

**ELECTROCHEMICAL, QUANTUM CHEMICAL
CALCULATION, QSAR AND MOLECULAR DYNAMICS
SIMULATION STUDIES ON SOME CARBAZOLE DERIVATIVES
AS CORROSION AND BIOCORROSION INHIBITORS FOR MILD
STEEL IN ACIDIC MEDIUM**

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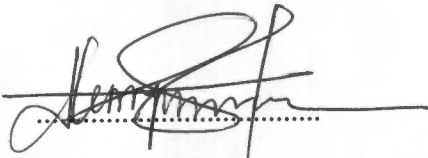
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DECLARATION

I declare that this thesis and the work contained therein are carried out by me and appropriate references were cited where the intellectual properties of other researchers were referred.

A handwritten signature in black ink, appearing to read 'Henry U. Nwankwo', written over a horizontal dotted line.

Henry U. Nwankwo

May 2017

DEDICATION

In loving memory of my mother Lady Ezinne Chioma Roseline Nwankwo (Oso di akpa-aku).

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ABSTRACT

The efficiency of sixteen (16) carbazole (CZ) derivatives as corrosion inhibitors for mild steel (MS) in 1 M HCl and sulphate reducing bacteria (SRB) dominated medium have been investigated by electrochemical and weight loss (WL) techniques. The sixteen carbazoles considered in this study include unsubstituted carbazole and additional fifteen substituted derivatives. The rationale was to compare the corrosion inhibition properties of the derivatives with the unsubstituted carbazole, in order to distinguish the effects of the substituent groups on corrosion inhibition property of carbazole. The adsorption strengths and corrosion inhibition properties of these compounds were studied for MS in 1 M HCl solution at 303 K using electrochemical, quantum chemical calculation and molecular dynamics (MD) simulation techniques.

The weight loss method was used to quantify the inhibition efficiencies of these carbazoles for MS in *Desulfovibrio vulgaris* (*D. vulgaris*) and *Desulfococcus multivorans* (*D. multivorans*) induced biocorrosion. Surface morphology techniques using scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and Fourier transform infrared (FT-IR) spectroscopy were employed to reaffirm film-forming properties of the investigated carbazoles.

All the reported CZs were found to reduce MS corrosion in both 1 M HCl and SRBs media. Analysis of potentiodynamic polarization data indicated that the studied carbazoles are mixed-type inhibitors with predominantly cathodic effects at maximum concentrations. Adsorption of the compounds was best described by the Freundlich adsorption isotherm (for GROUPS II, III and IV) and the Langmuir adsorption isotherm (for GROUPS I and V). The thermodynamic adsorption parameters suggest competitive physisorption and chemisorption mechanisms for GROUPS I and V; strong chemisorption mechanisms for GROUPS III and IV; and physisorption mechanisms for Group II compounds. The observed trends of their inhibition efficiencies for MS in 1 M HCl obtained at maximum inhibitor concentrations are: THCHZ > EHCZDCA > HCHZ > DBCZ > CZ (for GROUP I); THCHCA > MTHCHZ > MCZCA (for GROUP II); CZPD > DBCPCZ (for GROUP III); HTHCHZ > CZAA > DMCZ (for GROUP IV); ECZ > 9-ECZ > ENCZ > CZE (for GROUP V). Electrochemical impedance spectroscopy (EIS) measurements suggested that the studied CZs adsorbed on MS surface to form protective film that resembles a pseudo-capacitor. The inhibition efficiencies observed were found to increase with inhibitor concentrations.

On the other hand, the trends of inhibition efficiencies due to weight loss recorded in SRB medium are such that: CZ > EHCZDCA > DBCZ > THCZ > HCZ (for GROUP I); THCZCA > MCZCA > MTHCZ (for GROUP II); DBPCZ > CZPD (for GROUP III); HTHCZ > DMCZ > CZAA (for GROUP IV in the presence of *D. vulgaris* specie); HTHCZ > CZAA > DMCZ (for GROUP IV in the presence of *D. multivorans* specie); and 3-ECZ > ENCZ > CZE > 9-ECZ (for GROUP V).

SEM images obtained for MS in SRB and 1 M HCl media revealed that the studied CZs adsorbed on the metal surface forming highly cohesive protective layer that shielded the MS surface from the aggressive effect of the acid and SRB media. EDX examinations revealed MS surfaces that are consistent with respective test solutions. FTIR spectra of the corrosion products on MS surface retrieved from SRB media revealed similar features as the ones obtained in the acidic medium. Moreover, a distinctive broad band was observed at 1000 cm^{-1} for all the MS coupons recovered from the SRB consortium and can be attributed to Fe-S bond formed as a result of reduction of SO_4^{2-} to S^{2-} .

Quantum chemical data obtained correlate fairly well with electrochemical inhibition efficiencies and suggest that most of the quantum chemical descriptors could also be employed in explaining the inhibitory activities of these carbazoles in SRB dominated medium. The HOMO, LUMO, Mulliken atomic charge distributions, electron density distributions and the electrophilic Fukui function (f^-) were generally centred mostly on the N-atom of the carbazole ring and the C=C π -electrons centres of the fused aromatic rings.

MD simulations confirmed that the carbazoles were adequately adsorbed on MS surface in near-flat orientation, and the values of adsorption and deformation energies were also calculated for the lowest energy configurations of Fe(110)/inhibitor systems. The MD simulations results corroborated electrochemical inhibition efficiencies except for GROUPS IV and V, with such anomaly attributed to the exclusion of covalent interactions during molecular simulations.

Based on these findings, this work has proposed approaches to monitoring corrosion of metals that spans across various redox regimes and biochemical conditions.

LIST OF ABBREVIATION

AFM	Atomic Force Morphology
AFS	Atomic Force Spectroscopy
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared
BFM	Biological Force Microscopy
BFS	Biological Force Spectroscopy
BLYP	Becke-Lee, Yang and Parr
CE	Counter Electrode
CLSM	Confocal Laser Scanning Microscopy
CV	Cyclic Voltammetry
DFT	Density Functional Theory
EDX	Energy Dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
EPS	Extracellular Polymeric Substances
ESEM	Environmental Scanning Electron Microscopy
FMO	Frontier Molecular Orbitals
FTIR	Fourier transforms infrared
GC	Gradient-Corrected
GTO	Gaussian-Type Orbital
HF	Hartree-Fock
HOMO	Highest Occupied Molecular Orbital
IE	Inhibition Efficiency
IFM	InfiniteFocus Microscope
IP	Ionization Potential
IR	Potential
LDA	Local Density Approximation
LSI	Laser Spray Ionization
LUMO	Lowest Unoccupied Molecular Orbital
MD	Molecular Dynamics
MIC	Microbially Influenced Corrosion
MICI	Microbiologically Influenced Corrosion Inhibition
MS	Mass Spectroscopy/ Mild Steel

MP	Molar Polarizability
MV	Molar Volume
NVC	<i>N</i> -vinylcarbazole
OCP	Open Circuit Potential
PDP	Potentiodynamic Polarisation
QSAR	Quantitative Structure Activity Relationship
RE	Reference Electrode
SCF	Self Consistent Field
SEM	Scanning Electrode Microscopy
SRB	Sulphate Reducing Bacteria
STO	Slater-Type Orbital
STXM	Scanning Transmission X-ray Microscopy
TGA	Thermogravimetric Analysis
VWN	Vosko, Wilk and Nasair
WE	Working Electrode
WL	Weight Loss
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray powder Diffraction
ZRA	Zero Resistance Ammetry
HCl	Hydrochloric acid
SCC	Stress Corrosion Cracking
PCE	Platinum Counter Electrode
MV	Molecular Volume
FRA	Frequency Response Analyzer
PGSTAT302N	Metrohm Autolab Potentiostat/Galvanostat
LF	Low Frequency
C_{dl}	Double Layer Capacitance
R_s	Resistor
R_{ct}	Resistance of Charge Transfer
CPE	Constant Phase Element
IUPAC	International Union of Pure and Applied Chemistry
CZ	Carbazole
DBCZ	3,6-dibromocarbazole

HCZ	2-hydroxycarbazole
THCZ	1,2,3,4-tetrahydrocarbazole
EH CZDCA	9-(2-ethylhexyl)carbazole-3,6-dicarboxaldehyde
TH CZCA	2,3,4,9-tetrahydro-1H-carbazole-8-carboxylic acid
MTH CZ	6-methyl-2,3,4,9-tetrahydro-1H-carbazole
MCZCA	9-methyl-9H-carbazole-3-carboxylic acid
DBPCZ	3,6-Dibromo-9-phenylcarbazole
CZPD	3-(9H-carbazol-9-yl)-1,2-propanediol
CZAA	9-Carbazoleacetic acid
DMCZ	1,4-Dimethyl-9H-carbazole
HTHCZ	N'-hydroxy-2,3,4,9-tetrahydro-1H-carbazole-1-carboximidamide
9-ECZ	9-Ethylcarbazole
3-ECZ	3-ethylcarbazole
ENCZ	3-Ethyl-3-nitrocarbazole
CZE	9H-carbazole-9-ethanol

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CHAPTER 1

INTRODUCTION

1.1. Introduction and problem statement

The term corrosion can be defined as the gradual deterioration of materials as a result of reaction with their contact environment [1]. Corrosion affects a wide range of materials such as metals, plastics, woods, ceramics and polymers. Metallic corrosion proceeds via a spontaneous process that consists of the inverse of metallurgical processes, where the finished metals revert to their natural form of lower free energy, i.e. chemical minerals. All environments tend to be corrosive to a certain degree as substances that bring about corrosion are common around us. Those substances include air, acids, alkalis, salts, sulphur dioxide, ammonia, hydrogen sulphide, fuel gases, microbes and water.

Metals and their alloys are used in many applications due to their numerous useful properties. Mild steel has found application in a wide range of equipments as a preferred material in construction works and industries. This can be attributed to its relatively low cost and good mechanical strength [1].

Challenges posed by the need to remove undesirable scale and rust in numerous industrial processes involving acidic medium contributes to corrosion concern. The refining of crude oil, acid pickling, acid descaling, industrial cleaning, oil-well acid in oil recovery and the petrochemical industries all involve extensive use of acid solutions [2]. The periodic spillage of products such as gas and oil resulting in environmental catastrophe are often attributed to the wear of storage tanks and pipelines caused by metal corrosion. The stringent environmental legislations and huge penalty for defaulters put in place by various nations further highlight the need to combat corrosion-related problems in industries.

Pitting, inter-granular, concentration cell, uniform or general, galvanic, refinery and microbial corrosion are few types of corrosion that have received attention in the past few years.

A study conducted by Rajasekar *et al.* [3] revealed that about 20% of all damages caused by corrosion are influenced by microorganisms. Most recent study conducted by Miller *et al.* [4] alluded that cost of damages due to microbially influenced corrosion (MIC) stood at nearly 50% of all corrosion cost which amounted to 140 billion USD in the US alone. The deterioration of metal due to the activities of microbes is referred as biocorrosion or microbially influenced corrosion. MIC has been studied extensively by Videla. In one of such study [5], it was suggested that the mechanism of biocorrosion follows the same electrochemical process as the traditional or universal corrosion [6]. In some industrial plants such as filtration systems, reverse osmosis membranes, residual water treatment systems, sewage treatment facilities, underground pipes, ships, closed cooling systems and portable

water distribution systems, there can be an accumulation of undesired deposits of biological nature (i.e., biofilms) [7, 8]. Microbial colonization of metals and alloys of some components of industrial plants is caused by the formation of biofilms composed of bacteria, extracellular polymeric substances (EPS), particulate matter of different origin and mainly water [7, 8]. Biofilms, or surface-attached microbial communities, are both ubiquitous and resilient, and are believed to be responsible for the remarkable persistence of bacterial populations in the face of changing environmental conditions [9, 10].

Although previous studies have been devoted to investigating how biofilms form, develop, and detach, the relationships of these events to their metabolism and dynamics are not yet been unravelled [9]. Nevertheless, lack of skilled professionals in the field of biocorrosion study has persisted [11].

As corrosion ultimately results in the formation of rust (ferric oxide), it poses huge threats to industries, environment, humans and a host of other materials such as ceramics, metals and polymers. These threats may include, increase in maintenance cost, loss of production, loss of aesthetic and mechanical properties of the corroding material, polluted environment, job losses as well as putting food security at risk. Biocorrosion on the other hand remains a huge challenge that affects industrial components and ranges from heavy microbiological contamination with consequent energy and efficiency losses to structural failures due to biocorrosion attack. Overall, it is estimated that about 3.7 billion US Dollars is spent annually to mitigate corrosion-related problems in oil and gas industry alone [12].

Various measures have been used over the years to combat threats to equipment surfaces, industrial machinery, metal components and structures against corrosion. The use of inhibitors has remained the most viable method [2, 13-23] from cost-effective and environmental protection standpoints to abate the corrosion of metals in harsh acidic environments.

To this end, organic compounds containing nitrogen, oxygen and sulphur have been investigated and found to be effective corrosion inhibitors of mild steel in sulphuric and hydrochloric acids [2, 13]. As a result, large families of naturally occurring products that contain mixtures of these compounds have been explored as they are also biodegradable in nature [13]. Notable amongst this study include Ostovari *et al.* [2], Martinez *et al.* [24], Gunasekaran *et al.* [25], Srivasthava *et al.* [26] and Saleh *et al.* [27]. These groups of organic molecules containing donor atoms such as nitrogen and sulphur have been found to easily adsorb on the metal surface by displacing water molecules to form a compact barrier film [28]. The availability of lone pairs and π electrons in corrosion inhibitor molecules facilitates

electron transfer process from the inhibitor to the metal, thus forming a coordinate covalent bond. The effectiveness of the chemisorption bond depends largely on the electron density in the donor atoms of the functional group as well as the polarizability of the group [28]. In addition to these properties, a study conducted by Ostovari *et al.* [2] revealed aromaticity, steric effects, nature of the corrosive medium, structure and charge of metal surface as other physicochemical properties that determine the effectiveness of molecules as corrosion inhibitors on metal surfaces.

On the other hand, the use of synthetic compounds as effective corrosion inhibitors is not new, however, their high toxicity to both human beings and environment has shifted focus to more biodegradable compounds [29]. Most synthetic or inorganic corrosion inhibitors behave as passivators or deposits of rarely soluble salts on metal surfaces [30]. Their hazardous effects range from temporary to permanent damage to organs such as livers and kidneys. Their toxicity most often manifests during the synthesis of the compounds or their use [2].

At the moment, researchers are attempting to correlate the structure of corrosion inhibitors with their effectiveness of adsorption at the metal-solution interface. To this end, semi-empirical methods of calculation have been employed successfully in previous studies to measure macroscopic or quantum-chemical properties [31]. These include dipole moment, the highest occupied molecular orbital (HOMO) energies, lowest unoccupied molecular orbital (LUMO) energies, the HOMO-LUMO energy gap and the regions of highest electron density of the HOMO levels.

In corrosion inhibition studies, understanding adsorption phenomena is of great importance. For this reason, Barriga *et al.* [32] have reported that the use of molecular simulations is useful in finding the low-energy adsorption sites on both periodic and non-periodic substrates or in investigating the preferential adsorption of mixtures of adsorbate components.

To this end, this doctoral research study investigates a new set of carbazole derivatives with a common carbazole nucleus but differ only in the type and position of substituent atoms or groups. The set of compounds chosen for the proposed study has not been considered elsewhere as corrosion and biocorrosion inhibitors. This study will make original contributions to knowledge in the area of corrosion and biocorrosion sciences, electrochemical science, quantum chemical study and molecular simulations. Furthermore, attempts will be made to rationalize the biocorrosion activity of carbazole derivatives using

weight loss technique and surface morphology to explore the interaction with the metal-inhibitor interface.

1.2. Carbazole and its derivatives

Carbazoles are a unique class of aromatic heterocyclic [33] organic compounds with a tricyclic structure, consisting of two six-membered benzene rings fused on either side of a five-membered nitrogen-containing ring [34]. Carbazole and its derivatives can be found in nature. A few sources include coal tar and higher plants of the genus *Murraya*, *Glycosmis*, and *Clausena* from the family *Rutaceae* [35]. The structure of carbazoles is based on the indole structure in which a second benzene is fused onto the five-membered ring. The structural formula of carbazole is shown in Figure. 1.1 whilst some physical properties are presented in Table 1.1.

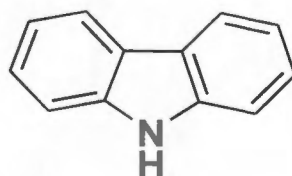


Figure. 1.1. Structure of carbazole.

Table 1.1. Some physical properties of carbazole.

Molecular formula	C ₁₂ H ₉ N
Molecular weight	167.20656 g/mol
Physical state	White crystal
Melting point	246.3 °C

1.2.1. Applications of carbazoles

Carbazole and its derivatives have found extensive industrial, biological and commercial applications. They have been used in the manufacture of organic photoconductors and electroluminescence devices [36, 37]. More recently as anion receptors [38], antioxidant [39], antidiabetic [40], antimitotic [41], antimicrobial [42-44], antivascular [45], antitumour [46], anticancer [47-51], antipsychotic [52], and anticonvulsant [53] agents. Carbazoles have also been used to greatly enhance the thermal stability or glassy-state durability of organic compounds upon incorporation of a carbazole moiety in the core

structure [37]. It is as a result of these numerous biological activities, that there is a need to explore carbazole and its derivatives as a potential biocorrosion inhibitor.

Few studies have been conducted on the self-assembly of carbazole and its derivatives on metal surfaces. Wang *et al.* [34] investigated the corrosion inhibition properties of carbazole and *N*-vinylcarbazole against copper in 0.5 M NaCl solution using electrochemical techniques. Synthesis, characterization and corrosion inhibition properties of poly(*N*-vinylcarbazole-co-glycidyl methacrylate) coatings on low nickel stainless steel has been reported by Gopi *et al.* [54]. A similar study was reported elsewhere by Abdallah *et al.* [55] on the synergistic effect of some halide ions on the inhibition of zinc corrosion in hydrochloric acid by tetrahydrocarbazole derivatives.

1.3. Research aim and objectives

The aim of this study is to carry out an extensive study of (bio) corrosion inhibition activities of sixteen selected derivatives of carbazoles in 1 M HCl and SRB media. The specific objectives of the work include to:

- ✓ Investigate corrosion inhibition efficiency of the studied compounds on MS corrosion in 1 M HCl solution.
- ✓ Utilize weight loss technique to quantify the protection efficiency of these carbazoles for MS biocorrosion in SRB media.
- ✓ Elucidate the influence of carbazole derivatives on (bio)corrosion of mild steel.
- ✓ Calculate the molecular quantum chemical parameters most relevant to their action as corrosion inhibitors and correlate the values with experimental results.
- ✓ Apply quantitative structure activity relationship (QSAR) approach to investigate the possible correlation of some quantum chemical parameters with the reported experimental inhibition efficiency.
- ✓ Propose the mechanism of adsorption of this new set of compounds onto mild steel surfaces following the results from adsorption isotherms and molecular dynamics (MD) simulations.

CHAPTER 2

LITERATURE REVIEW

2.1. Background of corrosion

The verb “corrode” was originally coined from the Latin word “*corrodere*”, which connotes “to gnaw into pieces”. In essence, corrosion in whichever form it occurs, results to the deterioration and the subsequent alteration of intrinsic properties of the material. Materials on the other hand, have been defined as substances used in the fabrication of machines, processing equipment, and other manufactured products [56]. Corrosive environments are almost ubiquitous and may be a gas, liquid, solid or even hybrid solid-liquid. The extent of corrosion depends to a large extent on the aggressiveness of the environment and the material in question. Figure 2.1 is an illustration of corroding materials under different aqueous media from simple to a more complex corrosion mechanism.

