO at 303K

Inhibitor	R^2	K_{ads} (L/mol)	$-\Delta G^o_{ads}$ (kJ/mol)
DMT	0.99624	1805.054	29.0124
DMT-GO	0.99930	16528.925	34.5921
DPT	0.99967	4219.409	31.1518
DPT-GO	0.99998	35714.285	36.5333
DNT	0.98981	877.192	27.1942
DNT-GO	0.99967	9009.009	33.063

6.4. Potentiodynamic polarization (PDP)

Figures 6.34-6.36 represent the Tafel polarization curves of uninhibited and inhibited MS corrosion at 303K. It can be observed that the corrosion current densities of both anodic and cathodic reactions significantly decreased after adding an increasing amount of DMT, DPT, and DNT inhibitors[407]. The significant reduction in anodic and cathodic branches is accompanied by a slight move of corrosion potential towards the anodic side. However, it is observed that each inhibitor's concentration has a different effect on the corrosion potential. Some added concentrations led to a visible move towards anodic corrosion potentials, whereas DNT had a slight move. The obtained corrosion parameters (corrosion current density, corrosion potential, efficiency, the anodic and cathodic Tafel slopes, and the anodic and cathodic interaction coefficient) are recorded in Table 6.9. It is observed that when the inhibitor is introduced the E_{corr} slightly shifted towards less negative values and the maximum shift is 52.666 mV towards the anodic region. According to Ahmed Al-Amiery et al.,[421] If E_{corr} is less than 85 mV, the inhibitor is considered a mixed-type corrosion inhibitor. In this study, all the inhibitors are mixed type inhibitors, implying that DMT, DPT, and DNT interfere with both the dissolution of the metal (anodic reaction) and the reduction of oxygen (cathodic reaction), thereby reducing the overall corrosion rate. The corrosion current density (i_{corr}) of MS in the presence of DMT, DPT, and DNT leads to a decrease in corrosion current densities by inhibiting both the anodic and cathodic reactions involved in corrosion, promoting the formation of a protective layer, and altering the electrochemical kinetics at the metal surface[422]. Continuous i_{corr} is indirectly proportional to inhibitor concentration as reflected in the %IE, which is markedly improved as the DMT, DPT, and DNT concentrations increased with 94.03%, 96.30%, and 92.34% respectively. Furthermore, as the concentration of the inhibitor increases, there is a change in the values of β_c and β_a , but no clear trend. The fact that the DMT, DPT, and DNT values of f_a and f_c in Table 6.9 are less than 1 suggests that the inhibitor molecules that were adsorbed affected both the cathodic and anodic reactions[255, 423-425].

When DMT, DPT, and DNT inhibitor is used the E_{corr} on the Tafel plot shifts towards less negative but when the Graphene oxide is added into the inhibitor solution the E_{corr} moves toward negative[426, 427]. This means that the inhibitor is effectively in slowing down the cathodic reactions, such as the reduction of oxygen or hydrogen evolution, thereby shifting the corrosion potential to a more negative value. The anodic and cathodic interaction coefficient (f_a and f_c) values further support the conclusion that the cathodic reaction is being inhibited

more significantly due to the f_a values being greater than f_c [428]. The GO affects the inhibitor reaction because the result without the GO indicates that the anodic reaction is denominationally inhibited.

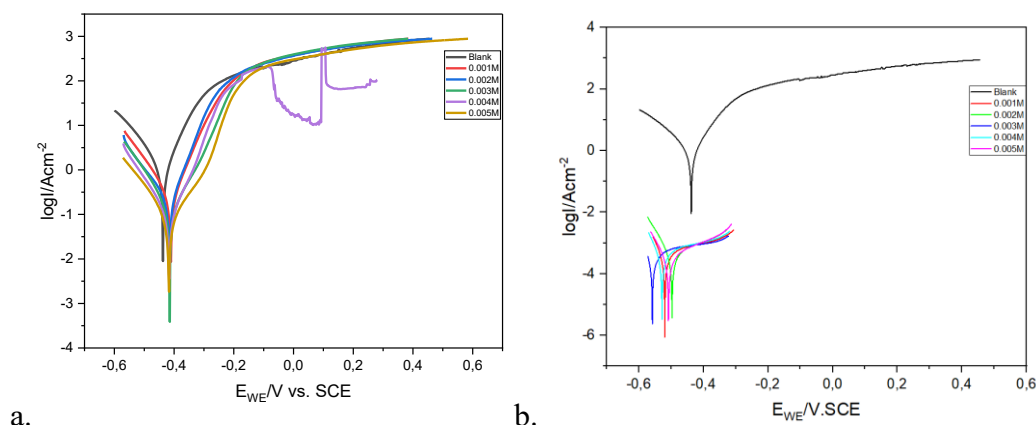


Figure 6. 34: Tafel PDP curves for MS dissolution in 1 M HCl with and without different concentrations of a. DMT and b DMT-GO at 303 K

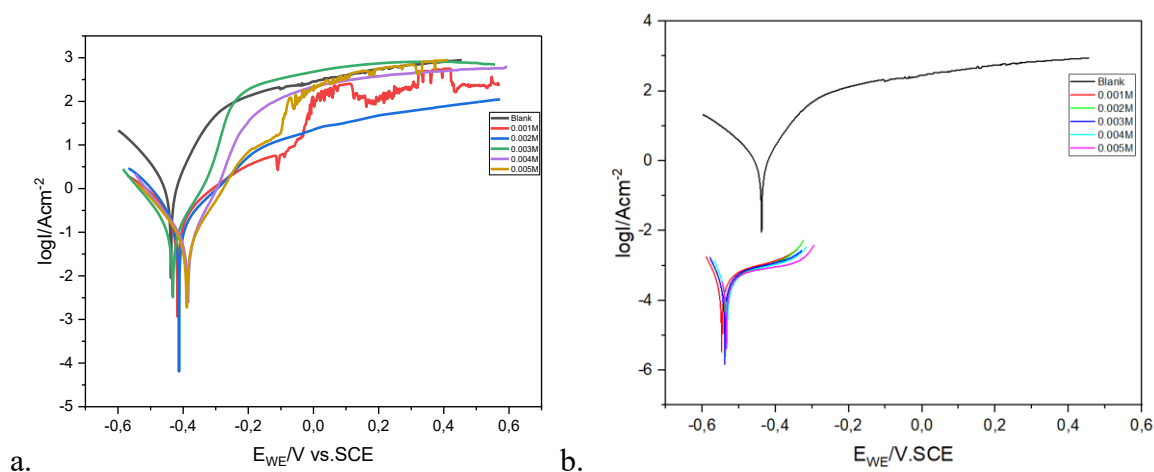


Figure 6. 35: Tafel PDP curves for MS dissolution in 1 M HCl with and without different concentrations of a. DPT and b DPT-GO at 303 K