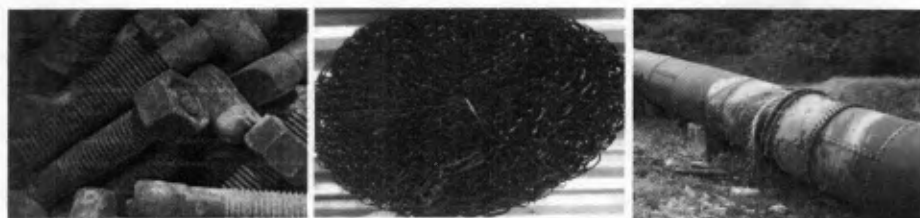


Figure 2.1. Materials undergoing corrosion under different aqueous media [57, 58].

Corrosion proceeds through a series of oxidation (anodic) and reduction (cathodic) reactions of chemical species in direct contact, or in the vicinity of the metallic surface.

The anodic reaction involves dissolution of the metal according to the following anodic equation (Equation 2.1).



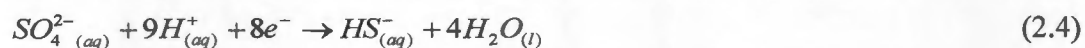
In cathodic reaction, the electrons produced in the anodic reaction are consumed by the adjacent cathodic reaction. This can proceed in two possible steps, either the reduction of hydrogen ion to produce hydrogen gas (Equation 2.2) or in neutral environments where dissolved oxygen is reduced to form hydroxide (Equation 2.3).



The resulting electron transfer process from zero valent metal to an external electron acceptor causes the release of the metal ions into the surrounding medium which ultimately leads to deterioration of the metal.

In other environments largely dominated by corrosive microorganisms such as sulphate reducing bacteria, MIC cannot be ruled out. SRB are typically Gram-negative that

are known to utilize available sulphate as the terminal electron acceptor to generate sulphide, which further aggravates the corrosion process. Equation 2.4 illustrates a typical electron acceptor reaction of SRB that ultimately results to the formation of hydrogen sulphide [59].



Consequently, it is imperative to highlight the following forms of corrosion:

General Corrosion: This form of corrosion is often referred as uniform surface corrosion. It emanates from direct chemical attack on the metal surface. During the process of general corrosion, only the surfaces of the metal are attacked. General corrosion is widely studied. It is therefore one of the forms/ types of aqueous corrosion investigated in this doctoral thesis.

Microbiologically induced corrosion: Another form of aqueous corrosion investigated in this thesis is MIC. MIC occurs when certain bacterial or extracellular polymeric substances bind onto the surfaces of metals. Anaerobic bacteria are chiefly responsible for MIC. Bacterial groups responsible for biocorrosion of metals and alloys include sulphate, iron and carbon dioxide reducing bacteria, sulphur, iron and manganese oxidizing bacteria. Sulphate reducing bacteria (SRB), however, are most often blamed for MIC due to their ability to coexist in naturally occurring biofilms with a wide bacteria community, including fermentative bacteria. This coexistence often results in a synergistic community that can induce electrochemical processes through cooperative metabolism [60].

SRB thrive in a variety of environments such as in sediments of marine, fresh waters, oil storage tanks and pipes, acid mine drains, sewage, and within the earth's subsurface [59, 61].

Microbial activity within biofilms formed on metal surfaces can drastically affect the kinetics of cathodic and/or anodic reactions and can also relatively modify the chemistry of a given protective layers thereby accelerating or inhibiting corrosion [5, 6].

Over time, metal surfaces under MIC attack develop pitting corrosion [62]. The menacing effect of this type of corrosion also depends hugely on the type and nature of bacteria.

Pitting Corrosion: Amongst all the various forms of corrosion, pitting corrosion is the more localized type and causes more havoc at microscopic level on a metal surface [63]. Metals that usually form protective film, such as aluminium and magnesium, are prone to pitting corrosion. White or grey powder often forms as a by-product of pitting corrosion. The powder residue is a common indication that pitting corrosion has occurred. However, tiny

pits or holes can be seen on the metal surface as soon as the powder is wiped out. Further damage can be caused on the metal when these small surface holes penetrate deeply into the structural chamber. In instances where conditions that exacerbate pitting corrosion cannot be managed, materials rich in alloy content can be used to provide relief to the problem [63].

Galvanic Corrosion: Galvanic corrosion takes place when two dissimilar metals joined together under electrochemical action are kept in an electrolyte. Ultimately, rust can be seen at the joints between the metals [63].

Fretting Corrosion: Another name for fretting corrosion is wear or friction corrosion [63]. It is universally defined as the attack that is expedited by the relative motion of contacting surfaces. Two heavy stationary surfaces can be affected by this type of corrosion at their interfaces the moment they start to move. As the two surfaces move against each other, they create friction, leaving behind an abrasive wear called fretting. During the friction process, the protective film on the metallic surface is eroded and this further exposes the surfaces. In essence, while many corrosion processes are driven by electrolyte, fretting corrosion is driven by this rubbing action [63]. From a practical standpoint, the use of lubricant and installation of a fretting-resistant material between the two surfaces in contact have been successfully applied to curb the menace of this form of corrosion.

Crevice Corrosion: This is often referred as shielded corrosion due to the fact that it occurs at regions where the metal surface is shielded from direct interactions with oxygen [64]. Some metals that have the tendency to form passive films during the corrosion process usually break down in those regions.

Stress Corrosion Cracking: In a situation where certain conditions are met, both crevice and pitting corrosion can give rise to stress corrosion cracking. The occurrence of this form of corrosion can manifest itself in the form of a brittle fracture on a ductile material. Some of the conditions necessary for stress corrosion cracking to occur include temperature above 60 °C, presence of aggressive ions and tensile stress [64].

Other less prominent corrosion forms include corrosion fatigue, filiform, exfoliation, active-passive cells and intergranular corrosion.

2.2. Electrochemical theory of corrosion

The modern day corrosion theory was developed based on the combination of the local cell model proposed by Evans [65] and the corrosion potential model proposed by Wagner and Traud [66] during the inception of twentieth century. The theory regards metallic corrosion as a coupled reaction comprising of two half-reactions, i.e. the anodic metal oxidation and the cathodic oxidant reduction. In any given corrosion system, four basic parts are often present. These are the anode, the cathode, the electrolyte and electrical connectivity. Their presence ensures the flow of current by the movement of electrons or ions in solution. The existence of potential difference between two regions on the metal surface ensures the metal surface is polarised into the anode (oxidation reaction) and the cathode (reduction reaction). In principle, it is generally regarded that the metal which is a bulk material maintains electrical connectivity between the anodic and cathodic parts in the aggressive environment, which acts as the electrolyte [67].

2.3. Measurement of electrochemical corrosion

Different electrochemical techniques have successfully been employed to probe the kinetics and mechanisms of electrochemical corrosion of vast metals or metal alloys in diverse corrosive solutions. Through their use, the nature and extent of electrochemical corrosion can be measured by some kinetic parameters obtained from different electrochemical theories. The most common techniques include the potentiodynamic polarization, Tafel plots, cyclic voltammetry, open circuit potential (OCP), linear polarization resistance (LPR), galvanostatic polarization, electrochemical impedance spectroscopy (EIS), etc. In the present doctoral research study, Tafel plots and electrochemical impedance spectroscopy are employed.

2.3.1. Potentiodynamic polarization and Tafel plots

This technique is undertaken in a three-electrode electrochemical cell system consisting of the metal (MS) whose corrosion process is being probed as the working electrode (WE), the reference electrode (RE), and the counter electrode (CE). All the electrodes are connected to a potentiostat which is a device that allows the user to alter the potential of the metal sample in a controlled manner and at the same time record the current that flows as a function of applied potential. Prior to any electrochemical corrosion measurement, it is advised that the entire system be allowed to attain a stable or equilibrium state popularly known as open-circuit potential (OCP). OCP has been defined as the

equilibrium potential assumed by the metal in the absence of electrical perturbations [68]. The corrosion current (i_{corr}) is the value of either the anodic or cathodic current at the OCP, and it is directly proportional to the corrosion rate of the WE (MS). The passage of current after the equilibrium electrode (metal) potential has been attained allows for the estimation of i_{corr} value from the current-potential curves. The current-potential curves obtained under steady-state conditions are generally referred to as polarization curves [69].

When the polarization curve is recorded under potentiodynamic condition, the curve is known as the potentiodynamic polarization curve. An ideal polarization is obtained when the curve is characterized by a horizontal region of a current-potential curve. Figure 2.2 represents a typical ideal polarization curve where the y-axis is the absolute current and the x-axis the electrical potential.

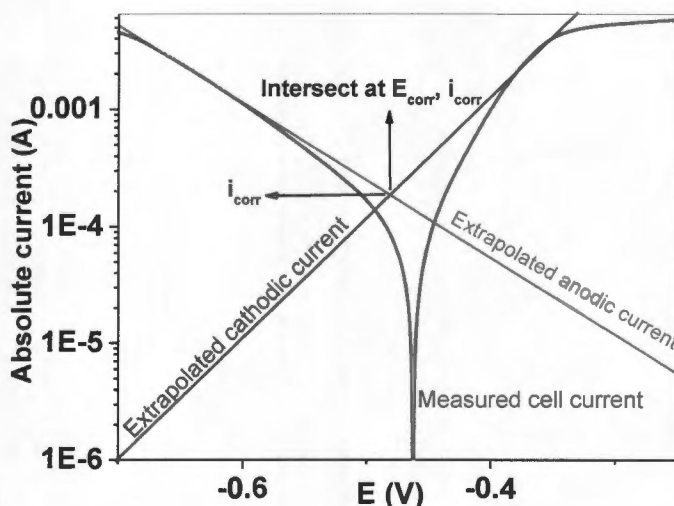


Figure 2.2. Polarization curve for a typical corrosion process showing the anodic, cathodic, measured current and classical Tafel plots.

The two straight lines in Figure 2.2 represent the theoretical current of the cathodic and anodic reactions, whereas the curved lines are the total current, which is the sum of cathodic and anodic currents. In addition, the sharp point in the curve is the point where the current reverses polarity as the reaction changes from cathodic to anodic, or vice versa [69]. Figure 2.2 also shows a typical Tafel analysis performed by extrapolating the linear segments of i versus E plot to their point of intersection, that is, E_{corr} . The corresponding cathodic or anodic value at the point of intersection is referred to as the i_{corr} . However, many real-world corrosion processes are too complex to exhibit excellent linear Tafel regions that will ensure

accurate resolution of i_{corr} by conventional extrapolation as shown in Figure 2.2. The main complexities often experienced during corrosion processes have been described by Kelly *et al.* [70] and include:

(i) *Corrosion products or impurities*: this complication occurs when impurities such as oxide films or other corrosion products are deposited on the surface of the WE. This may alter the surface morphology of the WE which may eventually affect the values of the constant parameters in the Butler-Volmer equation.

(ii) *Potential (IR) drop*: potential (IR) drop otherwise known as the ohmic (IR) drop emanates when the flow of cell current encounters impediment due to the cell solution resistance. Its manifestation is in the form of differing controlled potential and measured potential. It can however be minimized by using proper cell geometry or IR-compensation tool in the potentiostat.

(iii) *Concentration polarization*: this is often experienced when the rate of a reaction is dependent on the rate at which reactants arrive at the surface of the WE. In most cathodic reactions, this anomaly occurs at higher currents when diffusion of oxygen or hydrogen ion is not fast enough to sustain the kinetically controlled rate.

(iv) *Mixed control process*: the occurrence of more than one cathodic or anodic reaction simultaneously can aggravate the theoretical model of electrochemical corrosion test.

(v) *Preferential dissolution*: this occurs when one component of the alloy preferentially undergoes dissolution before other components.

The presence of one or more of these complications may result to potentiodynamic polarization curves that do not exhibit well-defined linear segments. Numerous sophisticated iteration algorithms have been developed and incorporated into most modern corrosion test software that fit the Butler-Volmer equation. The most striking importance of the curve-fitting technique is that it does not require a well-behaved linear region of the curve.

An electrochemical reaction under kinetic control obeys the Tafel equation of the form [69, 70]:

$$i = i_0 e^{\pm \frac{2.303(E - E_0)}{\beta}} \quad (2.5)$$

where the sign $\pm$ denotes the equation is valid for both anodic and cathodic reactions; i is the current resulting from the reaction, i_0 is the exchange current; E is the electrode/applied potential; E_0 is the equilibrium potential (constant for a given reaction), and β is the reaction's Tafel constant (constant for a given reaction, i.e. anodic or cathodic, given in volts/decade);

the term $E-E_0$ is known as the overpotential, usually given as η . The reaction Tafel constant (β) can exist as either anodic or cathodic reaction or both and may be expressed as [69]:

$$\beta = \pm \frac{2.303RT}{\alpha nF} \quad (2.6)$$

where α is the transfer coefficient; n is the number of electrons involved in the reaction; R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$); T is the absolute temperature and F is the Faraday constant ($96,500 \text{ Cmol}^{-1}$).

Since the Tafel equation given in Equation 2.5 only describes the behaviour of an isolated half-reaction, when real-world corrosion system involves two half reactions. There is therefore, the need to combine the Tafel equations for the anodic and cathodic reactions. The combination resulted to the Butler-Volmer equation [56, 69]:

$$i = i_{corr} \left(e^{\frac{2.303(E-E_{corr})}{\beta_a}} - e^{-\frac{2.303(E-E_{corr})}{\beta_c}} \right) \quad (2.7)$$

where i is the measured current from the cell; i_{corr} is the corrosion current; E is the electrode/applied potential; E_{corr} is the corrosion potential; β_a and β_c are the anodic and cathodic Tafel slopes, respectively.

2.3.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy or AC impedance technique involves the application of a sinusoidal perturbation in the form of potential or current to the cell in a certain range of frequencies. The use of negligible excitation amplitudes in the range of 5-10 mV during EIS measurement ensures minimal or no perturbations of the electrochemical test system [71]. This in particular has given EIS an edge over other electrochemical techniques.

For a typical electrical circuit that consists of resistance (R) as the circuit element that impedes the flow of electrical charge, the relationship of resistance, voltage (E) and current (I) can be illustrated using the Ohm's law:

$$R = \frac{E}{I} \quad (2.8)$$

The Ohm's law given in Equation 2.8 however is a generalization that is often applicable to an ideal resistor. In a real world scenario, electrical circuits are better described with a more complex element such as impedance (Z). Both resistance and impedance to a certain degree

share similar purpose, i.e., resisting the flow of electrical charge. In addition, impedance does this without the limitations and oversimplifications such as non-frequency dependency of resistance values and in-phase relationship between current and voltage that are inherent in the design of the Ohm's law. In a typical electrochemical cell, electron flow can be affected by slow electrode kinetics, slow preceding chemical reactions and slow diffusion. All these anomalies can be considered analogous to the resistors, capacitors, and inductors since they too can as well resist the flow of charges in an electric circuit. The total impedance in a circuit is therefore the combined individual effect of all its resistors, inductors and capacitors [71].

The measurement of electrochemical impedance is often carried out by applying an AC potential to an electrochemical cell and afterwards measuring the AC current through the cell. The AC voltage is a sinusoidal excitation signal that can be represented as [69, 71]:

$$E_t = E_o \sin(\omega t) \quad (2.9)$$

where E_t is the potential/voltage at time t , E_o is the amplitude of the signal, and ω is the radial frequency. The relationship of radial frequency ω (in radians/second) with frequency f (in Hertz) takes the form:

$$\omega = 2\pi f \quad (2.10)$$

In a typical electrochemical cell, its response to the small excitation signals applied is usually pseudo linear [71]. In a pseudo system of this nature, the current response to the sinusoidal potential is often a sinusoid at the same frequency though shifted in phase in such a manner that the current response can be represented using an equation similar to Equation 2.9 as:

$$I_t = I_o \sin(\omega t + \phi) \quad (2.11)$$

where I_t is the current at time t , I_o is the current amplitude, ϕ is the phase angle shift between the potential and current. Consequently, a similar equation to the Ohm's law can be formulated using the sinusoidal potential and current as [71]:

$$Z = \frac{E_t}{I_t} = \frac{E_o \sin(\omega t)}{I_o \sin(\omega t + \phi)} = Z_o \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (2.12)$$

where Z and Z_o are the total impedance and impedance magnitude respectively. When Euler's relationship and vector analysis are introduced, Equation 2.12 takes the form of [71]:

$$Z = Z_o(\cos \phi + j \sin \phi) = Z_o \cos \phi + j Z_o \sin \phi = Z_{re} + Z_{im}j \quad (2.13)$$

where $j = \sqrt{-1}$, Z_{re} and Z_{im} are the real and imaginary parts of the impedance respectively.

2.3.2.1. EIS spectra and equivalent circuits

During EIS measurements, various plots are generated. These plots are collectively referred as EIS spectra. The plots can take the form of the Nyquist and Bode plots. The Nyquist plot represents the imaginary part of the impedance (Z_{im}) against the real component (Z_{re}) such that the impedance is represented as a vector arrow of length $|Z|$ inclined to the horizontal (Z_{re}) axis at an angle, ϕ (often referred as phase angle) as shown in Figure 2.3. The vertical axis of Figure 2.3 is negative and each point on the plot corresponds to the impedance at one frequency. In addition, the lower values of Z_{re} correspond to higher frequency values while the higher values represent points taken at lower frequencies [71]. The phase angle is expressed as:

$$\phi = \arg(Z) = \tan^{-1}\left(\frac{Z_{im}}{Z_{re}}\right) \quad (2.14)$$

The semicircle observed in Figure 2.3 is a characteristic of a single time constant [71]. Since the frequency range and the corresponding phase angles recorded during impedance measurements are not displayed by the Nyquist plots, the use of the Bode plots becomes inevitable. The use of Bode plots ensures that more parameters are derived and provides information about the circuit [71]. The plots comprise the plots of logarithm of frequency on the horizontal axis and both the phase-shift and the absolute values of the impedance on the vertical axis as shown in Figure 2.4.

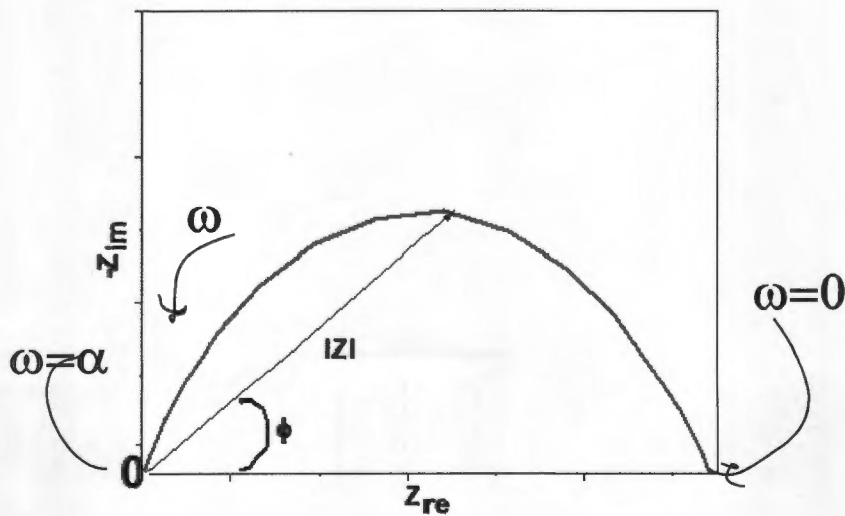


Figure 2.3. Nyquist plot showing the relevant components of the plot.

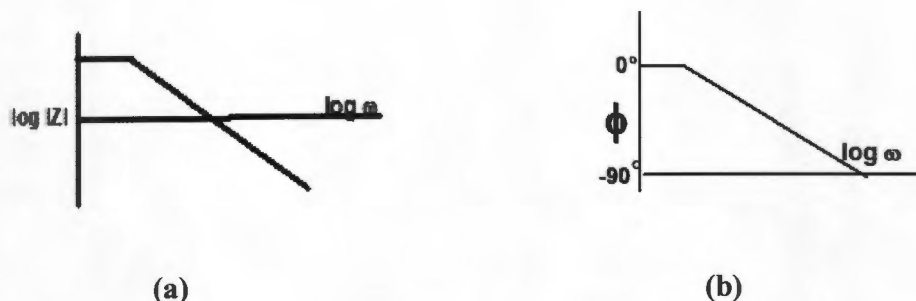


Figure 2.4. Representative Bode plots with one time constant showing the plots of logarithmic values of impedance values (a), and the phase angles against logarithmic frequency values (b) [71].

The process of analysing EIS spectra involves fitting the experimental data into appropriate equivalent circuit model that ensures proper description of the entire processes that took place on the WE surface [15]. In essence, the surface of the WE immersed in electrolyte solution behaves like an electrical circuit in which circuit elements such as resistors, capacitors and inductors can be connected in series or parallel.

In principle, the impedance of a resistor has no imaginary component, and the current through the resistor is in phase with the voltage, that is, the phase shift is 0° . The impedance of a capacitor however, has only the imaginary component, which is a function of both frequency and capacitance. In addition, the current through a capacitor is usually 90° out of phase with the voltage across it, that is, the current leads the voltage. The impedance of a capacitor is inversely proportional to the frequency, consequently at high frequencies a capacitor behaves as a short circuit with its impedance tending towards zero. At low frequency regions, a capacitor behaves like an open circuit while the impedance tends towards infinite value. Similarly, the inductor also has only imaginary part in its impedance and the current through it is always 90° out of phase with the voltage drop across it, in a manner that the current lags behind the voltage. An inductor therefore behaves like a short circuit at low frequencies and a large impedance at high frequencies.

EIS spectra are usually processed by constructing simple equivalent circuit models using approximate configurations of circuit elements to make initial guesses followed by iteratively fitting the experimental data to the theoretical circuit model. In a real electrochemical set-up however, the WE surface usually involves more complex electrochemical and/or physical processes that cannot always be explained by simple circuit elements but rather a combination of two or more circuit elements [15]. To this end, modern

potentiostats for EIS studies are now equipped with state-of-the-art software programs that carry out these iterations and produce results within seconds. Subsequently, the closeness of the theoretical data to the experimental results obtained are adjudged based on some statistical error values produced during the iteration steps.

In most practical corrosion processes, the Nyquist plots do not produce a semi-circle whose centre is on the horizontal axis. Rather, in most cases, the observed plot corresponds to the arc of a circle whose centre is below the real impedance axis. This anomaly has been ascribed as frequency dispersion as a result of the inhomogeneity or roughness of the WE electrode surface [72, 73]. Consequently, the constant phase element (CPE) is often introduced in the circuit in order to ensure a more accurate description of the process occurring at the electrode/electrolyte interface [74]. According to Hirschorn *et al.* [75] and Bojinov *et al.* [76], the CPE is ideal in describing electrochemical systems involving oxide films, metal/passive film interface and film/electrolyte interface.

The impedance of the CPE (Z_{CPE}) is expressed as:

$$Z_{CPE} = \left(\frac{1}{Y_0} \right) [(j\omega)^n]^{-1} \quad (2.15)$$

where, Y_0 is the CPE constant; ω is the angular frequency; j is the imaginary number and n is the phase shift (exponent) which can be used to gauge heterogeneity or roughness of the surface. The numerical values of n hovers between -1 and 1 in a manner that the CPE stands for a resistance, when $n = 0$, a capacitance, when $n = 1$, an inductance, when $n = -1$, and a Warburg impedance, when $n = 0.5$ [73]. The phase angle of the CPE is 90° when $n = 1$, as such CPE behaves like a true capacitor. In instances when n is close to unity, the CPE resembles a capacitor, but the phase angle is not exactly 90° but rather hovers below 90° at all frequencies.

2.4. Electronic structure methods

Electronic structure methods employ the laws of quantum mechanics in order to describe the molecular system. According to quantum mechanics, the energy and other related properties of a molecule may be obtained by solving Schrödinger equation:

$$H\Psi = E\Psi \quad (2.16)$$

where H is the Hamiltonian operator, Ψ is the wavefunction and E is the energy of the particle. The Hamiltonian operator includes both the kinetic energy term and the potential energy term. When the Hamiltonian operator is written to include both kinetic and potential terms and considering one dimension motion, it takes the form:

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (2.17)$$

For a three dimensional system, the Schrödinger equation can then be written as:

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(x,y,z) + V(x) \psi(x,y,z) = E \psi(x,y,z) \quad (2.18)$$

$$\text{where } \nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$$

Consider that the system of interest is a molecule with two electrons (e_1 and e_2) and two nuclei (N_A and N_B). In order to develop the Schrödinger equation, one needs to find all the kinetic energy terms and all the potential energy terms. The kinetic energy term related to the nucleus and electrons can be written as:

$$E_k(\text{nuclei}) = \frac{-\hbar^2}{2m} \nabla_{N_A}^2 + \frac{-\hbar^2}{2m} \nabla_{N_B}^2 \quad (2.19)$$

$$E_k(\text{electrons}) = \frac{-\hbar^2}{2m} \nabla_{e_1}^2 + \frac{-\hbar^2}{2m} \nabla_{e_2}^2 \quad (2.20)$$

The potential energy terms will include the repulsion term between electrons ($V_{e_1e_2}$), repulsion term between nuclei ($V_{N_A N_B}$), attraction term between electron 1 and nucleus A ($V_{N_A e_1}$), attraction term between electron 1 and nucleus B ($V_{N_B e_1}$), attraction term between electron 2 and nucleus A ($V_{N_A e_2}$), attraction term between electron 2 and nucleus B ($V_{N_B e_2}$). The mathematical form of each of these equations is given below:

$$V_{e_1e_2} = \frac{e^2}{4\pi\epsilon_0 r_{12}}, V_{N_A N_B} = \frac{Z^2 e^2}{4\pi\epsilon_0 r_{AB}}, V_{N_A e_1} = \frac{Z e^2}{4\pi\epsilon_0 r_{A1}}, V_{N_B e_1} = \frac{Z e^2}{4\pi\epsilon_0 r_{B1}}, V_{N_A e_2} = \frac{Z e^2}{4\pi\epsilon_0 r_{A2}},$$

$$V_{N_B e_2} = \frac{Z e^2}{4\pi\epsilon_0 r_{B2}} \quad (2.21)$$

These terms should then be combined to form a Hamiltonian operator and utilised to solve the Schrödinger equation (Equation 2.18). At the moment, it is not possible however, to study mathematically a system of two or more moving particles. Furthermore, it is still a mathematical challenge to obtain an analytical solution of the Schrödinger equation for a system with two or more potential energy terms. It is for this reason that several approximation approaches have been employed to solve the Schrödinger equation. In the next sections, we provide a brief explanation of some of these approximation approaches and the theory behind their development [78, 79].

2.4.1. Born-Oppenheimer approximation

The Born-Oppenheimer approximation is the first of the several approximations used to simplify the solution of the Schrödinger equation by separating nuclear degrees of freedom and electronic motions [77]. This approximation is based on the fact that the mass of a typical nucleus is thousands of times greater than that of an electron. In this respect, the nucleus move very slowly relative to the electrons. The movement of electrons is instantaneous with respect to changes in nuclear position; hence, the electron distribution within a molecular system depends wholly on the positions of nuclei (potential energy), and not on their motion (kinetic energy).

Several other approximations are utilised in the simplification of the Schrödinger equation. Electronic structure methods are characterized by their various mathematical approximations to the way in which the Schrödinger equation is solved.

2.4.2. Hartree-Fock (HF) approximation

This is another approximation method for the solution of the Schrödinger equation related to the multi-electron system. The simplest way of writing the wave function for a multi-electron system is that of considering the electrons as independent. This means considering that the motion of one electron is not influenced by the motion of the other electrons. Then the total wavefunction can be written as a product of functions, each of them depending on the coordinates of one electron. For example, consider a model of the hydrogen molecule in which there are two electrons, here denoted as e_1 and e_2 , and two nuclei, here denoted as H_A and H_B , as illustrated in Figure 2.5. The electronic Schrödinger equation takes the form:

$$\nabla_1^2 \psi_1 + \nabla_2^2 \psi_2 + \frac{2m_e}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r_{A1}} + \frac{e^2}{4\pi\epsilon_0 r_{B1}} + \frac{e^2}{4\pi\epsilon_0 r_{A2}} + \frac{e^2}{4\pi\epsilon_0 r_{B2}} - \frac{e^2}{4\pi\epsilon_0 r_{12}} - \frac{e^2}{4\pi\epsilon_0 r_{AB}} \right] \psi = 0 \quad (2.22)$$

According to the Hartree-Fock equation, the term $\frac{e^2}{4\pi\epsilon_0 r_{12}}$ can be considered negligible and equal to zero.

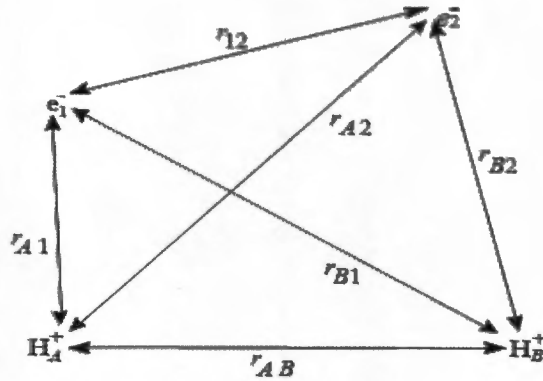


Figure 2.5. A schematic representation of the electron-electron, nucleus-electron and nucleus-nucleus interactions in the hydrogen molecule.

Once the term relating the interdependence of electron motion is removed, it becomes possible to consider that the Hamiltonian would be separable, and the total electronic wavefunction describing the motions of the two electrons would just be the product of two hydrogen atom wavefunctions:

$$\psi(r_1; r_2) = \psi_{H_A}(r_1) \psi_{H_B}(r_2) \quad (2.23)$$

This expression can be proven by considering the Hartree-Fock product:

$$\psi(r_1; r_2, r_3 \dots r_n) = \phi(r_1) * \phi(r_2) * \phi(r_3) \dots * \phi(r_n) \quad (2.24)$$

This equation however fails to satisfy the antisymmetry principle, which states that a wavefunction describing fermions should be antisymmetric with respect to the interchange of any set of space-spin coordinates (i.e., the three spatial degrees of freedom, and the intrinsic spin coordinate of the fermions, denoted as α or β). A better antisymmetric wavefunction is obtained if we can write the total wavefunction as a linear combination of permutations [78, 79].

$$\psi_{\text{total}}(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \sum (-1)^p \psi_1(k_1) \psi_2(k_2) \dots \psi_n(k_n) \quad (2.25)$$

where p is the number of transpositions performed on the starting $\psi_1(R_1) \psi_2(R_2) \dots \psi_n(R_n)$ to obtain the given term in the linear combination, $k_1, k_2, \dots, k_n$ are the coordinates resulting after the permutations and $1/\sqrt{n!}$ is the normalization factor. The factor $(-1)^p$ ensures that the wavefunction does not change sign for an even number of transpositions, but it changes sign for an odd number of transpositions.

Further approximations involve the replacement of the many-electron Hamiltonian operator with an effective one-electron Hamiltonian called the *Fock operator*. The Fock operator

contains all the one-electron terms of the Hamiltonian operator (kinetic energy and nuclei-electron attraction terms), and considers an effective potential perceived by one electron (i.e., each electron is subjected to a field that models the effect of the other electrons in the system). A problem that arises in considering an average value of the potential due to the presence of the other electrons is that one needs to know the electron distribution in order to evaluate the potential accurately, but the electron distribution can be known only after solving the Schrödinger equation. This demands an iteration procedure for the solution of the Schrödinger equation, commonly called the *Self Consistent Field* (SCF) procedure.

The SCF procedure is applied both to the study of atoms and to the study of molecules. This method is ideal for use in computers because it can be written as an algorithm. In the study of polyelectronic atoms, the Hartree SCF procedure considers the average potential that an electron perceives due to the charges of all the other $Z-1$ electrons and the nucleus. Initially, a "guess" average potential is utilized in the Hamiltonian operator, and the Schrödinger equation is solved. The solutions are then utilized to evaluate the average potential. If this differs significantly from the initial guess value, the new value is utilized to write the Schrödinger equation. This equation is then solved and the solutions are used to evaluate the average potential. The values are compared, and if they differ extensively the procedure is repeated. This procedure is repeated until the difference between the value found at the end of a cycle and the value utilized at the beginning of that cycle is less than a pre-fixed value called the *cut-off value*. Then we say that the procedure has converged (i.e. when the value returned by the equation, may be the value that was put in on that iteration). The absence of explicit electron-electron repulsion terms enables the replacement of the Schrödinger equation with Z equations, each of them depending on the coordinates of one of the electrons present in the atom. Therefore, the wavefunction of the atom can be written as a product of one-electron orbitals [80].

Since molecules contain more than one nucleus, Hartree-Fock calculations are more difficult in their case as compared to calculations for atoms, therefore, the potential cannot be assumed to have a spherical symmetry. In other words, while the atom is a one-centre problem, a molecule is a many-centre problem. The molecular orbital theory (as developed by Roothaan) provides a way for obtaining solutions to the Schrödinger equations. The wavefunction is expanded in terms of other functions (*basis set* functions), and the expansion coefficients are determined variationally [81]. The vibrational theorem states that "*the energy of any trial wavefunction E is always an upper bound to the exact ground state energy E_0* ".

The resulting equations are called the *Hartree-Fock-Roothaan equations*. The results of the calculations are a set of molecular orbitals ψ_i (as many as the functions in the basis set utilised) and the corresponding energies ϵ_i .

2.4.2.1. Basis sets

The selection of basis sets is necessary for the calculation of molecular properties. A basis set is a set of functions (called basis functions) which are combined in linear combinations (generally as part of a quantum chemical calculation) to create molecular orbitals. Therefore, for basis functions χ (usually centred on atoms), the linear combination of these orbitals would correspond to a molecular orbital ϕ :

$$\phi = \sum_i c_i \chi_i \quad (2.26)$$

where c_i are the expansion coefficients.

Generally basis set are formed from atomic orbitals, for instance, in the case of the H_2 molecule, the molecular orbital can be formed as a linear combination of the sigma (s) atomic orbital on one H atom (H_A) and the sigma atomic orbital on the other H atom (H_B). In this way, the molecular orbital (σ) for the hydrogen molecule can be written as:

$$\sigma \approx 1 S_{H_A} + 1 S_{H_B} \quad (2.27)$$

The larger number of basis functions selected to form molecular orbitals would yield more accurate approximations to the molecular orbitals. Usually the basis functions are formed from the Slater-type functions and the Gaussian-type functions [78, 82]. The Slater-type function (Figure 2.6a) has a mathematical form of:

$$\chi^{\text{STO}}(x, y, z) = N x^a y^b z^c e^{-\zeta r} \quad (2.28)$$

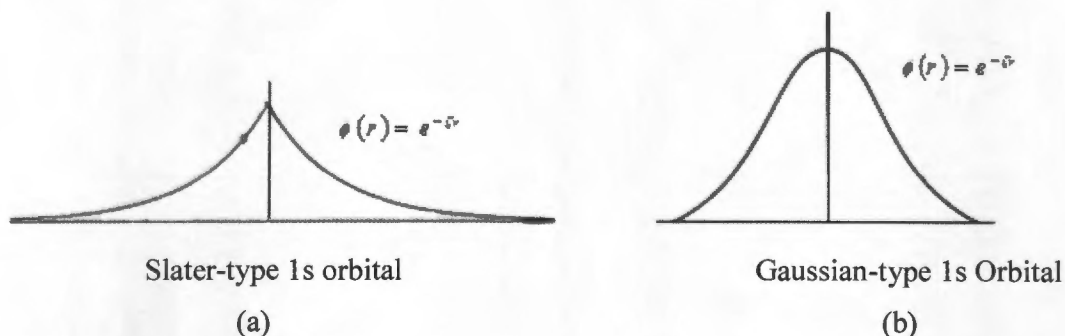


Figure 2.6. Graphical representations of the (a) Slater-type orbital and (b) the Gaussian-type orbital.

where, N is the normalization constant, a , b and c are parameters that control the angular momentum, ζ controls the width of the orbital (i.e., the large ζ gives tight function and smaller ζ gives diffuse function). Because of these characters, STO orbitals are likely to provide correct descriptions for the short-range and long-range behaviour of a molecular system. Gaussian function (Figure 2.6b) has the mathematical form:

$$\chi^{\text{GTO}}(x, y, z) = N x^a y^b z^c e^{-\zeta r^2} \quad (2.29)$$

The difference between the two types of orbitals is that STO are more accurate in describing molecular systems than GTO. However, STO is much more computationally expensive. Generally, molecular orbitals are formed by linear combinations of GTO with the objective of mimicking the STO.

2.4.2.2. Classification of Basis sets

Basis sets may be classified into different types depending on the number of Gaussian functions utilised to emulate an STO. These include hydrogen like orbitals, minimal basis set, valance split basis sets and diffuse basis set [78, 82-85]. Some of these basis set are described in the next paragraphs, giving information on their applicability and weaknesses.

Minimal basis set: This basis set describes only the most basic aspects of the orbitals, one basis function for each atomic orbital angular momentum component. It is the minimum number of basis functions χ that is needed to describe the ground states of the component atoms in a molecule. A water molecule (H_2O) would require seven basis functions (either STO or GTO types) in place of the seven atomic functions present in the water molecule which include, two 1s orbitals for each of the hydrogen atoms plus a 1s, 2s, 2 p_x , 2 p_y and 2 p_z atomic orbitals for the oxygen atom. A slater type orbital may also be approximated by a combination of two or more Gaussian type orbitals leading to such basis functions as STO-2G, STO-3G, etc. [78, 82-85].

All minimal basis sets however have some weaknesses including the fact that all the basis functions are either themselves spherical or come in sets that when taken together describe a sphere. This means that minimal basis sets are suited for describing molecular systems with spherical molecular environment and are not suitable for description of atoms with aspherical molecular environment. The second weakness of minimal basis sets is that the basis functions are atom centred instead of being between atoms [78, 82-85]. This shortcoming implies that

minimal basis sets are not able to describe electron distribution between nuclei, which is a major factor in chemical systems.

Double zeta: These basis sets are formed in such a way that each atomic orbital is expressed as the sum of two Slater-type orbitals [78, 82-85]. In the case of water for instance, which has seven atomic orbitals, the double zeta basis set is built in such a way that there are 14 basis functions, with two basis functions describing each of the atomic orbitals in the water molecule. The double zeta basis sets have to some extent reduced spherical character which can be described as having anisotropy character with respect to minimal basis sets [78, 82-85]; for example, the p orbitals in different directions can have effectively different sizes.

Split valence basis set: In a split-valence basis set the inner-shell atomic orbitals are represented by one basis function and the valence orbitals are represented by two or more basis functions [78, 85]. The 3-21G basis set for example has one contracted Gaussian function that describes the inner core orbital. This contracted Gaussian function is formed as a linear combination of three primitive Gaussian functions. In the valence atomic orbitals we distinguish between the inner and the outer valence atomic orbitals; the inner valence atomic orbital is described by two basis functions which are a linear combination of two primitive Gaussians; the outer valence atomic orbital is described by one primitive Gaussian function [78, 85]. In the case of O atom for instance, the inner core orbital is a 1s and is described by 3 Gaussian functions, the inner valence atomic orbital is the 2s and is described by 2 primitive Gaussian functions and the outer valence orbitals are the $2p_x$, $2p_y$ and $2p_z$, each is described by one primitive Gaussian function. The 6-31G basis set represents each inner-shell orbital with one contracted Gaussian function which is a linear combination of six primitive Gaussian functions and each valence orbital with two basis functions, one contracted Gaussian function that is a linear combination of three primitive Gaussians and one primitive Gaussian function [78, 82-85].