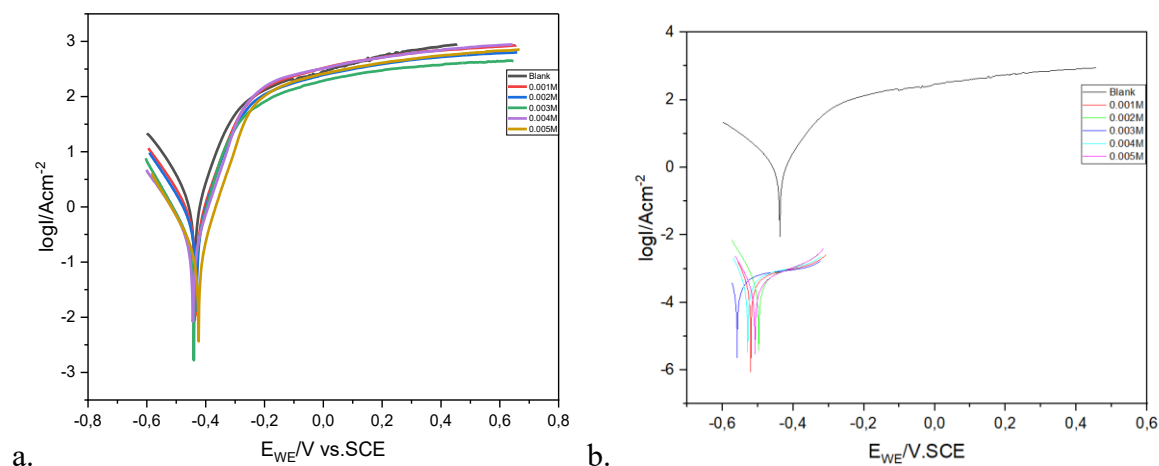


Figure 6. 36: Tafel PDP curves for MS dissolution in 1 M HCl with and without different concentrations of a. DNT and b DNT-GO at 303 K

Table 6. 9: Polarization of electrochemical parameters of MS at 303 K in 1 M HCl with and without different concentrations of DMT-GO, DPT-GO, and DNT-GO

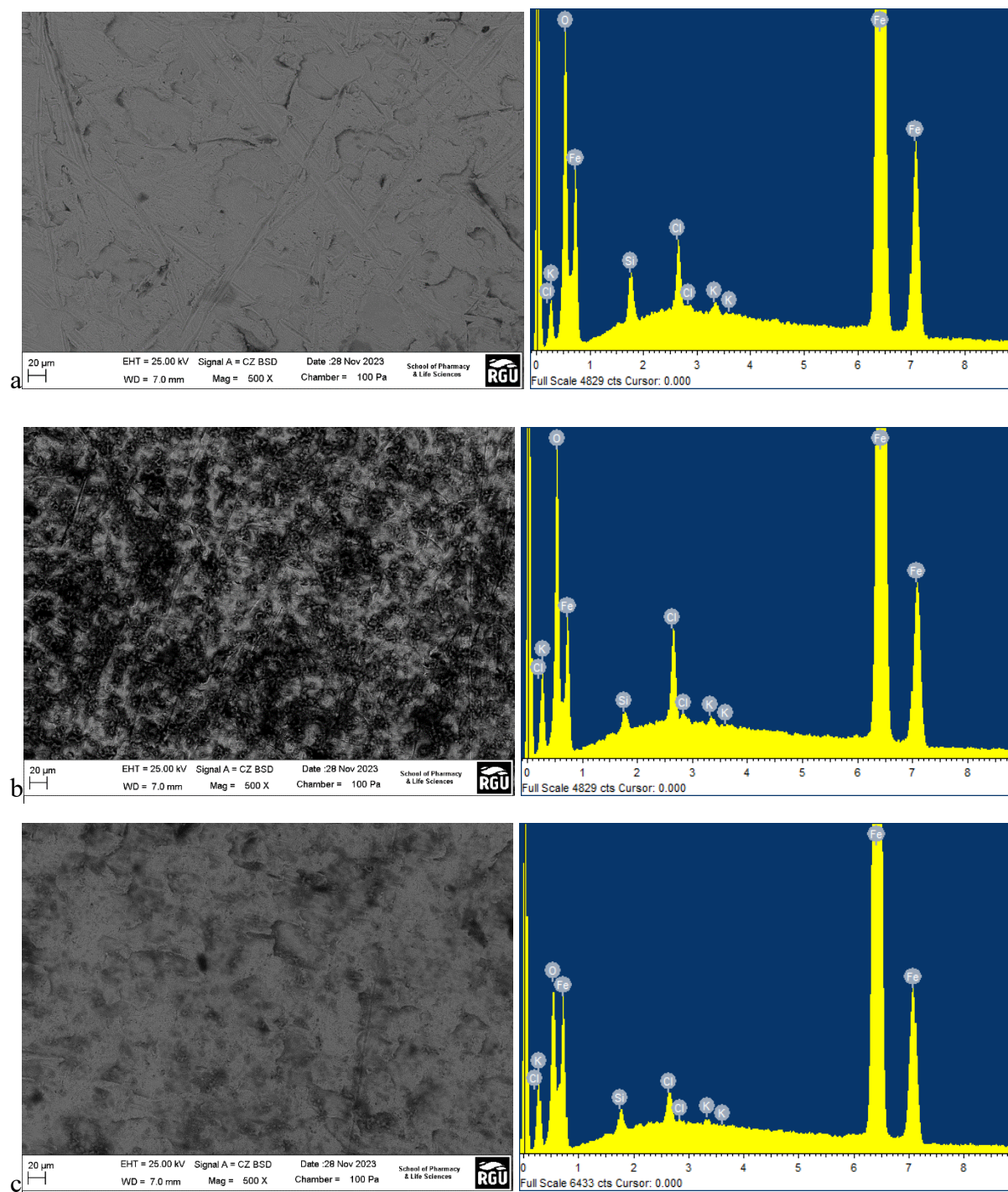
Con. (M)	-E _{corr} (mV)	I _{corr} (μA.cm ⁻²)	β _a (mV.dec ⁻¹)	β _c (mV.dec ⁻¹)	f _a	f _b	$\frac{f_a}{f_b}$	%IE _{PDP}
Blank	436.286	1351.762	82.8	129.7	-	-	-	-
DMT								
0.001	412.53	172.999	58.6	111.3	0.214	0.573	0.374	87.20
0.002	406.63	170.456	144.0	118.7	0.019	0.672	0.029	87.39
0.003	410.00	118.951	86.9	96.2	0.018	0.652	0.027	91.20
0.004	408.87	87.661	68.3	102.9	0.033	0.339	0.097	93.51
0.005	411.16	80.661	109.4	114.4	0.016	0.282	0.059	94.03
DMT-GO								
0.001	497.00	409.44	263.46	66.220	0.6305	0.1896	3.3271	69.71
0.002	519.30	532.15	408.71	62.395	1.0728	0.2025	5.2977	60.63
0.003	528.00	442.51	406.88	61.56	0.9909	0.1614	6.1901	67.26
0.004	507.80	383.52	223.18	66.818	0.6729	0.1634	4.1181	71.62
0.005	557.90	310.71	623.23	72.984	0.9978	0.0899	11.12	77.01
DPT								
0.001	421.00	203.785	166.5	133.8	0.137	0.168	0.814	84.92
0.002	415.37	129.783	133.8	89.3	0.082	0.121	0.676	90.39
0.003	425.86	86.414	77.6	102.6	0.055	0.070	0.788	93.60
0.004	432.73	67.434	76.5	77.0	0.047	0.052	0.911	95.01
0.005	383.72	49.927	66.3	98.4	0.016	0.063	0.265	96.30
DPT-GO								
0.001	538.50	354.47	188.25	68.956	0.9011	0.1192	7.5595	73.77
0.002	534.00	325.40	436.30	56.279	0.7834	0.1133	6.9143	75.92
0.003	546.50	319.02	227.90	68.363	0.8933	0.1008	8.8621	76.40
0.004	531.50	281.19	251.46	63.314	0.6569	0.0998	6.5821	79.19
0.005	537.20	233.00	177.04	52.911	0.5831	0.2296	2.5396	82.76
DNT								