Polarization functions: Both minimal basis sets and split-valence basis set functions are atom centred, which means that they cannot provide a good description of the region between atoms [78, 82-85]. This implies that the increase in the number of contracted Gaussian functions per atomic orbital does not necessarily result in a good quality basis set [82]. A better description of chemical bonds therefore, requires that other types of basis functions be

utilised. Polarized basis functions are usually utilized to account for the region between atoms [78, 82]. Polarized refers to the distortion of an electron cloud of a system as a result of the neighbouring species. Therefore contracted Gaussian functions that take into account the fact that the electron cloud of chemical species can be distorted need to be selected for studying such system. Such contracted Gaussian functions are called polarization functions and are constructed by adjusting the angular momentum parameters. The polarization basis functions are represented by the asterisk (*) at the end of the notation of the basis set, for instance, the 6-31G* (also denoted as 6-31G(d)) represents that polarization functions of the *d* type are added for each of the heavy atoms. When the polarization functions are also added on the H atoms the basis set is denoted as 6-31G** (also denoted as 6-31G(d,p)), where the second * represents the *p* functions added on the H atom [78, 82]. This type of functions are important in describing various phenomenon such as hydrogen bonding where the orbitals on the H atom are not necessarily spherical but are distorted because of the electron cloud of the neighbouring O atom.

Diffuse functions: Diffuse functions are constructed to take into account the fact that in some cases (e.g., anionic systems) the electron distribution may be further away from the nucleus. In order to take into account features that are away from the nucleus diffuse functions are needed. These functions are formed by adding very small zeta exponents to a basis set. These basis sets are represented by the + signs. One + means that we are accounting for the *p* orbitals [78, 85], while ++ signals that we are looking at *p* and *s* orbitals. When the diffuse functions are added to the *s* and *p* atomic functions, to describe the character of heavy atoms, the basis set is denoted as 6-31+G; when diffuse functions are also added to the *s* orbital on hydrogen atom, the basis function is denoted as 6-31++G [78, 85].

2.4.3. Density Functional Theory (DFT) method

DFT method is a computational approach that derives properties of the molecule based on a determination of the electron density of the molecule rather than the wavefunction. The electron density which is a physical property of all molecules is a function with three variables (i.e. *x*-, *y*-, and *z*-position) of the electrons. A functional is defined as a function of a function, for instance, the energy of the molecule is a functional of the electron density [77, 86-88]. The determination of the electron density is independent of the number of electrons involved. This is unlike the wavefunction, which becomes hugely complicated as

the number of electrons increases. Mathematically, the expression of the electron density in three dimensions can be represented as follows:

$$\text{Electron density} = \rho(x,y,z) \quad (2.30)$$

The energy of the molecular system is then expressed as:

$$\text{Energy} = F[\rho(x,y,z)] \quad (2.31)$$

There are three main categories of DFT methods, namely the local density approximation (LDA), the gradient-corrected (GC) and the hybrid methods [86, 87]. Each of these methods has their specific limitations and advantages. For instance, LDA methods utilize the assumption that the density of the molecule is uniform throughout the molecule, an assumption that has made the method remain very unpopular. An example of functional utilising the LDA method is the local spin density treatment of Vosko, Wilk and Nasair (VWN). Gradient corrected methods tend to some extent to account for the non-uniformity of the electron density. An example of the gradient-corrected correlation functional is the Becke-Lee, Yang and Parr (BLYP) [77, 87]. Hybrid methods attempt to incorporate most of the useful features from Hartree-Fock methods with some of the improvements of DFT mathematics. An example of hybrid functionals which describe the exchange functional and combine it with a local and/ or gradient-corrected correlation functional is the Becke's three-parameter formulation such as B3LYP and B3PW91 [89, 90].

2.4.3.1. Advantages of DFT methods over other *ab initio* methods

DFT methods are similar to *ab initio* methods in many ways. For instance, DFT calculations need about the same amount of computation resources as Hartree-Fock theory, the least expensive *ab initio* method. However, DFT methods unlike *ab initio* methods can be utilized for calculations involving metals, and are more specifically designed for the determination of kinetics problems. Density functional theory method is suitable in the study of molecules ranging from 40 to 100 atoms [91]. Furthermore, there is an inclusion of the effects of electron in DFT methods. For instance, they recognize the fact that electrons in a molecular system react to one another's motion and attempt to keep out of one another's pathway in their model. This recognition of the effects of electrons has made DFT methods to remain attractive. Hybrid methods such as B3LYP have often found application as a preferred method for reaction calculations [87, 88]. DFT methods also draw strength from their computational accuracy without the additional increase in computing time, an advantage emanating from the ability of DFT methods to scale three dimensionally (x-y-z coordinates) unlike the four dimensional *ab initio* methods. Due to these significant advantages, DFT

methods have extensively been applied in corrosion studies by Eddy and Ita [92], Abdel-Ghani *et al.* [93], Arslan *et al.* [20], Ghosh [91], Martinez and Štagljar [24] and Chakraborty *et al.* [94].

2.5. Gaussian program

The computational results that are presented in this thesis were performed using the Gaussian09 program. Gaussian09 program is capable of predicting many properties of molecules and reactions, such as thermochemical properties, nuclear magnetic resonance (NMR) properties, vibrational frequencies, atomic charges and electrostatic potentials, molecular orbitals, multiple orbitals, bond and reaction energies, molecular energies and structures, infrared and Raman spectra, reaction mechanisms, excitation energies and potential energy surfaces [88-90]. Gaussian09 program contains a detailed list of procedures relating to different approximation methods commonly known as different levels of theory.

Gaussian input is designed to be free-format and extremely flexible irrespective of the versions of the computer program, and it is not case-sensitive, and it allows keywords and options to be shortened to a unique abbreviation. Gaussian accepts molecule specifications in several different formats including Cartesian coordinates, Z-matrix format (internal coordinates) and mixed internal and Cartesian coordinates [77].

2.6. Quantum chemical parameters with relevance to corrosion inhibition

Quantum chemical approaches have been widely employed as a great tool in predicting the inhibition potentials of some organic compounds that are structurally related. This is supported by the strong correlations that have been established between the corrosion inhibition efficiencies of most compounds and some semiempirical parameters [30, 55, 92, 95]. Quantum chemical methods are particularly important in the study of electrochemistry and equip researchers with an appropriate means of probing the structure, reactivity and behaviour of corrosion inhibitors. In the subsequent subsections, we present the different quantum chemical parameters that are of interest to corrosion.

2.6.1. Frontier molecular orbitals (FMO) and reactivity of molecules

According to the FMO theory of chemical reactivity, the formation of a transition state is characterized by the interaction between the frontier orbitals (HOMO and LUMO) of the reacting species. The theory governing hard and soft nucleophiles and electrophiles has also directly been linked to the relative energy of the HOMO/LUMO orbitals. For instance,

hard nucleophiles have a low-energy HOMO; soft nucleophiles have a high-energy HOMO; hard electrophiles have a high-energy LUMO; and soft electrophiles have a low-energy LUMO. The energy of the two orbitals also play important role in understanding the corrosion inhibition ability of inhibitors. A higher E_{HOMO} for organic molecules facilitates the ease to donate electrons to the unoccupied d orbitals of metal, hence, resulting to a higher inhibition efficiency. At a lower E_{LUMO} for organic molecules, there is ease of acceptance of electrons from the d orbitals of metal resulting to a higher inhibition efficiency. Similar interpretations have been reported in literature [30, 31, 95-98]. In line with this concept, Martinez and Štagljar [24] alluded that in a corrosion system containing inhibitor, the inhibitor and the metal act as a Lewis base and a Lewis acid, respectively. It has also been reported [103] that molecular orbitals play a significant role in governing many chemical reactions and determining electronic band gaps in solids.

The energy band gap ($\Delta E = E_{LUMO} - E_{HOMO}$) has been employed as a characteristic parameter for metallic complexes [31, 97]. Most corrosion studies have explored the concept of $E_{LUMO} - E_{HOMO}$ gap to develop a theoretical model that can be used to quantitatively describe the structural stability and conformity in numerous molecular systems. Similar studies have linked the energy gap to the redox potential and electrical resistivities of the complexes. In summary, it has been established by previous studies [55, 92, 97], that inhibition efficiencies increase as the $E_{LUMO} - E_{HOMO}$ values decrease. Such trend depicts the stability of formed complexes, hence, chemisorption is evident. In addition, study conducted by Eddy and Ita [92] has explored the relationship between the energy band gap (ΔE), activation hardness and polarizability. A decrease in the value of ΔE connotes that the molecule is soft, and can be easily polarized.

Many other quantum chemical indices are also derivable from the frontier molecular orbital (FMO) energy parameters (E_{HOMO} and E_{LUMO}) using appropriate relations (Equations 3.5-3.8) as previously reported in literature [92].

2.6.2. Selectivity parameter: Partial atomic charges

Electrical charges in the molecule play crucial role as the driving force of electrostatic interactions hence are important in many chemical reactions and physicochemical properties of compounds. This has necessitated the use of charge-based descriptors as chemical reactivity indices or as measures of weak intermolecular interactions. Most computational methods use Mulliken population analysis for the calculation of the charge distribution in a molecule [92, 99]. The only limitation with Mulliken's definition is that both ionization

potential and the electron affinity relate to some mythical state of an atom called the valance state.

The adsorbability of an inhibitor on the metal surface is also related to the charges on the inhibitor molecule. The higher the negative partial atomic charge of the adsorbed centre, the more easily the atom donates its electron to the partially filled or vacant d orbital of the metal [20, 92, 96, 97].

2.6.3. Selectivity parameter: Fukui functions

Fukui functions ($f(r)$) were computed from the Mulliken atomic charges on the neutral, anionic and cationic forms of the inhibitor molecules in order to probe the local reactivity of each atom in the inhibitor molecules. This is defined in (Equations 3.9–3.11). The Fukui functions ($f(r)$) indicate the change in electron density at a given position when the number of electrons is changed (Equation 3.9), such that, largest value of f_k^+ (Equation 3.10) defines the most probable site in a molecule that will receive charge from the metal surface (electrophilic), largest value of f_k^- (Equation 3.11) defines the most probable site through which the molecule will back-donate charge to the metal surface (nucleophilic).

2.7. Quantum chemical study

A host of authors have employed various quantum chemical techniques in a bid to explore and correlate corrosion inhibition efficiency of molecules.

Arslan *et al.* [20] carried out quantum chemical calculations using the DFT method on four set of sulphonamides used as corrosion inhibitors for mild steel in acidic medium. Their study revealed that the entire sulphonamides are effective and harmless corrosion inhibitors for mild steel in 1.0 M HCl solution. The results obtained showed a strong correlation between experimental percentage inhibition efficiency and E_{HOMO} , E_{LUMO} , global hardness, polarizability, dipole moment and charges. Similar satisfactory correlations abound [34, 100]. Quantum chemical calculations based on AM1 semi-empirical method was reported by Behpour *et al.* [101] in their electrochemical, gravimetric and theoretical investigations of the inhibitory effect of thiosalicylaldehyde derivatives. The results revealed a good correlation between the corrosion inhibition efficiency and the calculated quantum chemical parameters. Another significant contribution in this regard was done by Yurt *et al.* [30] who revealed that significant correlations existed between experimentally obtained inhibition efficiencies and quantum parameters such as dipole moment, electronic charges, E_{HOMO} , E_{LUMO} and energy gap.

Correlation between the molecular structure and the corrosion inhibition efficiency of chestnut tannin in acidic solutions has been modelled by molecular dynamics, molecular mechanics and semiempirical quantum NDDO method with PM3 parametrization [24]. The quantum calculation results and the results obtained from the adsorption theory, gave a consistent picture of the studied corrosion system. Temkin adsorption isotherm was proposed. Bereket *et al.* [97] reported a satisfactory correlation among the experimentally obtained inhibition efficiencies and theoretically derived quantum parameters for a set of imidazole derivatives as corrosion inhibitors for iron in acidic medium.

2.8. Quantitative structure activity relationship (QSAR)

According to Ebenso *et al.* [102], the correlation of individual quantum chemical parameters with experimentally derived inhibition efficiency is usually less informative due to the complex nature of the adsorption process. To this end, it is therefore most appropriate to combine several quantum chemical parameters to form a composite index that could be correlated to the experimental inhibition efficiency. This is achieved by the use of quantitative structure-activity relationship approach whereby relevant mathematical equations are developed and used to relate the quantum chemical parameters to the observed inhibition efficiency. The set of equation obtained can be used to study and predict inhibition efficiency of related compounds in future.

The quantitative structure activity relationship study conducted by Murulana *et al.* [103] on some imidazolium-based ionic liquids gave strong correlation between experimentally obtained corrosion inhibition efficiency and two quantum chemical parameters. The information provided by QSAR is necessary especially towards the search for new ionic liquids with similar characteristics, and can be used to predict better corrosion inhibitors.

Bentiss *et al.* [104] reported a significant QSAR correlation between experimental and predicted charge-transfer resistance, R_{ct} using a linear resistance (LR) model indicating that the variation of the inhibitor effectiveness with the structure of thiadiazole derivatives can be unravelled in terms of electronic properties. They went on to conclude that the importance of QSAR approach cuts across finding the optimal group of parameters that might be used to predict and design the structure and overall molecule suitability as an effective inhibitor.

2.9. Molecular dynamics simulation in corrosion inhibition studies

The verification of experimental data has become a fundamental requirement for accurate analysis of corrosion inhibition systems. To this end, several molecular modelling

techniques have been expanded to probe metal surface interactions with inhibitor molecules in different media [105-109]. In the present work, considering the fact that both universal corrosion and biocorrosion of mild steel take place in aqueous media, molecular simulation was then used to identify low energy adsorption sites between the substrate-adsorbate system. Molecular simulation searches of the configurational space of iron-alanine system as the temperature is gradually decreased was reported by Khaled *et al.* [105]. The results further suggest that alanine molecules adsorb on Fe surface via the nitrogen or oxygen atoms with the lone pair electrons.

For Singh *et al.* [106], their Monte Carlo simulations study of green naphthyridine derivatives on the Fe(110) surface was carried out to model the mode of adsorption and the most stable low energy adsorption configurations. From the resulting energy parameters such as the total energy, adsorption energy and deformation energy, high negative adsorption energy values represent a more stabilized and stronger interaction between the iron and inhibitor. The results obtained from the simulations study correlate well with the trend of the experimental inhibition efficiency.

The simulation studies of L-glutamine molecules show that some of its configurations are unstable adsorption centres for the iron surface [107]. The most unstable configurations were attributed to those with more positive $E_{interaction}$ values.

Monte Carlo simulations incorporating molecular mechanics and molecular dynamics was used to study the corrosion inhibition of copper by benzotriazole derivatives in an aerated HCl [108]. The results revealed strong adsorption occurred at the thiazolyl and carbothioamide groups.

Feng *et al.* [109] highlighted the importance of molecular simulations in corrosion study as among other things, its potential application in the design and development of organic corrosion inhibitors. According to them, the choice of Fe(110) surface over Fe(100) and Fe(111) was based on the most densely packed and stable surfaces. The high negative value computed for 5,10,15,20-tetraphenylporphyrin molecules and iron surface indicates strong and stable interaction. The other two Fe surfaces have been criticized for their relatively open structures.

2.10. Mild steel: Composition, applications and disadvantages

Mild steels generally consist of between 1 to 2% of other alloy constituents by weight with the main constituent being iron [110]. Plain carbon steels are classified into three categories based on the percentage of carbon present in the steel. They include the low-

carbon or MSs with about 0.08-0.28% C, the medium-carbon steels with about 0.28-0.55% C, and the high-carbon groups comprising about 0.5-1.0% C [111]. In addition, manganese, nickel, vanadium, chromium, phosphorous, molybdenum, sulphur and silicon have all being used as alloying materials for iron [110, 111]. The amount of these substituents and carbon solely depends on the required properties of the alloy. The use of carbon steels has permeated various industrial applications including transportation, mining, chemical processing, construction, nuclear and fossil fuel power plants, process plants, marine structures etc. [110, 112]. The popularity of carbon steels relative to other metal alloys is due to their appreciable mechanical strength and cheapness [113-115]. Notwithstanding, each application of carbon steels has its concomitant corrosion burden that threaten its life span if adequate measures are not put in place. It is in a bid to minimize the corrosion burden that mild steel has remained the most popular. Nevertheless, MS is susceptible to corrosion attack in very aggressive environments such as solutions of strong acids and SRB dominated media that are often found in many industrial setups.

2.11. Corrosion control methods

Various methods have been adapted to combat corrosion of metal components. The choice of a particular corrosion control method cuts across factors such as the type of corrosion, type of material, nature of environment, control cost, etc. Central to all the corrosion control measures is the practice of either modifying the material or the active environment in a way that will retard the effect of corrosion [116]. The main corrosion control methods, mode of action and their associated problems that have been adapted to metal corrosion in aqueous acid are presented in Table 2.1.

Table 2.1. Methods employed to control metal corrosion in aqueous acid, their respective mode of action and associated problems.

Method	Mode of action	Associated problems
Material selection [110, 117-119]	Selection of materials based on the prevailing environment.	Often expensive.
Proper design [110, 120, 121]	Adoption of special designs that eliminates accumulation of water	(a) Complex method as design must adhere to other crucial criteria; (b) Designers may lack adequate knowledge
Cathodic [110, 122, 123] and anodic protection [110, 124, 125]	Modification of the electrochemical potential of the metal	Requires in-depth knowledge of corrosion mechanism
Protective coatings [110]	(a) Use of organic or inorganic materials that are relatively inactive. (b) Other useful properties can be blended with coating i.e., abrasion resistance.	Toxicity concerns
Corrosion inhibitors [110]	(a) Adsorb as a thin film on metal surface; (b) Induces the formation of thick corrosion product; (c) Changes the characteristics of the corrosive environment.	Toxicity concerns

On the other hand, Table 2.2 provides an insight into the main control measures for biocorrosion adopted worldwide, as well as the action and problems associated with their use.

Table 2.2. Methods employed to control biocorrosion, their respective mode of action and associated problems [7, 126-131].

Method	Examples	Mode of action	Associated problems
Physical cleaning	(a) Washing with brushes; (b) Injection of air or gas; (c) Manual cleaning.	Removes physical deposits.	(a) Abrasive method may damage protective film; (b) Not effective in removing thick biofilms.
Biocides	(a) Chlorine; (b) Ozone; (c) Bromine; (d) Aldehydes.	Prevention, inhibition or elimination of microorganisms.	High toxicity.
Protective or antifouling coatings	(a) Raisings; (b) Antifouling paints.	Formation of protective film.	(a) Used as nutritional source by some bacteria; (b) High toxicity
Corrosion inhibitors	(a) Amines; (b) Phosphate esters; (c) Ammonium nitrate.	Formation of protective film.	(a) They are metabolized by some bacteria, causing increased microbial growth and increased rate of corrosion; (c) High toxicity.

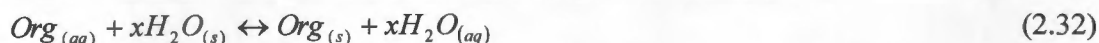
These methods have been combined together in the past to effectively combat the metal exposure to biocorrosion [7, 127].

The choice of corrosion inhibitors offers a cost-effective, convenient and eco-friendly means to abate mild steel corrosion in aqueous hydrochloric acid and SRB dominated environment.

2.11.1. Use of organic molecules as corrosion inhibitors

It has been established by numerous past studies including Singh [132] that organic compounds containing heteroatoms with high electron density, such as oxygen, sulphur, nitrogen and phosphorous as well as those containing multiple bonds are effective corrosion inhibitors. This is attributed to reasonable adsorption centres offered by such class of organic compounds.

The adsorption of organic inhibitor molecules from an aqueous solution can be regarded as a quasi-substitution process between the organic compound in the aqueous phase, $Org_{(aq)}$, and water molecules at the electrode surface, $H_2O_{(s)}$ [96] (Equation 2.32):



where x is the size ratio representing the number of water molecules replaced by one molecule of organic inhibitor.

Adsorption isotherms on the other hand have been vastly employed in determining the mechanism of organo-electrochemical reactions. The most common adsorption isotherms that are often cited in corrosion studies are those developed by Langmuir, Temkin, Frumkin, Kastening Holleck, Flory Huggins, Parsons, Dhar-Flory Huggins, Bockris-Swinkels and El-Awady-Abd-El-Nabey-Aziz [96].

Weight loss and electrochemical measurements of three eco-friendly thioureas derivatives were explored by Torres *et al.* [133]. The polarization curves demonstrate that the studied thioureas derivatives were successfully adsorbed onto the metal surface thereby lowering both anodic and cathodic current densities. The electrochemical impedance diagrams of the studied thioureas derivatives show that the inhibition efficiency increases with increased concentration of the inhibitors. It was suggested that the presence of sulphur atom in the moiety may have played important role in the inhibition process. The adsorption process for the two substituted thioureas obeyed the Langmuir isotherm.

Experimental and quantum chemical study on four sulphonamides as corrosion inhibitors for mild steel in aqueous HCl was investigated by Murulana *et al.* [100]. All the four studied

sulphonamides displayed good corrosion inhibition efficiency. The results from the potentiodynamic polarization measurements showed that the sulphonamides under probe are mixed-type corrosion inhibitors for mild steel. On the other hand, electrochemical impedance spectroscopy revealed that the four inhibitors were easily adsorbed onto the surface of mild steel thereby preventing further corrosion. Overall, there was a satisfactory correlation of the results obtained from weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. The four sulphonamides obeyed the Langmuir adsorption isotherm. The inhibitory effect of three thiosalicylaldehyde derivatives in HCl for mild steel was expanded by electrochemical, gravimetric and theoretical techniques [101]. The inhibition efficiencies obtained from the experimental methods increased as the concentration of all three inhibitors increased. The adsorption of the Schiff bases on the steel surface was said to obey the Langmuir's isotherm.

2.11.2. Eco-friendly corrosion inhibitors

Search towards environmentally benign corrosion inhibitors has intensified in recent times. To this end, numerous eco-friendly molecules such as ionic liquids and amino acids have been expanded.

Murulana *et al.* [103] explored some imidazolium-based ionic liquids using experimental and quantum chemical techniques. The results obtained from the weight loss, electrochemical analysis and quantum chemical calculations show a good correlation between experimentally derived inhibition efficiency and a composite index of quantum chemical parameters. The studied set of ionic liquids obeyed the Langmuir adsorption isotherm. The corrosion inhibition efficiency was enhanced as the alkyl chain attached to the imidazolium moiety increases.

The inhibition effect of amino acids and hydroxy carboxylic acids on pitting corrosion of aluminium alloy 7075 was investigated by Bereket and Yurt [134]. The polarization curves obtained showed that the addition of amino acids to NaCl solutions resulted to more effective shifting in pitting potential (E_{pit}) values to noble directions in acidic solutions.

Ashassi-Sorkhabi *et al.* [135] conducted a study to investigate the inhibition effect of three amino acids against steel corrosion in HCl solution by potentiodynamic polarization method. The studied amino acids acted as corrosion inhibitors for steel in HCl solution through adsorption on the steel surface. The adsorption of the amino acids followed the Langmuir isotherm.

The quest for greener corrosion inhibitors has necessitated substantial corrosion studies focusing on numerous plant extracts. For instance, Gunasekaran and Chauhan [25] employed weight loss and electrochemical impedance spectroscopic techniques to investigate the inhibition effect of *Zenthoxylum alatum* plant extract on the corrosion of mild steel in aqueous orthophosphoric acid. The plant extract was found to considerably reduce the corrosion of steel. Similar plant extract has been used to probe the corrosion of mild steel in aqueous HCl solution [13]. The corrosion inhibition efficiency of the studied *Zenthoxylum alatum* plant extract was found to increase as the plant extract concentration increased. Another significant work in this regard was done by Satapathy *et al.* [29]. The inhibition efficiency of mild steel in 1 M HCl was found to increase as the concentration of *Justicia gendarussa* plant extract increased. The polarization studies revealed that the plant extract acted as a mixed-type inhibitor. The adsorption of the inhibitor molecules on the mild steel surface was found to obey Langmuir adsorption isotherm. Study conducted by Ostovari *et al.* [2] revealed that the henna constituents used as corrosion inhibitor acted as a mixed-type inhibitor for corrosion of mild steel in 1 M HCl. This study suggested the mechanism of chemisorption whilst corrosion inhibition was slightly enhanced via oxygen scavenging.

2.11.3. Use of carbazole and its derivatives in corrosion studies

The use of carbazole and its derivatives in corrosion study have not been expanded. Few corrosion studies focusing on carbazole derivatives however, abound. The inhibition efficiencies of carbazole and *N*-vinylcarbazole for copper in NaCl solution as described by Wang *et al.* [34] were determined by electrochemical impedance spectroscopy and potentiodynamic polarization measurements. Both measurements gave satisfactory corrosion inhibition efficiency. The Frumkin adsorption isotherm was proposed for both carbazole and *N*-vinylcarbazole.

Gravimetric, potentiodynamic polarization and quantum chemical techniques were employed to study corrosion inhibition efficiency for zinc by tetrahydrocarbazole derivatives [55]. The inhibition efficiencies were found to increase with the increase of inhibitor concentration. The inhibitive effect was due to the adsorption of inhibitor molecule on the zinc surface whilst the adsorption process followed the Langmuir isotherm. The values of experimentally derived inhibition efficiencies showed a good correlation with some quantum chemical parameters.

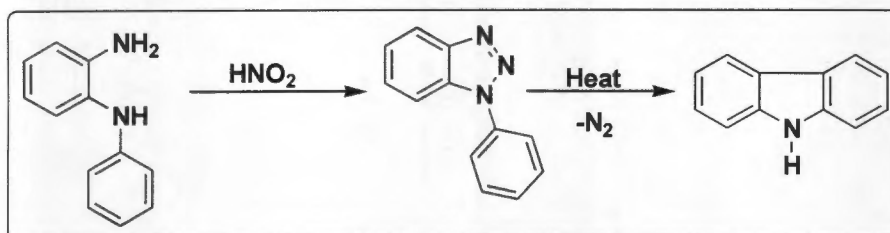
2.11.3.1. Carbazoles as pharmacological agents

The pharmacological activity of carbazole and its derivatives has been extended to various diseases such as cancer and cardiovascular disorders. Kaushik *et al.* [14] evaluated anticancer, antibacterial and antifungal activity of some newer carbazole derivatives, and found them active on all the three microorganisms. Some novel thiazolidinonylcarbazoles were successfully evaluated for their antipsychotic and anticonvulsant activities by Kaur *et al.* [52].

In view of their broad biological activity, carbazole derivatives are receiving significant attention at the moment. A study, however, focusing on biocorrosion inhibition potential of carbazole and its derivatives has not been expanded.

2.11.3.2. Synthesis of carbazole

With the growing number of interest and wide applications of carbazoles, numerous synthetic strategies have been developed over the years. Famous amongst the list is the Graebe-Ullmann reaction, which involves the conversion of *N*-phenyl-1, 2-diaminobenzene to a diazonium salt which immediately forms a 1,2,3-triazole. The triazole is unstable and at high temperatures nitrogen is released resulting in the formation of carbazole. The synthetic route is shown in Scheme 2.1.



Reaction Scheme 2.1. Carbazole synthetic route.

2.12. Biocorrosion study

The harmful effect of microorganisms that eventually results to MIC is not new [136-140]. Surface analytic techniques and electron microscopy have been used extensively to unravel the nature of microbially influenced interfacial processes [136-143]. Analytical mass spectroscopy (MS) has the ability to detect large molecules, deal with complex mixtures, monitor microbiological systems and elucidate molecular interrelationships in such systems. The extensive use of modern MS remains a powerful tool in deepening understanding of the interfacial chemistry governing biocorrosion processes. Atomic force spectroscopy (AFS),

atomic force microscopy (AFM), biological force spectroscopy (BFS), biological force microscopy (BFM), X-ray powder diffraction (XRD), energy dispersive X-ray (EDX), scanning transmission X-ray microscopy (STXM) and laser spray ionization (LSI) are few more techniques used in the study of biocorrosion.

Omoike *et al.* [144] employed attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to investigate the adsorption mechanism of *Bacillus subtilis* and *Pseudomonas aeruginosa* to goethite surface in the presence of phosphodiester groups. The use of ATR-FTIR allows for quick acquisition of spectral data on hydrated samples in a bid to unravel the adsorption mechanisms. The study revealed that inner-sphere complexation of carboxyl groups with Fe metal centres of hydrous oxide surfaces proceeds via a ligand-exchange mechanism.

A novel mechanism for MIC in cases where carbon steel surfaces are heterogeneously covered by biofilms comprising of anaerobic Fe(III) reducing bacterium *Shewanella oneidensis* have been reported by Miller *et al.* [4]. Zero resistance ammetry (ZRA) in a split chamber configuration was used to show the corrosion inhibition characteristics of *S. oneidensis* on carbon steel whereas corrosion rates were probed using weight loss technique. The surface characteristics of the different carbon steel coupons in medium were unravelled using confocal laser scanning microscopy (CLSM).

The biocorrosion of 1020 carbon steel coupons in natural seawater over a 1-year period was investigated by Lee *et al.* [145] using weight loss and polarization resistance techniques. The coupons were examined afterwards using ESEM, XRD and SEM in order to characterize the corrosion morphology, biofilm structure and corrosion product composition.

The effect of *Desulfovibrio vulgaris* on carbon steel coupons was studied by Chen *et al.* [146]. The extent of carbon steel corrosion was probed by mass loss technique whilst the coupons surfaces were examined by SEM and CLSM. The results of SEM and CLSM showed a more severe pitting than uniform corrosion. Both surface techniques revealed similar dynamics of cell-carbon steel association with characteristic reductions in surface coverage and biofilm thickness as exposure time increased.

Similar pitting corrosion was reported by Wang *et al.* [147] in their investigation involving corrosion of carbon steel C1010 in the presence of iron oxidizing bacterial such as *Acidithiobacillus ferrooxidans*. The standard Weight loss procedure ASTM D2688-05 was used to examine the extent of corrosion. The surface of the cleaned and dried metal coupons was analyzed using an infiniteFocus microscope (IFM) in order to obtain surface

characteristics whilst the corrosion products obtained was analyzed using Raman spectroscopy.

Venzlaff *et al.* [148] on the other hand employed potentiodynamic measurements and EIS to probe the precipitate-covered iron coupons that were previously incubated with SRB strains. The use of EIS allowed for some insights into the conductive and dielectric properties of the precipitate formed on the iron coupons due to the activities of the microorganisms.

Electrochemical and surface analytical techniques were used to study the MIC resistance characteristics of a 304L-Cu stainless steel against *Escherichia coli* [149]. The surface morphologies were investigated under optical microscope, SEM, XPS and EDS. EDS was used to study the chemical compositions of the Cu-rich precipitates. CLSM micrographs in addition, provided further evidence that localized corrosion took place on the specimens with *E. coli* after 21 days.

In recent times however, studies focusing on the protective roles of some bacterial biofilms for metal corrosion have emerged [140, 142, 143]. Bano and Qazi [150] for instance, investigated the antagonistic activity of some non-corrosive *Bacillus coagulans* for mild steel biocorrosion using weight loss technique. The results revealed that the non-corrosive *Bacillus* isolates not only hindered the intensity of MIC, but they protected the mild steel from abiotic corrosion too.

2.13. Surface analysis

In a bid to gain further insight into the nature of interaction or sites on which the metal ion is likely to interact with inhibitor molecules, various surface analysis techniques have been employed in previous (bio)corrosion studies. One of such studies involved the use of the FTIR spectroscopy to unravel the preferred site of four sulphonamides with mild steel surface [100]. The disappearance of the SO₂ functional group during the corrosion inhibition process was attributed to the formation of a complex between the O and the Fe atoms.

Wang *et al.* [34] employed XPS and FTIR to explore the nature of the interaction between the copper surface and the self-assembled films of carbazole and *N*-vinylcarbazole. The results obtained from the XPS and FTIR revealed that *N*-vinylcarbazole molecules adsorbed onto the copper surface through a Cu-N bond, thereby producing a tilted orientation from the copper surface.

SEM micrographs obtained after 20 days exposure of aluminium 7075 coupons to solutions of 0.05 M NaCl containing amino acid revealed few numbers of pits with small size [134].

The results obtained from the XPS and FTIR studies as reported by Gunasekaran and Chauhan [25] revealed the formation of an organo-metallic complex such as Fe-plant extract. Similar organo-metallic complex formation has been reported by Chauhan and Gunasekaran [13] using SEM, XPS and FTIR.

To explore the topographical features of the exposed mild steel in 1 M HCl medium containing the inhibitor molecules, atomic force microscopy (AFM) and electron spectroscopy (ECSA) were used as described by Satapathy *et al.* [29]. The results obtained from both techniques showed the formation of a stable Fe-inhibitor complex that ultimately protected the mild steel from corroding.

In order to elucidate the surface characteristics of the mild steel after electrochemical test, SEM and EDS were carried out for the corrosion inhibition of mild steel in 1 M HCl henna extract and its constituents [2]. The results revealed the disappearance of pits which was attributed to adsorption of henna extract on the metal surface after the inhibitor was added.

The scanning electron micrographs images of the acid etched bare steel, steel immersed in 1 M H₂SO₄ and steel in 1 M H₂SO₄ + 2×10^{-2} M inhibitor were reported by Hasanov *et al.* [96]. From the images they obtained, clear morphological differences can be observed.

CHAPTER 3

MATERIALS AND METHODS

3.1. Experimental details

3.1.1. Materials, equipment, methods, apparatus and reagents

3.1.1.1. *MS electrodes*

Mild steel coupons with percentage weight compositions 0.17 % C, 0.46 % Si, 0.017 % S, 0.019 % P, and the remainder iron was used for both aqueous electrochemical corrosion and biocorrosion weight loss tests. Mild steel coupons were mechanically cut into 1 cm x 1 cm. The mild steel coupons for electrochemical measurement were embedded in a Teflon holder using epoxy resin, exposing a surface area of 1 cm². Prior to each measurement, mild steel surface was mechanically polished on Struers MD PianoTM 220 (size: 200 dia) mounted on Struers LaboPol-1 machine to expel traces of epoxy resin from the surface. The surface was then ground using progressively finer SiC papers of grit size in the range 200-600 to achieve a mirror-like finish. The coupons were then cleaned in a sonicating acetone bath for 30 mins, followed by sonication in ethanol and finally wiped with clean paper towel and air-dried.

3.1.1.2. *Materials and reagents*

The sixteen (16) carbazole derivatives used as corrosion inhibitors in the study were obtained from Sigma-Aldrich Company 3050 Spruce Street, St. Louis, MO, USA and used without further purification. The molecular structures, groupings, IUPAC names and adopted abbreviations of the studied CZs are presented in Tables 3.1-3.5. The atom numberings in Tables 3.1-3.5 are used for discussion of results in the later part of the thesis. Absolute ethanol 99.8 %, Tin(II) chloride dihydrate and glutaraldehyde solution (25 %) were supplied by Sigma-Aldrich; hydrochloric acid and acetone (Merck, Modderfontein, South Africa); antimony trioxide from Acros. The chemicals were used without further purification.

3.1.1.3. *Carbazole derivatives*

The choice of carbazole derivatives as corrosion inhibitors in this investigation is premised on their poorly documented anticorrosion activities as well as their vast natural sources. In addition, the carbazole derivatives were selected as biocorrosion inhibitors based on the conviction they will offer good value when cost versus effectiveness are considered. Their selection as (bio)corrosion inhibitors were further supported by the presence of aromatic rings network, pi-electrons and certain heteroatoms in the molecules of the compounds. The carbazole derivatives were divided into five groups based on some levels of similarity and inherent variation in their molecular structure, substituent functional groups

and unique electrochemical behaviour. Some relevant information about the carbazole derivatives and adopted abbreviations with which they are referred are presented in Tables 3.1-3.5.

Table 3.1. GROUP I: CZ, DBCZ, HCZ, THCZ and EHCZDCA.

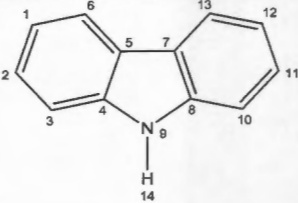
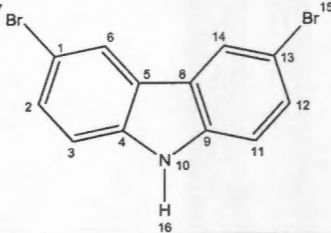
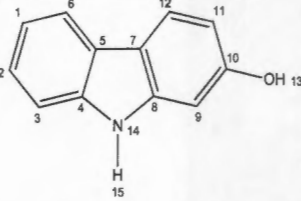
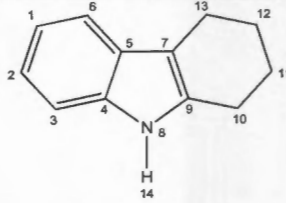
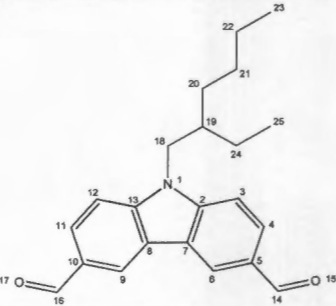
Structure of inhibitor	IUPAC name	Abbreviation	Molecular formula and mass
	Carbazole	CZ	Molecular formula: $C_{12}H_9N$ Molecular mass: 167.07g/mol
	3,6-dibromocarbazole	DBCZ	Molecular formula: $C_{12}H_7Br_2N$ Molecular mass: 322.89g/mol
	2-hydroxycarbazole	HCZ	Molecular formula: $C_{12}H_9NO$ Molecular mass: 183.07g/mol
	1,2,3,4-tetrahydrocarbazole	THCZ	Molecular formula: $C_{12}H_{13}N$ Molecular mass: 171.10g/mol
	9-(2-ethylhexyl)-3,6-dicarboxaldehyde	EHCZDCA	Molecular formula: $C_{22}H_{25}NO_2$ Molecular mass: 335.19g/mol

Table 3.2. GROUP II: THCZCA, MTHCZ and MCZCA.

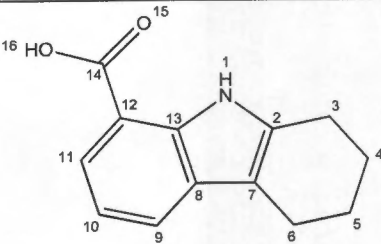
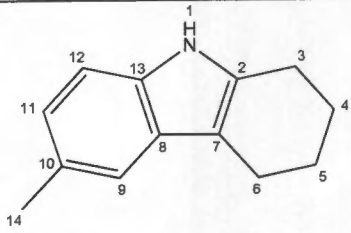
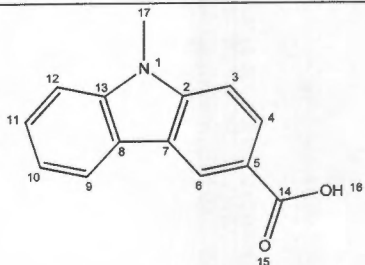
Structure of inhibitor	IUPAC name	Abbreviation	Molecular formula and mass
	2,3,4,9-tetrahydro-1H-carbazole-8-carboxylic acid	THCZCA	Molecular formula: $C_{13}H_{13}NO_2$ Molecular mass: 215.09g/mol
	6-methyl-2,3,4,9-tetrahydro-1H-carbazole	MTHCZ	Molecular formula: $C_{13}H_{15}N$ Molecular mass: 185.12g/mol
	9-methyl-9H-carbazole-3-carboxylic acid	MCZCA	Molecular formula: $C_{14}H_{11}NO_2$ Molecular mass: 225,08g/mol

Table 3.3. GROUP III: DBPCZ and CZPD.