0.001	412.89	252.295	174.4	168.8	0.163	0.214	0.761	81.33
0.002	419.60	217.124	166.3	139.2	0.145	0.181	0.801	83.93
0.003	434.51	185.858	52.5	105.7	0.132	0.139	0.947	86.25
0.004	420.05	126.767	60.2	108.4	0.071	0.108	0.657	90.62
0.005	404.97	103.784	81.6	115.1	0.052	0.100	0.518	92.32
DNT-GO								
0.001	528.50	415.19	298.57	85.611	0.9354	0.1508	6.2029	69.28
0.002	508.00	404.16	209.73	70.934	0.7108	0.1719	4.1349	70.10
0.003	519.90	400.16	303.65	82.618	0.8126	0.1553	5.2324	70.40
0.004	534.70	389.22	321.66	70.272	0.9451	0.1348	7.0111	71.21
0.005	532.70	306.45	231.11	69.197	0.7263	0.1078	6.7374	77.32

6.5. Scanning electron microscopy (SEM) and energy-dispersive X-ray Spectroscopy (EDS)

The surface morphology of MS was examined by SEM/EDS in a 1 M HCl solution, both with and without 0.005M DMT, DPT, and DNT. The SEM/EDS analysis was conducted on two environmental systems: uninhibited and inhibited systems (Figures 6.33). The results were compared to those obtained for the polished but untreated samples. The SEM images of MS metal electrodes exposed to a 1 M HCl solution without protective measures reveal significant surface damage. Energy Dispersive X-ray Spectroscopy (EDS) was conducted in conjunction with SEM to provide compositional analysis of the corroded surfaces. The SEM images reveal many cavities and significant pits on the surfaces of the electrodes. The presence of chloride ions (Cl^-) in the HCl solution and their ability to penetrate metal surfaces are indicative of their aggressive nature, leading to corrosion. The occurrence of deep penetration suggests that the passive oxide layer, if it exists, has been compromised, resulting in more significant harm. EDX spectra reveal the presence of high concentrations of Cl on the electrode surfaces. This confirms that chloride ions from the HCl solution have indeed interacted with and penetrated the metal. Peaks corresponding to elements that form corrosion products, such as oxygen (O) can be seen, indicating the degradation of the metal surface. When the MS surface is treated with the corrosion inhibitor (DMT, DPT, and DNT), the SEM analysis reveals significant improvements in surface morphology compared to untreated samples. The surface morphology of the inhibited MS is much smoother compared to the untreated surface and the surface of MS shows a significant reduction in the number and depth of pits and cavities. This is because DMT, DPT, and DNT inhibitor forms a protective layer on the surface, which prevents the chloride ions from penetrating and causing corrosion. For EDS MS surfaces show significantly lower concentrations of chlorine (Cl), suggesting that the inhibitor effectively blocks the

chloride ions from penetrating the metal surface. The intensity of peaks of Fe is higher in the inhibited sample compared to the uninhibited one for both inhibitors. This indicates less material loss and better preservation of the metal surface[166, 429].



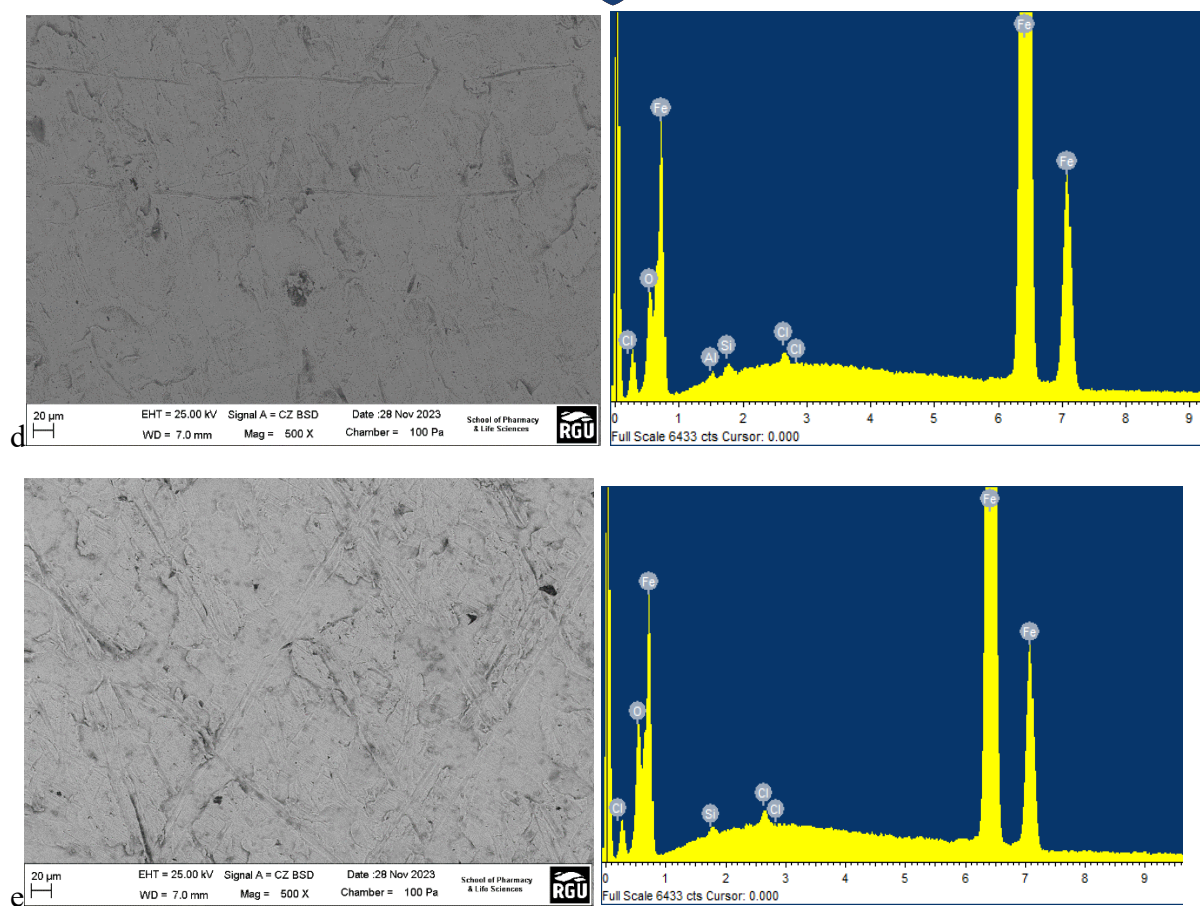


Figure 6.33. SEM images and EDX spectra of a. unexposed-polished MS surface, b. MS immersed in uninhibited 1M HCl, and MS immersed in c. DMT, d. DPT, and e. DNT-inhibited 1 M HCl solution

6.6. Water contact angle measurements

The contact angle between a stationary water droplet and a metal surface is influenced by the polarity of the water molecules, as well as the presence of surface sites, impurities, and the roughness of the metal surface. These parameters can be utilized to confirm the binding of an inhibitor on the metal surface[430-432]. Figures 6.36a-e display contact angle images of the surfaces of the MS sample for (a) untreated metal, (b) the immersed in HCl test solution, treated with inhibitor (c) DMT, (d) DPT, (DNT) adsorption. The contact angle of water droplets on untreated MS surfaces was 91.364° . When MS surface is subjected into HCl solution, the contact angle decreases to 55.150° [430, 433-435]. Generally, a metal surface is considered hydrophilic when the water droplet contact angle is less than 90° , and when it is greater than 90° , the contact angle is hydrophobic [436-438]. The immersed MS sample for this study is considered hydrophilic, same as several author results. This shows that the acidic solution severely damaged the surfaces, allowing the water droplet to spread over the large area of the

surfaces. With the introduction of an inhibitor into a 1M HCl solution the contact angle increased and became more than 90° for all inhibitors suggesting poor wettability[372, 429, 439-441].

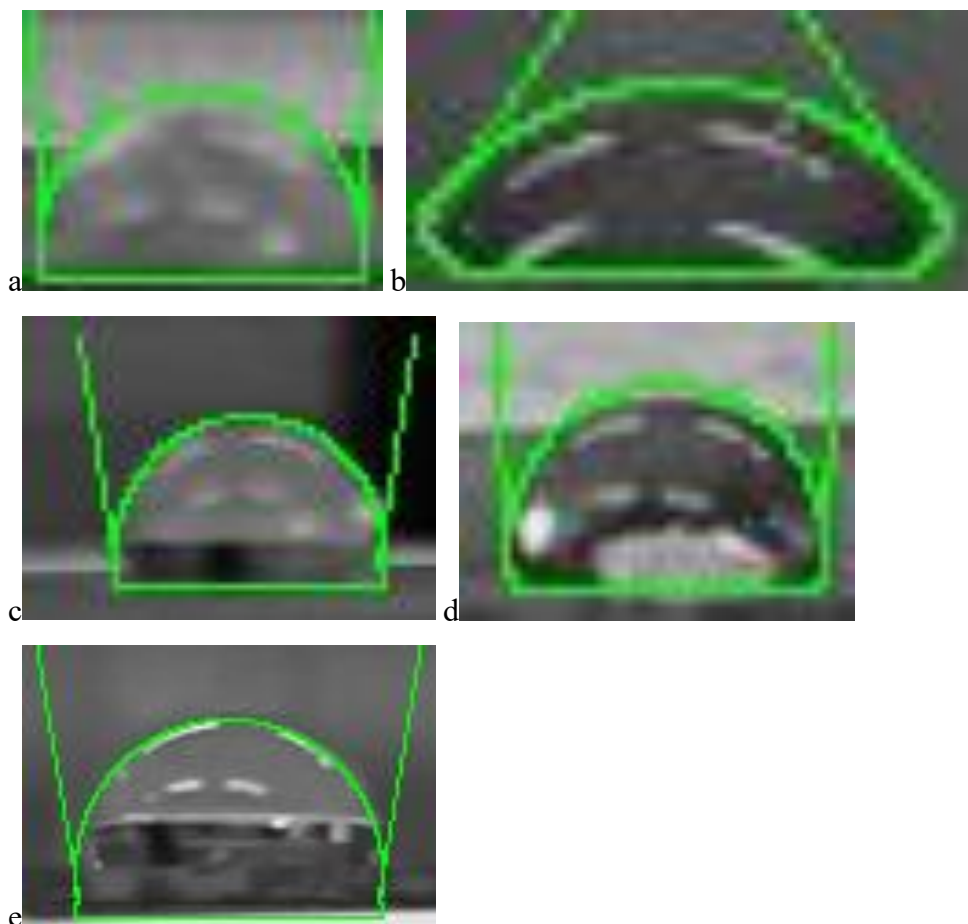


Figure 6. 34: Surface wettability behaviour of (a) untreated MS sample 91.364° , (b) MS sample after 6 hours of immersion in 1 M HCl medium with no inhibitor 55.150° , and (c) in the presence of 0.005M of DMT 99.594° , (d) DPT 93.937° , and (e) DNT 99.867°

6.7. Fourier transform infrared Spectroscopy (FTIR) analysis of corrosion products on the Al surfaces

FTIR analysis was performed to investigate the interaction of an inhibitor with a metal surface. The metal used in this study was MS; the inhibitors were DMT, DPT, and DNT. The objective was to compare the FTIR spectra of MS with and without DMT, DPT, and DNT to understand the inhibitor's effect on the metal surface. The FTIR spectra of MS without and with DMT, DPT, and DNT inhibitors are shown in Figures 6.35-6.37, respectively. In the spectrum of MS without the inhibitor, characteristic peaks at $\approx 3400\text{ cm}^{-1}$ (O-H stretching), $\approx 1600\text{ cm}^{-1}$ (O-H bending), and $\approx 580\text{ cm}^{-1}$ (Fe-O stretching) were observed. The O-H stretching peak at 3400 cm^{-1} decreased in intensity in Figure 6.35-6.36, indicating reduced surface hydroxyl groups

due to inhibitor adsorption. In Figure 6.37, the appearance of peaks at ≈ 1500 cm suggests the formation of DNT-metal complexes. The increased O-H stretch peak suggests that DNT may be inducing the formation of hydroxyl groups on the MS surface, possibly through adsorption and interaction with surface water molecules.