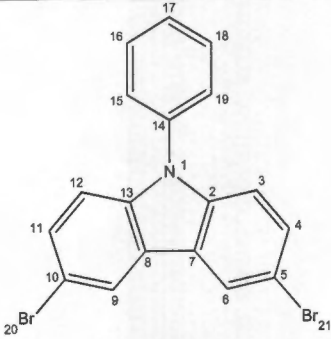
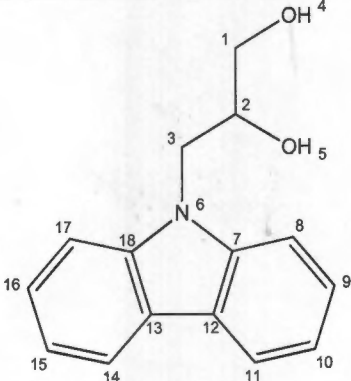
Structure of inhibitor	IUPAC name	Abbreviation	Molecular formula and mass
	3,6-Dibromo-9-phenylcarbazole	DBPCZ	Molecular formula: $C_{18}H_{11}Br_2N$ Molecular mass: 398.93g/mol
	3-(9H-carbazol-9-yl)-1,2-propanediol	CZPD	Molecular formula: $C_{15}H_{15}NO_2$ Molecular mass: 241.11g/mol

Table 3.4. GROUP IV: CZAA, DMCZ and HTHCZ.

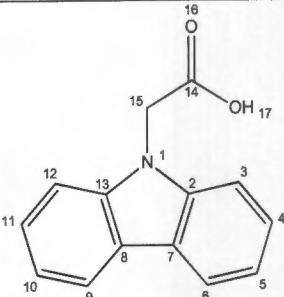
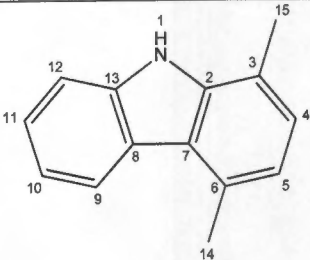
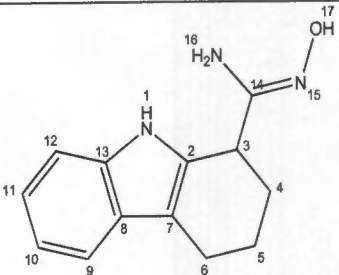
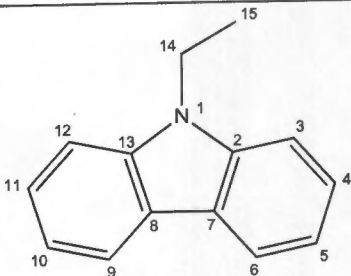
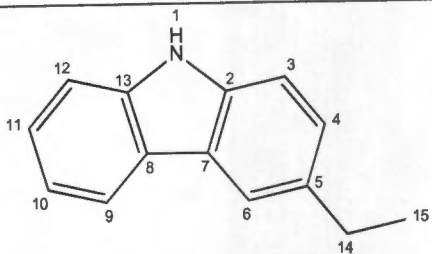
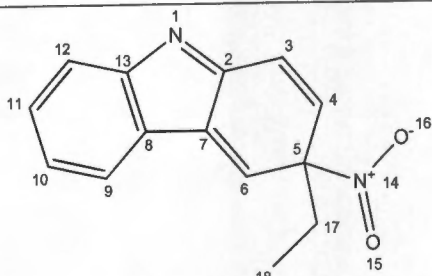
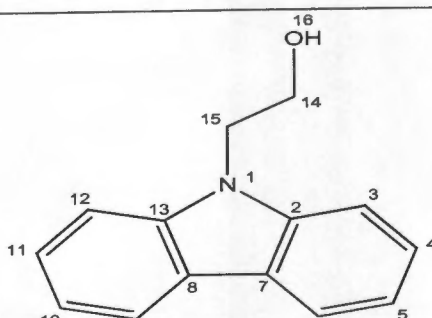
Structure of inhibitor	IUPAC name	Abbreviation	Molecular formula and mass
	9-Carbazoleacetic acid	CZAA	Molecular formula: $C_{14}H_{11}NO_2$ Molecular mass: 225.08g/mol
	1,4-Dimethyl-9H-carbazole	DMCZ	Molecular formula: $C_{14}H_{13}N$ Molecular mass: 195.10g/mol
	N'-hydroxy-2,3,4,9-tetrahydro-1H-carbazole-1-carboximidamide	HTHCZ	Molecular formula: $C_{13}H_{15}N_3O$ Molecular mass: 229.12g/mol

Table 3.5. GROUP V: 9-ECZ, 3-ECZ, ENCZ and CZE.

Structure of inhibitor	IUPAC name	Abbreviation	Molecular formula and mass
	9-Ethylcarbazole	9-ECZ	Molecular formula: C ₁₄ H ₁₃ N Molecular mass: 195.10g/mol
	3-ethylcarbazole	3-ECZ	Molecular formula: C ₁₄ H ₁₃ N Molecular mass: 195.10g/mol
	3-Ethyl-3-nitrocarbazole	ENCZ	Molecular formula: C ₁₄ H ₁₂ N ₂ O ₂ Molecular mass: 240.09g/mol
	9H-carbazole-9-ethanol	CZE	Molecular formula: C ₁₄ H ₁₃ NO Molecular mass: 211.10g/mol

3.1.1.4. Aggressive solutions

The aggressive blank solution of 1 M HCl was prepared by diluting the analytical grade 32% with distilled water. The stock solutions of the inhibitors were prepared using 1:1 mixture of acetone and ethanol as a co-solvent at a quantity of 2.4 % (by volume) of the solution. The inhibitor concentrations in the range of 100 to 1000 ppm were used in the (bio)corrosion study.

3.1.1.5. SRB culture

The sulphate-reducing bacterium *Desulfobrio vulgaris* (*D. vulgaris*, ATCC, No. 7757) was purchased from Leibniz Institute DSMZ-German Collection Microorganisms and Cell Cultures. The culture medium was prepared by adding 2.0 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 5.0 g of sodium citrate, 1.0 g of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 1.0 g of NH_4Cl , 0.5 g of K_2HPO_4 , 3.5 g of sodium lactate, 1.0 g of yeast extract into 1000 ml of distilled water. The final pH of the SRB culture medium prior to MS incubation was 7.4. The pre-cultures of SRB strains were grown on H_2 and subsequently flushed with N_2 for 30 min to prevent contamination by dissolved sulphide and H_2 into the incubations.

3.1.1.6. Electrochemical measurements

A three-electrode glass cell with a capacity of 50 mL was used for the purpose of these measurements. 10 mL of 1 M HCl was used as electrolyte without and with various concentrations of inhibitors. The carefully prepared MS coupons embedded in a Teflon holder using epoxy resin was used as WE. A Ag/AgCl reference electrode and a high purity platinum foil were used as the reference and counter electrodes respectively.

The overall setup and measurements for electrochemical study were carried out as described in literature [73]. All electrochemical measurements were conducted at 30⁰ C using AUTOLAB PGSTAT 302N obtained from Metrohm. The temperature was maintained using a thermostated water bath. Electrochemical methods such as potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were employed to probe the electrochemical corrosion process on the surface of the prospective metal specimens. PDP measurements were undertaken after 30 minutes of mild steel immersion in the aggressive solutions by sweeping the potential between -0.25 to +0.25 V at the scan rate of 0.5 mVs⁻¹. Previous research studies have demonstrated that 30 minutes was sufficient for OCP

stabilization for an electrochemical system comprising of MS in acidic medium [73, 151-158].

Electrochemical kinetic parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c , β_a) and corrosion current density (i_{corr}) were obtained from Tafel plots generated from electrochemical study. The IE_p was calculated by using Equation 3.1.

$$IE_p = 100 \left(1 - \frac{i_{corr}}{i_{corr}^0} \right) \quad (3.1)$$

where i_{corr}^0 and i_{corr} are corrosion current densities in the absence and presence of inhibitors respectively.

EIS measurements were carried out at the OCP by analysing the frequency response of the electrochemical system in the range of 10 mHz to 100 kHz at 10 mV root-mean-square (rms) amplitude. The impedance spectra were fitted into appropriate equivalent circuit to obtain relevant electrochemical parameters including the charge transfer resistance (R_{ct}), solution resistance (R_s) and inhibition efficiency (IE_I).

The corrosion inhibition efficiency was extrapolated from R_{ct} according to Equation 3.2.

$$IE_I = 100 \left(\frac{R_{ct} - R_{ct}^0}{R_{ct}} \right) \quad (3.2)$$

where R_{ct} and R_{ct}^0 are the charge transfer resistance in the presence and absence of inhibitor respectively.

3.1.1.7. Biocorrosion study: weight loss measurements

Corrosion rates due to the activities of *D. vulgaris* on MS coupons were probed using weight loss analysis as prescribed by ASTM method G01-03 [137, 159, 160]. Prior to immersion of mild steel in SRB medium, the shiny coupons were cleaned in a sonicating acetone bath for 30 mins, followed by sonication in ethanol. MS coupons were further sterilized by soaking in ethanol for 48 hours and later air-dried. The initial weight of the mild steel was then recorded before exposure to SRB. The sterilized mild steel coupons were exposed to SRB for a period of 9 days, after which they were retrieved, rinsed in distilled water, wire brushed, and immersed in Clark's reagent (1000 mL, 12.1 M HCl, 20 g antimony trioxide, and 50 g tin chloride) for 30 seconds to remove surface oxides, biofilm and other corrosion product. The use of Clarke's solution has been encouraged as an effective means of removing base metal that accumulates on the surface of metallic coupon [161]. The coupons were further rinsed with distilled water, air-dried and weighed. Washing (in Clark's solution and distilled water), drying and weighing were repeated until a steady weight was recorded, indicating complete removal of biofilms and corrosion products.

The weight loss investigation was carried out in triplicates and average weight loss was recorded in each case to ensure reproducibility.

Corrosion rate was calculated using the equation:

$$CR = \frac{\Delta W}{AT} \quad (3.3)$$

where CR is the corrosion rate ($\text{g.cm}^{-2}.\text{d}^{-1}$); ΔW is the average weight loss (g) of mild steel coupons; A is the surface area (cm^2) and T is the duration of immersion in days. From the calculated CR values, inhibition efficiency ($\%IE_{WL}$) was derived using the relationship:

$$\%IE_{WL} = \frac{CR_1 - CR_2}{CR_1} \times 100 \quad (3.4)$$

where CR_1 and CR_2 are the corrosion rate values in the absence and presence different concentrations of CZs, respectively.

3.1.1.8. Quantum chemical calculations

In order to probe the effect of different substituents in the carbazole (common nucleus) on corrosion efficiency and mechanism, gas phase quantum chemical calculations were performed using density functional theory (DFT) method comprising the Becke three-parameter hybrid functional together with the correlation functional, which includes both local and non-local terms (B3LYP), and the split-valence double-zeta polarized basis set (6-31G(d)). Full geometry optimizations were carried out on neutral molecules. Previous study by Chen *et al.* [162] has alluded that carbazoles undergo protonation in very strong acids (e.g., half-protonation at -8.5 M sulfuric acid). In the present study, 1 M HCl solution was used, therefore the protonated forms of the studied compounds was not considered.

Calculations were also carried out in water phase in order to investigate the effect of solvent on quantum chemical parameters of carbazoles. The Polarizable Continuum Model (PCM) implemented in G09W was used to study solvent effects. This method creates the solute cavity via a set of overlapping spheres.

Quantum chemical parameters expected from the calculations included the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy band gap ($\Delta E = E_{LUMO} - E_{HOMO}$) and ionization potential (IP). Global electronic chemical potential (μ), electronegativity (χ) and chemical hardness (η) were also calculated. Many of these quantum chemical indices are only derivable from the frontier molecular orbital energy parameters (E_{HOMO} and E_{LUMO}) using appropriate relations (Equations 3.5-3.8) as previously reported in literature [92].

$$\mu = -\frac{1}{2}(IP + EA) \quad (3.5)$$

$$\chi = \frac{1}{2}(IP + EA) \quad (3.6)$$

$$\eta = \frac{1}{2}(IP - EA) \quad (3.7)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (3.8)$$

where $IP = -E_{HOMO}$ and $EA = -E_{LUMO}$ according to Koopmann's theorem.

Fukui functions ($f(r)$) were computed from the Mulliken atomic charges on the neutral form of the inhibitor molecules in order to probe the local reactivity of each atom in the inhibitor molecules. The equations are defined in equations (3.9–3.11). The Fukui functions ($f(r)$) indicate the change in electron density at a given position when the number of electrons is changed (Equation 3.9), such that, largest value of f_k^+ (Equation 3.10) defines the most probable site in a molecule that will receive charge from the metal surface (electrophilic), largest value of f_k^- (Equation 3.11) defines the most probable site through which the molecule will back-donate charge to the metal surface (nucleophilic).

$$f(r) = \frac{\partial \rho(r)}{\partial N_{electron}} \quad (3.9)$$

$$f_k^+ = \rho_{k(N+1)}(r) - \rho_{k(N)}(r) \quad (3.10)$$

$$f_k^- = \rho_{k(N)}(r) - \rho_{k(N-1)}(r) \quad (3.11)$$

where ρ_k in the equations refers to the atomic charge on atom k ; N , $(N+1)$ and $(N-1)$ represent the number of electrons in the neutral system, in the system in which an electron has been added (anionic system) and in the system in which the electron has been subtracted (cationic system) respectively.

For this purpose, ground state full geometry optimization was first carried out on the N -electron system after which single point calculations was carried out at the same level of theory on $(N+1)$ -electron system. Other quantum chemical parameters such as molecular volume (MV), and hydrophobicity ($\log P$) were also calculated using Spartan 10 V1.01 program [163].

3.1.1.9. Quantitative structure activity relationship (QSAR) studies

Quantitative structure activity relationship (QSAR) approach was applied to investigate the possibility of correlating quantum chemical parameters with the reported experimental inhibition efficiency. Quantum chemical parameters that were used in the QSAR studies include molecular orbital energies, dipole moment and global softness. The

suitability of the resulting models in describing the dependence of inhibition efficiencies of the studied compounds on a set of quantum chemical descriptors was adjudged based on the correlation coefficient (R^2) values, mean square error (MSE) and root mean square error (RMSE) values. The QSAR analyses were carried out with the aid of the XLSTAT software code used as a Microsoft Excel add-in [164]. The linear equations/models were generated based on the propositions of Lukovits *et al.* [165, 166].

3.1.1.10. Molecular dynamics (MD) simulations

In corrosion inhibition studies, understanding adsorption phenomena is of great importance. For this reason, Barriga *et al.* [32] have reported that the use of Monte Carlo simulations is useful in finding the low-energy adsorption sites on both periodic and non-periodic substrates or in investigating the preferential adsorption of mixtures of adsorbate components. The adsorption locator module implemented in the Materials studio 6.0 software supplied by Accelrys was used for the simulation. The carbazole molecules were modelled and optimized using the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. Fe(110) crystal surface was employed as the representative metallic surface. The Fe(110) crystal surface was obtained by cleaving the crystal structure of Fe into 110 plane and optimize the surface to minimum energy using the COMPASS force field. A 10x10 supercell of Fe(110) was built from the optimized crystal surface and a vacuum slab of 7 nm was built above the plane.

The optimized inhibitor molecule was used as the adsorbate and made to interact with the surface atoms of the Fe(110) using the adsorption locator module. A maximum distance of 10 Å was maintained between the adsorbate and the selected atoms of Fe(110) surface. Ultra-fine convergence criteria was used for all optimization and simulation jobs, while the temperature was ramped down from 1×10^5 K to 100 K as the simulations went through 10 cycles at 100,000 steps per cycle.

The energy of interaction (E_{M-Inh} , kJ.mol⁻¹) of the adsorption between the inhibitor molecule and the metal surface was calculated using Equation 3.12. Binding energy ($E_{binding}$, kJ mol⁻¹) is related to $E_{interaction}$ according to Equation 3.13:

$$E_{interaction} = E_{Total} - (E_{Surface} + E_{Inh}) \quad (3.12)$$

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

This is in accordance with previous studies conducted elsewhere, for instance, Eddy and Ita [92], Barriga *et al.* [32] and Khaled [105].

3.2. Surface morphology studies

3.2.1. Scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) study

For corrosion tests in acidic medium, MS specimens with freshly pre-treated surface as described earlier were immersed in 1 M HCl in the absence and presence of 100 ppm of the investigated CZs. Thereafter, the specimens were retrieved, washed with distilled water, air-dried and used SEM and EDX analyses. For MIC study, the MS coupons inoculated in SRB incubator for 9 days were used. The retrieved coupon whose surface is covered with biofilm was immersed in 2.5 wt % glutaraldehyde for 8 hours and subsequently washed with a graded series (30%, 50%, 70%, 100% v/v) of ethanol for dehydration [160, 167], and finally stored in a desiccator and later utilised for SEM and EDX analyses. The SEM images with simultaneous elemental characterization using EDX were obtained using FEI Quanta FEG 250 Environmental Scanning electron microscope (ESEM) under an acceleration voltage of 15 kV in high vacuum.

3.2.2. Fourier transforms infrared (FTIR) spectra

FTIR spectra of the pure CZs, and the adsorbed film of CZs on mild steel surface after immersion in acidic solution containing 100 ppm CZs for 3 hours were recorded. Similarly, FTIR spectra of the adsorbed film of CZs on mild steel retrieved from SRB incubation after 9 days were also recorded. The corrosion product in powder form obtained after the immersion periods were subsequently analysed. FTIR spectra were recorded on Cary 670 or Bruker alpha-P FTIR spectrometer in the wavenumber range $400 - 4000\text{ cm}^{-1}$.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. GROUP I: CZ, DBCZ, HCZ, THCZ, and EHCZDCA

GROUP I consists of five carbazole derivatives as listed in Table 3.1. The compounds were studied for their adsorption and (bio)corrosion inhibition activities in 1 M HCl and *D. vulgaris* media using electrochemical, theoretical and weight-loss techniques. Surface morphology techniques such as scanning electron microscopy and Fourier transform infrared spectroscopy were employed to describe the nature and composition of adsorbed films on MS surfaces. The five carbazoles examined in this group comprise of unsubstituted carbazole and extra four substituted derivatives. The rationale behind it was to collate the corrosion inhibition potentials of the derivatives with the parent compound, in order to scrutinize the effects of the substituent groups on corrosion inhibition property of carbazole.

It is worthy of mention that work done on this set of carbazoles has been published in Scientific Reports Journal and the following portions of results and discussions on this set of compounds basically refer to the published work [168].

4.1.1. Electrochemical studies

4.1.1.1. Potentiodynamic polarization (PDP) studies

Potentiodynamic polarization studies were explored to unfold the mechanism of the MS decomposition at the anode and the build-up of hydrogen at the cathode in the absence and presence of different concentrations of CZs. The current-potential curves for MS corrosion in 1 M HCl in the absence and presence of different concentrations of CZ and DBCZ are displayed in Figure 4.1, while that of other three compounds are shown in Figure AI-1 (Appendix I). On close inspection of Figure 4.1, it is clear that the addition of the inhibitors diminish the rate of both anodic and cathodic corrosion reactions with the latter being more remarkable.

In addition, the relevant electrochemical parameters such as corrosion current density (i_{corr}) and anodic and cathodic Tafel slopes (b_a and b_c respectively) were procured by extrapolating the linear Tafel sections of the polarization curves to the E_{corr} . The results of the electrochemical parameters in conjunction with the inhibition efficiencies are presented in Table 4.1. A shift in E_{corr} less than 85 mV is regarded as a feature of mixed-type inhibitive effect of a corrosion inhibitor [169]. Therefore, it can be inferred that the studied CZs are mixed-type inhibitors with paramount effects on cathodic reaction. The inhibition efficiency was found to improve with concentration for the five CZs studied, with the highest $\eta\%$ accomplished at 500 ppm for each compound.