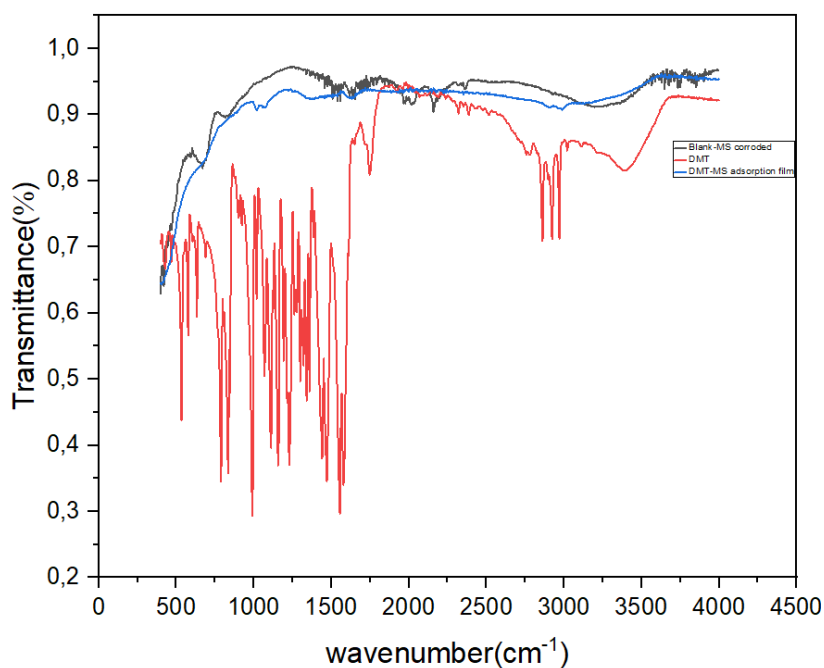


Figure 6. 35: The FTIR spectrum of the adsorption film formed on the MS surface compared to the crude DNT and corrosion products formed on MS (Blank MS corrosion products).

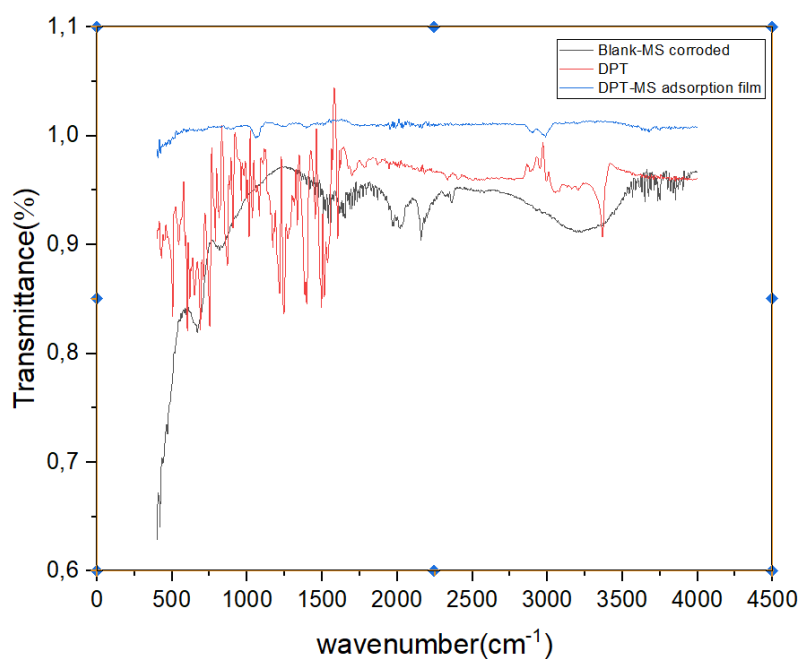


Figure 6.36: The FTIR spectrum of the adsorption film formed on the MS surface compared to the crude DPT and corrosion products formed on MS (Blank MS corrosion products).

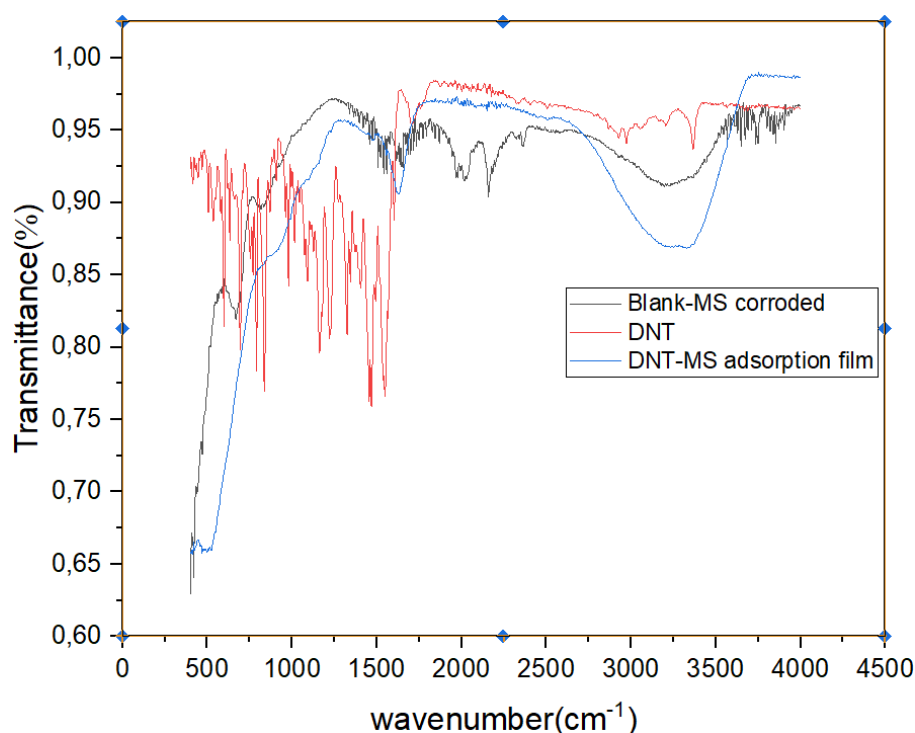


Figure 6.37: The FTIR spectrum of the adsorption film formed on the MS surface compared to the crude DNT and corrosion products formed on MS (Blank MS corrosion products).