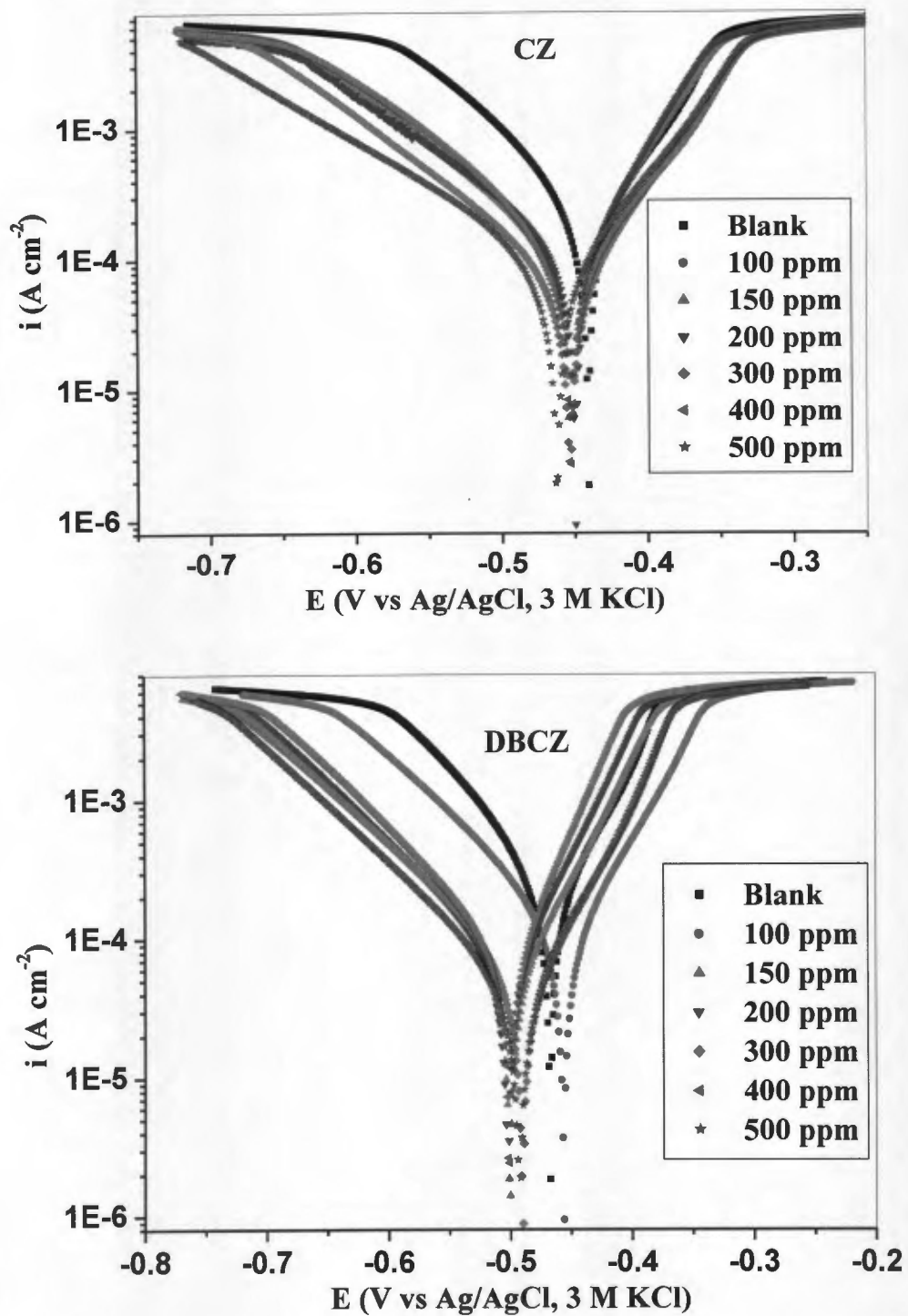


Figure 4.1. Polarization curves for mild steel in absence and presence of different concentrations of CZ and DBCZ.

Table 4.1. Tafel polarization parameters for MS in 1 M HCl solution in absence and at different concentration of carbazoles.

Inhibitor	Conc (ppm)	b_a (mV/dec)	b_c (mV/dec)	$-E_{corr}$ (mV)	i_{corr} ($\mu A\ cm^{-2}$)	$\eta\%$
Blank	-	98.93	72.08	452.72	236.22	-
CZ	100	123.75	69.18	497.80	133.63	43
	150	130.55	63.02	500.26	129.70	45
	200	137.05	80.27	505.95	114.25	52
	300	107.39	87.41	433.62	111.17	53
	400	143.94	77.47	478.54	84.46	64
	500	56.65	96.62	493.23	60.42	74
DBCZ	100	124.18	79.70	440.76	141.88	40
	150	125.43	80.36	482.89	103.72	56
	200	124.25	67.24	490.84	88.37	63
	300	134.98	78.26	486.05	86.04	64
	400	54.66	110.41	498.77	78.45	67
	500	124.80	68.77	482.55	51.18	78
HCZ	100	118.57	64.35	481.27	102.65	57
	150	94.46	83.61	449.77	85.24	64
	200	65.93	121.99	480.15	82.04	65
	300	144.64	56.71	489.62	57.74	76
	400	133.06	64.09	491.49	53.51	77
	500	60.00	99.82	492.14	46.17	80
THCZ	100	123.25	87.50	484.01	140.20	41
	150	55.66	111.29	495.39	82.23	65
	200	159.60	75.19	481.00	68.17	71
	300	58.50	121.49	488.13	68.40	71
	400	59.53	85.81	487.35	46.74	80
	500	119.46	92.87	505.37	12.77	95
EHCZDCA	100	116.50	64.23	472.42	129.45	45
	150	85.54	58.28	476.72	114.62	51
	200	111.46	56.71	492.41	83.67	64
	300	129.79	85.22	482.57	70.99	70
	400	54.08	107.58	491.63	41.59	82
	500	125.62	70.18	490.80	21.51	91

As can be observed in Table 4.1, there appear certain concentrations where increases in concentrations do not make any remarkable difference in the values of $\eta\%$. For instance, in CZ, this occurs between 200 ppm to 300 ppm; DBCZ (200-400 ppm); HCZ (150-200 ppm) and THCZ (200-300 ppm). There is however an apparent improvement in values of $\eta\%$ for all the concentrations of EHCZDCA.

4.1.1.2. EIS measurements

Electrochemical impedance spectroscopy (EIS) was employed to advance the understanding of adsorption of the studied inhibitor molecules on MS surface during the electrochemical corrosion reactions occurring at the metal/electrolyte interface [72]. The impedance spectra of MS in 1 M HCl in the absence and presence of different concentrations of CZ and DBCZ are presented in Figures 4.2 and 4.3 for the Nyquist and Bode plots respectively. Similar plots for other three (HCZ, THCZ and EHCZDCA) can be found in Figure AI-2 and AI-3 (Appendix I) respectively.

The Nyquist plots exhibit depressed semicircles with large capacitive loop at low frequency. On the other hand, the Bode plots exhibit one time constant. This implies that the corrosion of MS in the studied media is dominated by single charge transfer process. The depression in Nyquist semicircles is a popular feature of solid electrodes which is generally referred as frequency dispersion as a result of the inhomogeneity or roughness of the electrode surface [72].

Increases in the diameter of the capacitive loop of the Nyquist plots with unchanged characteristic features can be observed in the presence of the inhibitors. This implies that the inhibitive action of the investigated CZs is as a result of the adsorption of their molecules on the MS surface without affecting the corrosion mechanism [74]. The gentle widening of phase angle maxima at intermediate frequency in the presence of the studied CZs implies the emergence of a protective film of the inhibitor molecules on the MS surface [170].

The equivalent circuit recruited in the fitting of impedance spectra is shown in Figure 4.3. Similar equivalent circuit was utilized for the subsequent groups of carbazoles reported in this thesis. The constant phase element (CPE), is inserted in the circuit in order to guarantee a more precise description of the process occurring at the electrode/electrolyte interface [74]. The impedance of the CPE (Z_{CPE}) is mathematically expressed as:

$$Z_{CPE} = \left(\frac{1}{Y_0} \right) [(j\omega)^n]^{-1} \quad (4.1)$$

where, Y_0 is the CPE constant; ω is the angular frequency; j is the imaginary number and n is the phase shift (exponent). Electrochemical parameters acquired from the fitting of the impedance spectra are recorded in Table 4.2. The electrochemical behaviour of the CPE is comparable to the value of n , which in turn is comparable to the surface inhomogeneity [169]. The values of R_s and Y_0 do not form a definite trend with increasing concentration of the studied inhibitors. However, it can be observed that the values of R_s are generally higher

than the blank. The high R_s values confirm the relatively low conductivity media in the presence of the inhibitors. R_{ct} typifies the charge-transfer resistance whose value is an estimate of electron transfer across electrode/electrolyte interface and it is inversely proportional to corrosion rate [74]. The R_{ct} values presented in Table 4.2 can be seen to improve with improvements in the concentration of the inhibitors. This connotes that the impedance of the MS electrode surface to flow of charges across metal-electrolyte interface increases with increasing concentration of the inhibitors.

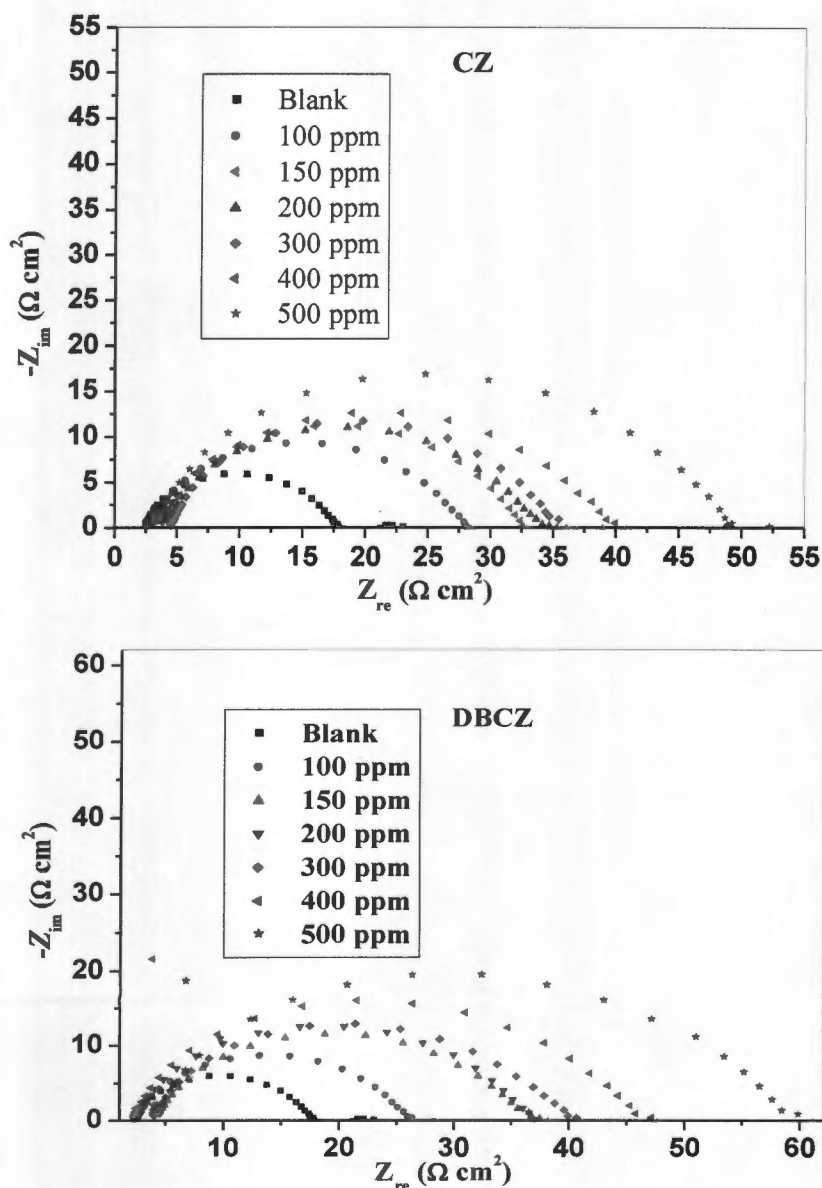


Figure 4.2. Nyquist plot for mild steel in 1 M HCl in the absence and presence of different concentrations of CZ and DBCZ.

Table 4.2. Electrochemical impedance parameters obtained for MS in 1 M HCl in absence and presence of different concentration of carbazoles.

Inhibitor	Conc (ppm)	R_s ($\Omega \text{ cm}^{-2}$)	R_{ct} ($\Omega \text{ cm}^{-2}$)	Y_0 ($\mu\text{S s}^n \text{ cm}^{-2}$)	n	$\eta\%$
Blank	-	2.50	16.6	677	0.84	-
CZ	100	3.0	27.9	487	0.81	41
	150	3.61	32.1	382	0.82	48
	200	3.70	34.9	513	0.75	52
	300	4.57	35.1	553	0.82	53
	400	3.35	42.0	525	0.74	60
	500	3.37	51.7	428	0.81	68
DBCZ	100	2.38	25.9	817	0.80	36
	150	4.82	37.0	454	0.78	55
	200	2.43	38.5	492	0.80	57
	300	3.78	43.6	550	0.75	62
	400	2.22	50.5	485	0.80	67
	500	4.01	62.6	335	0.80	73
HCZ	100	3.06	38.4	472	0.81	57
	150	3.04	41.5	491	0.72	60
	200	2.50	42.3	507	0.81	61
	300	2.65	57.7	404	0.81	71
	400	4.28	59.5	307	0.81	72
	500	4.52	87.7	379	0.79	81
THCZ	100	3.73	27.7	536	0.82	40
	150	2.97	46.1	448	0.81	64
	200	4.26	52.9	550	0.73	69
	300	3.97	54.0	402	0.80	69
	400	3.99	71.8	416	0.78	77
	500	2.31	374	186	0.65	96
EHCZDCA	100	1.87	28.8	628	0.83	42
	150	1.78	33.7	624	0.83	51
	200	2.29	37.8	515	0.81	56
	300	3.64	42.2	563	0.76	61
	400	3.37	79.4	416	0.77	79
	500	3.43	206	134	0.81	92

The observed increases in R_{ct} with increase in inhibitor concentration may be due to increase in the number of inhibitor molecules that adsorb on MS surface, and subsequent decrease in the exposed surface area of the MS to the aggressive solution. The improved R_{ct} with improvement in inhibitor concentration also translates to high inhibition efficiency ($\eta\%$).

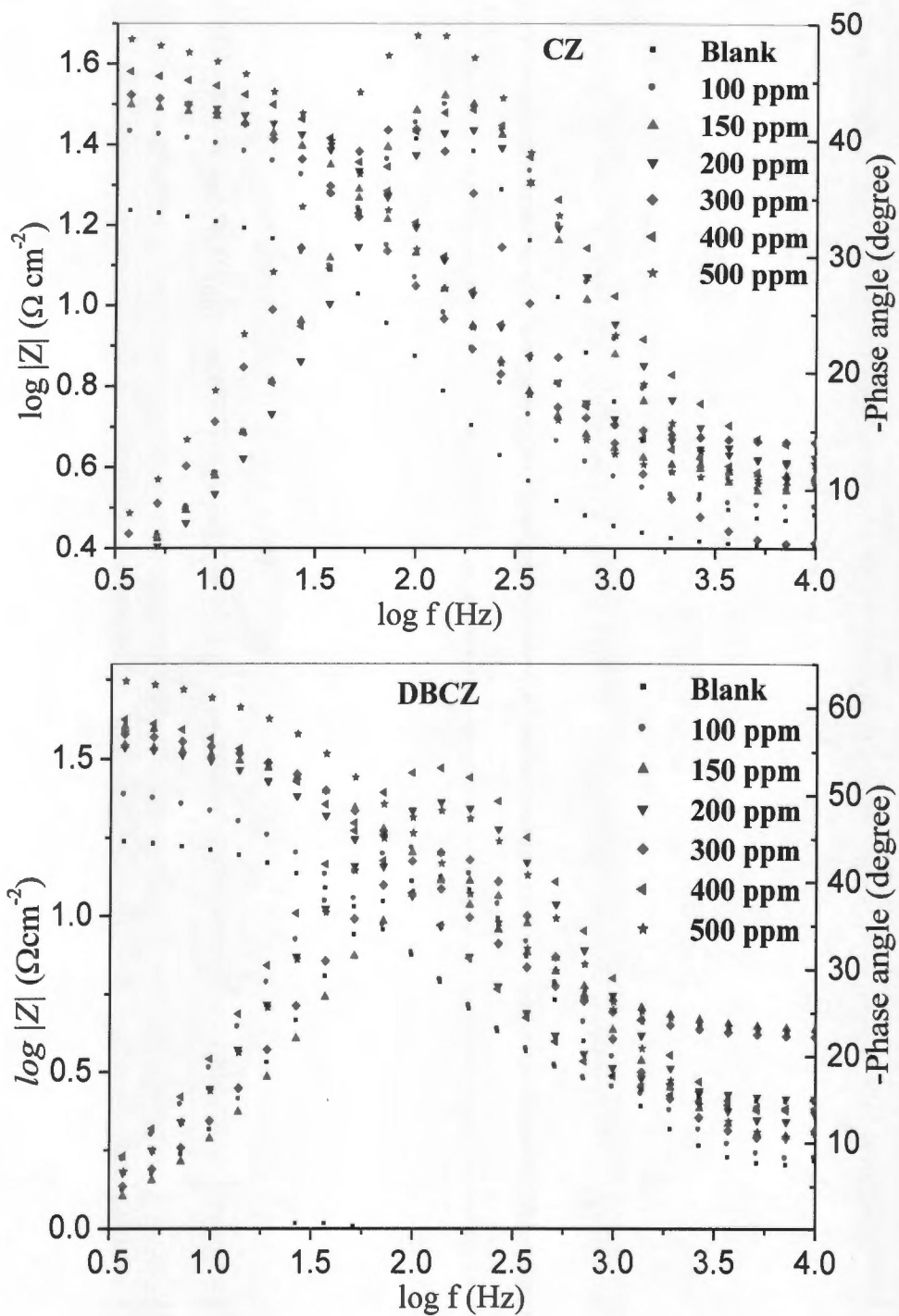


Figure 4.3. Bode impedance modulus and phase angle plots for mild steel in 1 M HCl in absence and presence of different concentration of CZ and DBCZ.

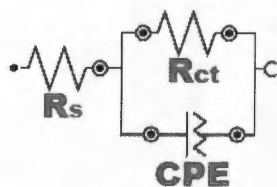


Figure 4.4. Equivalent circuit employed for the fitting of impedance spectra.

Table 4.3. The slopes (S) of the Bode impedance modulus plots at intermediate frequencies and the maximum phase angles (α) for mild steel in 1 M HCl solution in the absence and presence of 500 ppm inhibitors.

Inhibitor	$-S$	$-\alpha$
Blank	0.30	40.47
CZ	0.38	48.94
DBCZ	0.50	48.25
HCZ	0.47	49.60
THCZ	0.39	50.73
EHCZDCA	0.53	59.91

The alterations of impedance modulus and phase angles with frequency are presented in Figure 4.3. The impedance at upper limit frequency correlates to the Ohmic resistances of the protective film and the solution entrapped between the working electrode and the reference electrode. At high frequencies, $\log|Z|$ tends to proceed towards zero and the phase angle (α) descends rapidly to 0° [170]. This response is ascribed to resistive behaviour of the electrode/electrolyte interface and the impedance magnitude is analogous to the solution resistance. A linear plot of $\log|Z|$ vs $\log f$ with a slope (S) of -1 and a phase angle (α) of -90° at intermediate frequencies is a well-known feature of perfect capacitive behaviour of electrode/electrolyte interface [169, 170]. The values of S and α as recorded in Table 4.3 reveal that the electrochemical systems of MS in 1 M HCl in the absence and presence of CZs exhibit pseudo-capacitive behaviour. The values of S and α for the inhibitor-containing systems are predominantly nearer to the threshold values for a pure capacitor. This clearly indicates that the inhibitor molecules form pseudo-capacitive adsorbed film on MS surface that subsequently protect the MS surface from direct attack by aggressive acidic ions in solution.