6.8. Structures and binding energies for the inhibitor...Fe interacting species

The body-centered cubic (BCC) flat surface of Fe(100) was chosen because it has the lowest energy, indicating that it is the dominant surface on real Fe crystals[442-447]. Figure 6.38-6.40 shows the optimized inhibitor...Fe structures and the nearest heteroatom bond distance. Table 8.2 reports the adsorption energies (ΔE , kcal/mol), binding energies (ΔE_{bind} , kcal/mol), relative energies (ΔE , kcal/mol), and bond distances ($\text{\AA}$) between the Fe(100) surface and the inhibitor molecule. The adsorption behavior of the DMT, DPT, and DNT inhibitors on the Fe surface reveals intriguing insights into its interaction mechanisms, as elucidated through DFT calculations. Two distinct adsorption orientations (perpendicular and horizontal) have been identified, both involving the interaction of the inhibitor molecule with the Fe(100) surface. In Figure 6.38, the DMT molecule adsorbs perpendicularly onto the Fe(100) surface. The oxygen atom forms a direct bond with the Fe atom, leading to a robust Fe...O interaction with a distance of 2.971 $\text{\AA}$. This perpendicular arrangement likely allows for strong orbital overlap between the

oxygen lone pairs and the Fe d-orbitals, contributing to the stability of the adsorption[448-451]. The alternative configuration involves the DMT molecule lying almost parallel to the Fe(100) surface, with the oxygen atom still interacting with the Fe atoms at a distance of 2.858Å. This distance is indicative of stable adsorption, potentially facilitated by van der Waals forces in addition to the Fe...O interaction.

In Figure 6.39, the DPT molecule has three possible arrangements for adsorption on the Fe(100) surface, either in a horizontal or perpendicular orientation. The benzene ring and nitrogen atom have adsorbed horizontally on the Fe(100) surface, with a distance of 3.757Å. The nitrogen atom has formed a perpendicular orientation to the Fe(100) surface, with a distance of 2.878Å. The adsorption also occurs through an aromatic ring. The perpendicular alignment of DPT-c promotes effective orbital overlap between the π -electrons of the aromatic ring and the d-orbitals of the Fe atoms, increasing the adsorption's stability. The perpendicular orientation of the benzene ring could result in a contract that affects the Fe surface, perhaps causing changes in its chemical reactivity and electrical characteristics[452-455].

Figure 6.40 illustrates three possible arrangements of DNT inhibitors on the Fe(100) surface. The DNT-a molecule is attracted to the Fe surface due to its horizontal layout, which allows for strong π - π interactions between the benzene ring and the Fe surface. This interaction is responsible for the stability of the adsorption since van der Waals forces and π -d interactions drive it. The benzene ring's horizontal orientation on the Fe surface offers wide coverage, which has the ability to provide a more uniform and protective layer. Referencing DNT-c, when the inhibitor DNT arranges itself through the chlorine, the bond of chlorine breaks and has a large relative energy(11.2798Kcal/mol), indicating not to be stable. One chlorine forms a bond with an iron surface, and the other chlorine bond often breaks and moves away from the organic inhibitor due to a combination of electronic and structural interactions at the atomic level. This situation happens because chlorine atoms have a high electronegativity, strongly attracting electrons. When an organic inhibitor containing chlorine approaches the iron surface, there can be significant electronic interactions between the chlorine and iron atoms. These interactions can cause the chlorine to become more strongly attracted to the iron surface than the rest of the DNT molecule[456-458].

Table 6.8 shows that all inhibitor (DMT, DPT, and DNT) adsorption energies are negative, indicating that the adsorption is a spontaneous reaction. In this study, the adsorption inhibitors on the Fe(100) surface exhibited adsorption energies greater than 100 kcal/mol. These high

adsorption energies indicate strong interactions between the inhibitors and the Fe(100) surface, suggesting the chemisorption process[319, 459-462]. The highest adsorption energy and binding inhibitor was 704.5889 kcal/mol for the DNT inhibitor, and the lowest was 649.1694 kcal/mol for the DMT inhibitor.

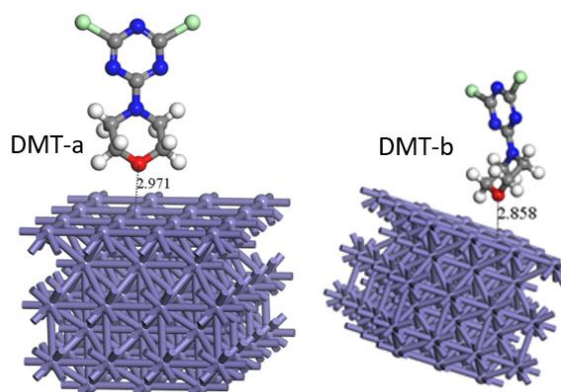


Figure 6.38: Different adsorption geometries of DMT molecules on the Fe(100) surface and the distance between the nearest nitrogen atom to the Fe surface.

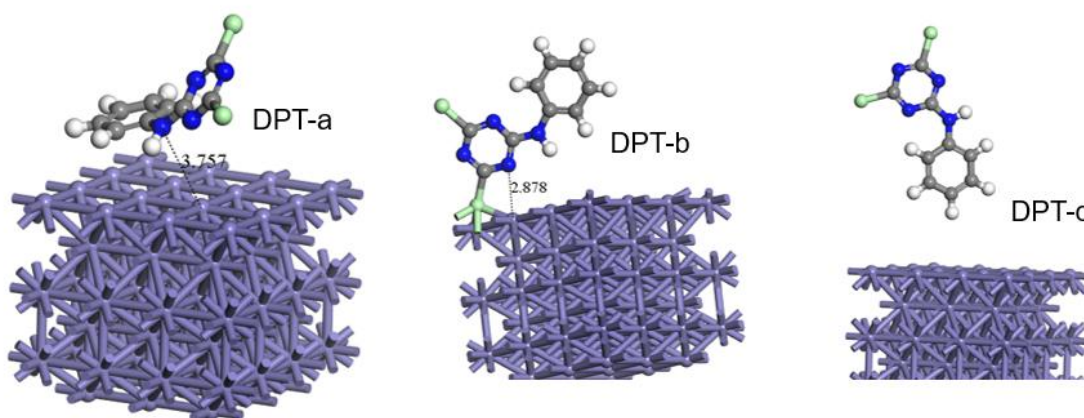


Figure 6.39: Different adsorption geometries of DPT molecules on the Fe(100) surface and the distance between the nearest nitrogen atom to the Fe surface.

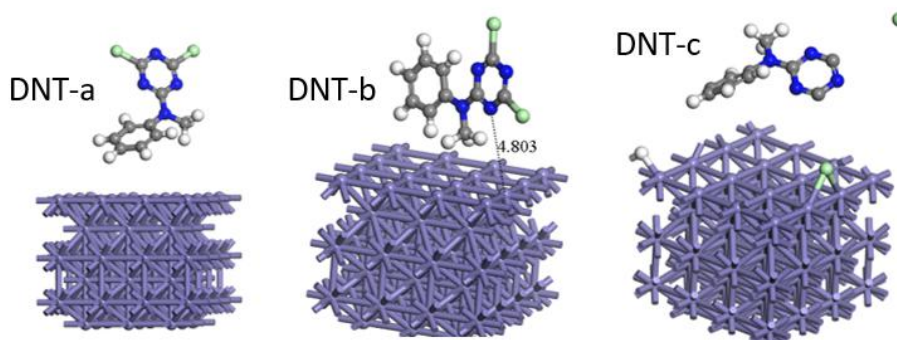


Figure 6.40: Different adsorption geometries of DNT molecules on the Fe(100) surface and the distance between the nearest nitrogen atom to the MS surface.

Table 6. 10: Optimised energies calculated for DMT(-1485.408986Ha), DPT(-1485.19083Ha), and DNT(-1524.443013Ha) adsorption sites on the Fe(100) surface(-6709.663301) and the distance between the nearest heteroatom to the metal surface.

Configuration	-E _{ads} (kcal/mol)	E _{binding} (kcal/mol)	ΔE (kcal/mol)	Bond distance (Å)
DMT				
(DMT...Fe)-a	649.1694	649.1694	0	Fe...O(2.971)
(DMT...Fe)-b	648.7440	648.7440	0.4254	Fe...O(2.971)
DPT				
(DPT...Fe)-a	678.5973	678.5973	0	Fe...N(3.757)
(DPT...Fe)-b	675.1661	675.1661	3.4312	Fe...N(2.878)
(DPT...Fe)-c	676.9689	676.9689	1.6284	-
DNT				
(DNT...Fe)-a	704.5889	704.5889	0	-
(DNT...Fe)-b	703.0096	703.0096	1.5793	Fe...N(4.803)
(DNT...Fe)-c	693.3091	693.3091	11.2798	-

Chapter 7: Comparison and summary

This chapter compares the key findings from the study, focusing on the performance of the synthesized inhibitors on aluminium and mild steel. A brief summary of the overall outcomes is also provided.

7.1. Comparison

The variation of inhibition efficiency between Al and MS is closely related to the electronic and steric characteristics of the inhibitor molecules, as well as the inherent nature of each metal surface. Although all three inhibitors are triazine-based and rich in nitrogen, their distinct substituents (morpholine in DMT, aniline in DPT, and N-methylaniline in DNT) leads to different adsorption behaviors on Al and MS. On aluminium, DNT demonstrated the highest %IE, reaching 95.02% at 313 K, with efficiency increasing as temperature rose. This trend indicates a chemisorption mechanism, where DNT forms strong chemical bonds with the Al surface or its oxide layer. The enhanced electron-donating ability of the N-methylaniline group, along with the aromatic system, likely promotes strong interactions with Al^{3+} surface sites, particularly at elevated temperatures where molecular activation is more favorable. In contrast, DMT and DPT showed declining %IE with temperature, suggesting physisorption, a weaker and thermally less stable interaction.

This behavior underscores DNT's structural suitability for temperature-stable adsorption on Al. However, on MS, the trend is reversed. DMT exhibited the highest %IE of 93.87% at 303 K, followed by DPT and DNT. The decrease in %IE for all inhibitors with increasing temperature points to physisorption as the dominant mechanism on MS. DMT's effectiveness can be attributed to the presence of both nitrogen and oxygen heteroatoms from the morpholine ring, which interact favorably with the vacant d-orbitals of Fe atoms, enhancing adsorption and protective film formation. While DPT offers π -electron interactions through its aniline group, its adsorption is slightly weaker. DNT, although highly effective on Al, showed the lowest inhibition performance on MS, likely due to its bulkier structure and greater steric hindrance, which may limit its ability to adsorb effectively onto the iron surface. Furthermore, E_a calculations support these trends. On Al, DNT showed a lower E_a than the blank, consistent with chemisorption. In contrast, DMT and DPT showed higher E_a values, characteristic of physisorption. On MS, all inhibitors had E_a values higher than the blank, further confirming that physical adsorption is dominant.

7.2. Summary

Techniques	Aluminium	Mild steel
Weight loss	➤ The %IE for DMT and DPT decreases with an increase in temperature. ➤ %IE for DNT increases with an increase in temperature. ➤ The highest %IE was 83.02%, 82.39%, and 95.02% for DMT, DPT, and DNT, respectively. ➤ The E_a for DMT and DPT was higher than blank, while DNT was lower than blank. ➤ DNT was the best inhibitor of AL compared to DMT and DPT ➤ DNT>DPT>DMT	➤ The %IE for DMT, DPT, and DNT decreases with temperature increases. ➤ The highest %IE was 93.87%, 90.20%, and 87.95% for DMT, DPT, and DNT, respectively. ➤ The E_a for all the inhibitors was higher than blank. ➤ DMT was the best inhibitor for MS compared to DPT and DNT ➤ DMT>DPT>DNT
Adsorption isotherm	➤ All inhibitors obey the Langmuir adsorption isotherm. ➤ Spontaneous reaction ➤ Mixed-type adsorption with lucky physisorption process	➤ All the inhibitors obey the Langmuir adsorption isotherm. ➤ Spontaneous reaction ➤ Mixed-type adsorption process
EIS	➤ The impedance spectra consist of capacitive loops at a higher frequency and inductive loops at a lower frequency. ➤ Circuit for data fitting: $R_s(Q R_{ct} (L_1/RL))$	➤ The impedance spectra consist of a capacitive loop ➤ Circuit for data fitting: $R_s(Q R_{ct})$ and $R_s(Q_1 R_{ct})(Q_2 R_3)$ for the concentration of 0.001M and 0.002M DPT

PDP	➤ The E_{corr} values shift towards positive values. ➤ More than 85mV ➤ All inhibitors are either anodic or cathodic inhibitors.	➤ MS PDP has a slight move towards a positive value compared to the PDP of Al ➤ Less than 85mV ➤ Mixed-type adsorption
SEM/EDX	➤ Pitting corrosion ➤ Traces of oxygen and carbon precipitate	➤ Uniform ➤ Trace of oxygen and chloride ions
Contact Angle	➤ The hydrophobicity of the Al surface is enhanced in the presence of DMT, DPT, and DNT.	➤ The hydrophobicity of the MS surface is enhanced in the presence of DMT, DPT, and DNT.
DFT	➤ Adsorption energies on the Al(111) surface are less than 100 kcal/mol. ➤ All of the compounds physically adsorb on the Al(111) metal surface. ➤ The highest adsorption energy and binding inhibitor was observed at 17.2688kcal/mol for the DNT inhibitor.	➤ The Fe(100) surface adsorption inhibitors exhibited adsorption energies greater than 100 kcal/mol. ➤ All compounds chemically adsorb on the Fe(100) surface. ➤ The highest adsorption energy and binding inhibitor was 704.5889 kcal/mol for the DNT inhibitor.

Chapter 9: Conclusions, recommendations, and future

This chapter provides a summary of the current study's findings and a review of significant research on substituted triazines as potential corrosion inhibitors. It includes recommendations and suggestions for future research derived from the current work.

9.1. Conclusions

This Study concluded that three substituent triazine compounds, namely 4,6-dichloro-2-morpholine-1,3,5-triazine (DMT), 4,6-dichloro-2-anilino-1,3,5-triazine (DPT), and 4,6-dichloro-N-methylanilino-1,3,5-triazine (DNT) were successfully synthesized, and their structures were confirmed using nuclear magnetic resonance spectroscopy (NMR), Fourier transforms infrared spectroscopy (FT-IR), and liquid chromatography-mass spectrometry (LC-MS). From the characterization of the compounds, it was certain that the synthesized compounds were mono products. Thermogravimetric Analysis (TGA) results showed that the DMT, DPT, and DNT inhibitors begin their degradation at 85.91°C, 181.007°C, and 253.82°C, respectively. Then, lower temperatures were used. Those compounds successfully showed excellent inhibitor properties for Al and MS corrosion in 1 M HCl as they promoted the formation of a passive or protective layer on the metal surfaces and reduced the corrosion rate.

Weight loss measurements revealed that the corrosion rate decreased upon the addition of DMT, DPT, and DNT for both aluminium (Al) and mild steel (MS). The inhibition efficiency (%IE) of all three inhibitors increased with rising inhibitor concentration, reaching an optimal effect at 0.005 M for both metals. Aluminium exhibited a more effective and possibly irreversible inhibition behavior compared to mild steel, particularly when DNT was used. This is supported by the observation that DNT's protective effect on Al improved with increasing temperature, indicating an endothermic adsorption process. At 313 K, DNT achieved the highest %IE of 95.02% on Al, suggesting strong chemisorptive interaction facilitated by molecular activation at elevated temperatures.

On the other hand, the %IE of DMT and DPT on Al decreased with temperature, reaching 83.02% and 82.39% at 303 K, respectively, indicating a less stable adsorption mechanism. In contrast to its excellent performance on Al, DNT exhibited the lowest inhibition efficiency on MS, with %IE decreasing at higher temperatures, where weak van der Waals interactions are disrupted by thermal agitation.

Among the three inhibitors on MS, DMT was the most effective, showing a maximum %IE of 93.87% at 303 K using 0.005 M. This high performance is attributed to the presence of nitrogen and oxygen heteroatoms in DMT, which promote strong coordination with the vacant d-orbitals of Fe, enhancing its adsorption and corrosion resistance. The weaker interaction between DNT and the iron surface of mild steel limits its protective capability compared to DMT and DPT, which may have structures more favourable for adsorption onto steel.

Observations were made on the increases in the thermodynamic ΔH_a and E_a values when the concentrations of DMT and DPT inhibitor increased up to 0.005M for Al. For MS, when the concentration of DMT, DPT, and DNT inhibitors increases the ΔH_a and E_a also increases. The rise in these parameters as the concentration of the inhibitor increases suggests the creation of a physical obstacle that hinders the transfer of corrosive charge and mass. This obstruction necessitates a greater amount of energy to facilitate the movement from the reactants to the activated complex. Alternatively, it has been suggested that the reduction in these factors results from the expansion of the surface area the inhibitor covers as the temperature rises.

DMT, DPT, and DNT adsorption onto Al and MS in 1M HCl obey kinetic-thermodynamics adsorption isotherm of Langmuir isotherm adsorption. The adsorption of the inhibitor onto metals is a spontaneous and mixed-type process according to free Gibbs energy. The negative value of enthalpy adsorption (ΔH°_{ads}) for the DMT inhibitor signifies that the adsorption of the inhibitor onto the Al surface is an exothermic process, releasing energy and stabilizing the system. The positive values of DPT and DNT indicate an endothermic nature, suggesting that the adsorption process of the inhibitor molecules to Al surface spontaneity and effectiveness depends on the temperature and entropy change. The enthalpy adsorption of all the inhibitors (DMT, DPT, and DNT) on the MS surface is an exothermic process.

The impedance spectra for Al consist of capacitive loops at a higher frequency and inductive loops at a lower frequency, while MS consists only of capacitive loops. From the PDP result the interaction coefficient of anodic and cathodic for all inhibitor molecules adsorbed on Al and MS indicates that the inhibitor is more effective in slowing down the anodic reactions. Using GO as a modification to DMT, DPT, and DNT inhibitors has increased the effectiveness of the inhibitor on MS.

DFT calculations supported experimental observations, showing that heteroatoms and π -bonds in the inhibitor structures contribute to stable interactions with metal surfaces. These findings highlight the potential of substituted triazines as efficient, structure-dependent corrosion inhibitors, with performance varying according to both metal type and operating temperature.

9.3. Recommendations and future studies

According to the results of this study, numerous recommendations are suggested to improve the use and efficiency of triazine as a corrosion inhibitor for aluminum and mild steel. Conducting extensive field testing in diverse industrial environments is recommended. This

will help validate laboratory results and assess triazine substitution inhibitors' real-world applicability and reliability under different operational conditions. It is recommended that the potential synergistic effects of mixing triazine with other established corrosion inhibitors be investigated to improve overall protection. Investigating the di and tri forms of the compounds and conducting a comparative analysis for future research is advisable. Studying these inhibitor's effectiveness in paint and cathodic protection is also advisable.

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