4.1.2. Adsorption isotherms

Thorough knowledge of interactions taking place between the corroding MS surface and inhibitor molecule during corrosion inhibition can be unravelled in respect of the adsorption characteristics of the inhibitor molecule [171].

The data obtained for the degree of surface coverage at 303 K (using the data obtained from polarization studies and listed in Table 4.1) were fitted into assorted adsorption isotherm models. At the end, only Langmuir and Freundlich adsorption isotherms gave adequate fittings with near unity values of the correlation coefficients (R^2). The universally accepted forms of adsorption models employed are:

$$\text{Freundlich isotherm: } \theta = K_{ads} C_{inh} \quad (4.2)$$

$$\text{Langmuir isotherm: } \frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (4.3)$$

where, θ is the degree of surface coverage; K_{ads} is the equilibrium constant of the adsorption/desorption process and C_{inh} is the concentration of the inhibitor. The value of K_{ads} is a gauge of the degree of adsorption where a high value of K_{ads} is attributed to strong adsorption of the inhibitor molecules on the metal surface [171,106]. The Freundlich and Langmuir adsorption isotherm plots depicted in Equations 4.2 and 4.3 respectively are presented in Figure 4.5 for all the studied compounds. The plots display requisite linearity with R^2 values ranging from 0.9717 to 0.9987 for Langmuir, and 0.901 to 0.9867 for Freundlich adsorption isotherms. This is a key observation that suggests a satisfactory level of fitness of the adsorption data to both models. Consequently, the Freundlich adsorption model in Equation 4.2 anticipates intercept at $\theta = 0$, while the slope of the Langmuir adsorption isotherm in Equation 4.3 should be unity. These conditions however, were not met by the two models as was adjudged by the values of slopes and intercepts listed in Table 4.4. The departure of the slope of a Langmuir adsorption plot from unity has been ascribed to potential interactions between the adsorbed inhibitor molecules [171], which the original form of the Langmuir adsorption model does not take into consideration.

The observed anomaly necessitated the use of a modified Langmuir adsorption isotherm of the form $C_{inh}/\theta = 1/K_{ads} + mC_{inh}$. In this modified model, m is the slope of the plot and can be deduced to an inherent factor in the surface coverage values. As a result, the intercept of the plots can be equated to $(1/m)K_{ads}$, from which K_{ads} can be calculated [168]. This approach was adopted to calculate the values of K_{ads} listed in Table 4.4. Therefore, the values of K_{ads}

were obtained using the Langmuir adsorption isotherm parameters since there is no similar simple modification for the Freundlich adsorption isotherm.

The change in Gibb's free energy of adsorption (ΔG_{ads}) was calculated by using the equation:

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}) \quad (4.4)$$

where ΔG_{ads} is the standard free energy of adsorption; R is the gas constant and T is the absolute temperature. The value of 55.5 is the concentration of water in solution in mol L^{-1} .

The calculated values of K_{ads} and ΔG_{ads} are presented in Table 4.4. Examination of the results in Table 4.4 shows the ΔG_{ads} values are negative as anticipated for an adsorption process, which connotes spontaneity of the adsorption process and solidity of the adsorbed film on the MS surface [72, 106]. The ΔG_{ads} values recorded in this work are more negative than -20 kJ mol^{-1} (for physisorption) and less negative than -40 kJ mol^{-1} (for chemisorption). This clearly demonstrates that the studied CZ molecules adsorb on MS surface in 1 M HCl through competitive physical and chemical adsorption mechanisms [72].

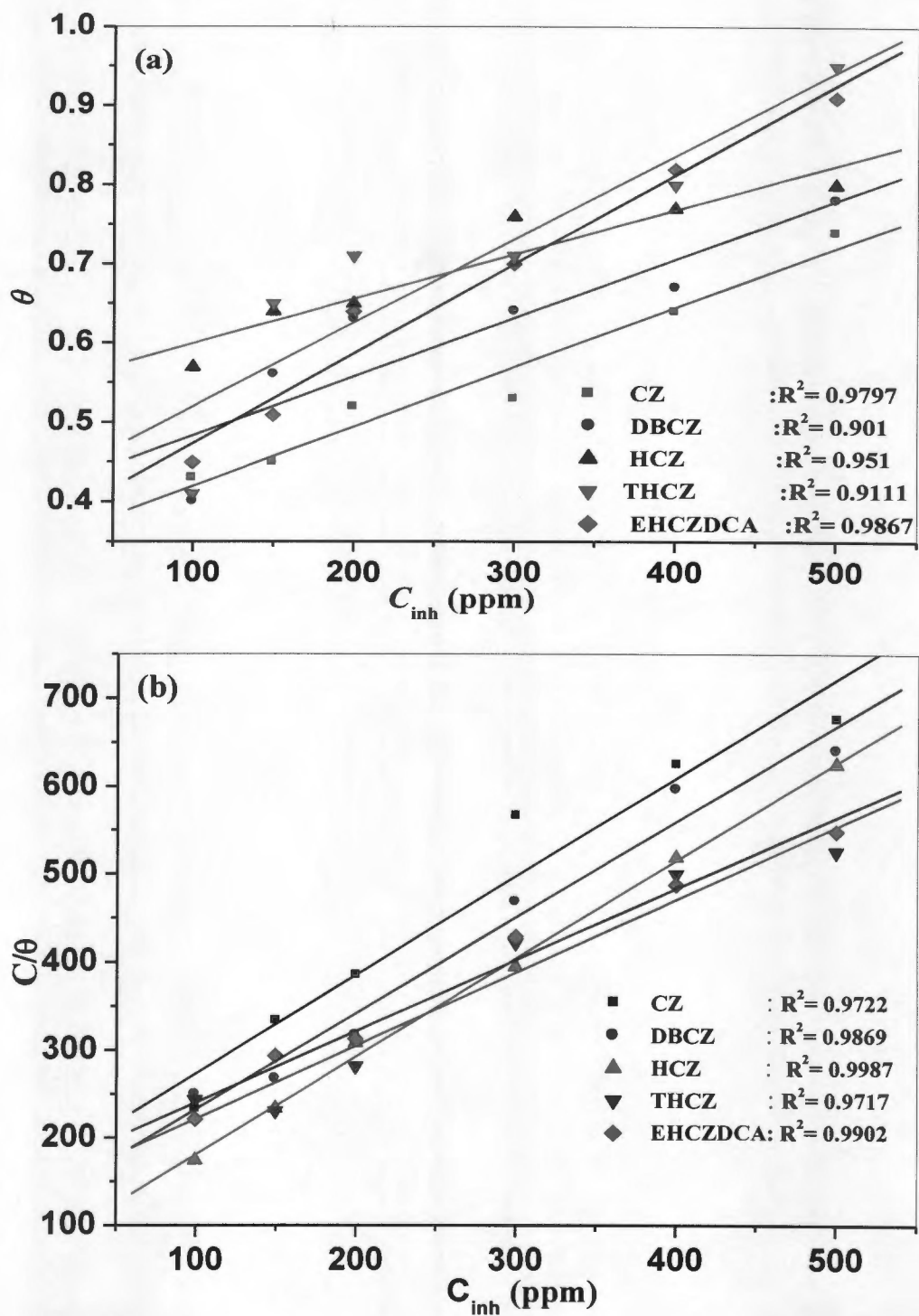


Figure 4.5. Adsorption isotherm plots of (a) Freundlich, (b) Langmuir for mild steel in the presence of carbazoles.

Table 4.4. Langmuir and Freundlich parameters for the adsorption of CZs on mild steel surface obtained from Tafel parameters at 303 K.

Isotherm	Inhibitor	Slope	Intercept	K_{ads}	$-\Delta G^{\circ}_{ads}$ (kJ/mol)
Langmuir	CZ	1.1208	161.4351	1035.71	27.61
	DBCZ	1.091	123.6561	2628.26	29.96
	HCZ	1.115	69.3895	2640.31	29.97
	THCZ	0.831	138.9895	1232.04	28.05
	EHCZDCA	0.8099	159.779	2099.40	29.39
Freundlich	CZ	7.5158×10^{-4}	0.345	-	-
	DBCZ	7.4105×10^{-4}	0.4095	-	-
	HCZ	5.6211×10^{-4}	0.5438	-	-
	THCZ	11.0×10^{-4}	0.415	-	-
	EHCZDCA	11.0×10^{-4}	0.3608	-	-

4.1.3. Biocorrosion study (weight-loss measurements)

SRB induced anaerobic corrosion of MS was investigated by weight-loss (WL) measurements and the extent of weight loss in the absence and presence of the studied inhibitors (CZs) are recorded as column plots in Figure 4.6. The order in terms of weight-loss values for MS exposed to pure and mixed SRB culture is such that $SRB > HCZ > THCZ > DBCZ \approx EHCZDCA > CZ$.

The appreciable WL observed in pure SRB strain is in good agreement with the pit image caused by the uninhibited corrosive environment [172]. Corrosion rate (CR) due to MIC was also computed using Equation 3.3 whilst inhibition efficiency from WL analysis ($\%IE_{WL}$) was deduced using Equation 3.4 and the results are presented in Table 4.5. All the studied compounds showed a great deal of corrosion mitigation efficiencies for MS in the SRB culture. The corrosion inhibitive effect of the studied CZs in the SRB media may be a combination of biocidal effect of CZs on the bacteria that are responsible for corrosion in the SRB media and the observed protection of the steel surface by adsorbed molecules of the tested CZs.

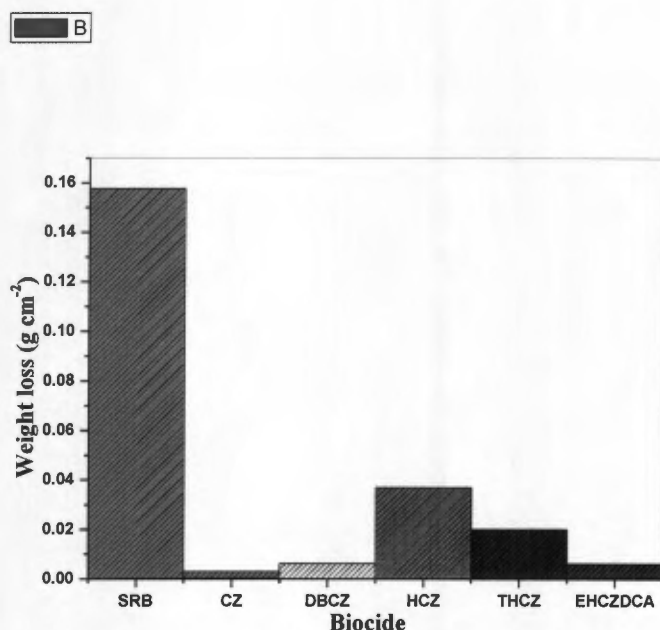


Figure 4.6. Weight loss measurements for mild steel exposed to SRB cultures after 9 days incubation with or without 100 ppm carbazoles at 310 K.

Table 4.5. The weight loss parameters obtained for mild steel exposed to SRB cultures after 9 days incubation with or without 100 ppm CZs.

Biocide	CR (g.cm ⁻² .d ⁻¹)	IE% _{WL}
SRB	1.97x10 ⁻² ±2.36x10 ⁻³	-
CZ	3.09x10 ⁻⁴ ±1.69x10 ⁻⁵	98.43±12.96
THCZ	2.17x10 ⁻³ ±1.16x10 ⁻⁴	88.97±11.67
EHCZDCA	9.17x10 ⁻⁴ ±2.05x10 ⁻⁵	95.34±11.62
HCZ	4.16x10 ⁻³ ±2.76x10 ⁻⁴	78.86±10.81
DBCZ	9.32x10 ⁻⁴ ±2.70x10 ⁻⁵	95.31±11.76

4.1.4. Surface morphology studies

4.1.4.1. SEM study

The SEM images of MS coupons exposed to the uninhibited and inhibited (CZ and DBCZ) acid media (for 3 h) and uninhibited and inhibited (CZ and DBCZ) *D. vulgaris* inoculated media (for 9 days) are presented in Figures 4.7 and 4.8 respectively. The rest of SEM micrographs can be found in Figures AI-4 and AI-5 (Appendix I). The coupon surfaces were examined cautiously to avoid removing the biological and/or chemical species formed

on the coupon surfaces. The entire MS coupons analysed revealed distinguishing surfaces after exposure to the respective media.

Figure 4.7a reveals the SEM micrograph of MS surface in 1 M HCl in the absence of inhibitors, which is marked by vastly corroded and vandalized surface. In the presence of 100 ppm of the studied CZs, the surface morphologies (Figures 4.7b and 4.7f) are marked by strongly localised preservative film, which proposes that the studied CZs adsorbed on MS surface and block it from immediate contact with the corrosive acidic ions.

Figure 4.8a shows the presence of passive film as well as conditioning layers on the MS coupons recovered from the SRB medium (without the inhibitors). In the presence of the investigated carbazole molecules, the coupon surfaces become more uniform than that of SRB medium (Figures 4.8b and 4.8f). A comparison of the steel surfaces revealed that the MS coupons recovered from the *D. vulgaris* inoculated media that contain the inhibitor molecules are covered with protective film of inhibitor molecules, while the one recovered from the blank *D. vulgaris* inoculated medium does not possess such film. Yuan *et al.* [173] uncovered that the absence of protective surface film tends to facilitate localised attack by sulphide ions, which most SRBs are known to produce. This accordingly initiates pitting or crevice corrosion, which is more pronounced for the MS surface inoculated in the uninhibited SRB medium as suggested by the large pit depth in Figure 4.8a [62].

In addition, the surfaces of MS coupons exposed to SRB cultures after 9 days incubation with or without 100 ppm CZs are marked by two distinguishing layers (with the exception of Figures 4.8a and 4.8d) that present both morphological and chemical features of the biofilm (developed) on the MS surface. The dark coating is made of reduced amounts of sulphides and high quantities of carbon-based materials and iron oxides. The light layer moreover consists of high quantities of sulphides, carbon-based materials and iron oxides. These revelations corroborate data recorded in the EDX elemental analysis.

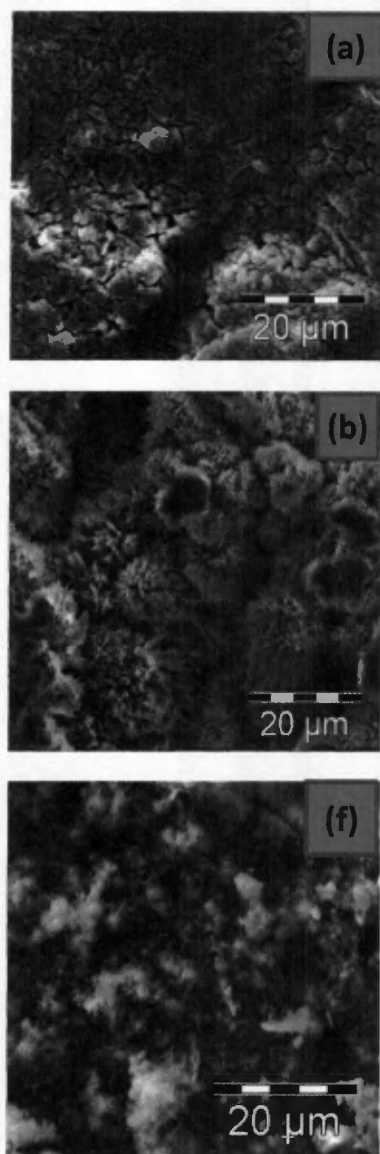


Figure 4.7. SEM images of mild steel surfaces immersed in 1 M HCl without and with 100 ppm of the studied inhibitors (a) blank (b) CZ (f) DBCZ.

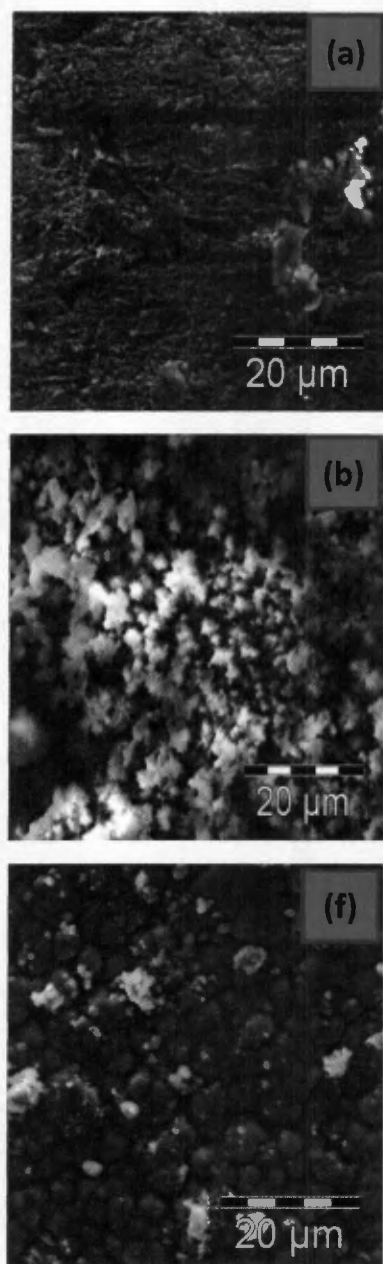


Figure 4.8. SEM images of mild steel surfaces immersed in SRB culture without and with 100 ppm of the studied inhibitors (a) blank (b) CZ (f) DBCZ.

4.1.4.2. EDX study

Elemental analysis using EDX technique was employed at different points on the corrosion crust for all the MS coupons and the effects of the assays are recorded in Table 4.6. It was established that the crystalline particles acquired from coupons immersed in 1 M HCl with or without 100 ppm of CZs compose of iron, chlorine, carbon, oxygen and trace of sulphur. MS surfaces in SRB media were dominated by iron, sulphur, phosphorous,

aluminium, oxygen and carbon. The identification of sulphur in all the samples further confirms the presence of SRB. The poor level of oxygen on the steel surface recovered from SRB blank (medium) compared to the presence of the investigated CZ molecules may be due to the reducing actions of SRB. SRBs are known for their ability to reduce sulphate and other oxidized species within their dominant environment. Elevated oxygen contents detected for the steel in the presence of the inhibitors (in SRB media) can be credited to the biocidal actions of the CZs on the bacteria, which sabotaged the reducing activity of SRB.

Table 4.6. EDX elemental constituents (in weight %) of mild steel surface retrieved from the acidic and SRB corrosive media without and with 100 ppm of the inhibitors.

Inhibitors	Fe	Mn	Ca	Cl	S	P	Al	Na	O	C
Acidic media										
1 M HCl Blank	34.55	-	-	34.6	-	-	-	-	23.99	6.86
CZ	55.98	-	-	5.49	-	-	-	-	34.63	3.91
DBCZ	55.32	0.48	-	2.05	0.24	0.07	0.4	0.27	36.24	4.92
HCZ	55.21	-	-	0.16	-	-	-	-	41.28	3.35
THCZ	50.06	0.16	-	0.35	-	1.68	0.09	0.07	22.95	24.64
EHCZDCA	48.89	0.18	-	3.15	1.08	-	0.07	-	39.91	6.71
SRB Culture media										
SRB Blank	76.57	0.15	0.47	-	0.21	0.77	0.1	-	8.9	12.83
CZ	49.92	-	-	-	0.08	-	0.07	-	39.57	10.37
DBCZ	61.15	-	-	0.11	0.07	0.08	0.07	-	24.27	14.23
HCZ	54.52	-	-	-	0.14	0.32	0.07	-	35.54	9.42
THCZ	51.66	-	-	-	0.14	0.42	0.06	-	38.7	9.03
EHCZDCA	50.88	-	-	-	0.19	2.77	0.14	0.38	36.5	9.13

4.1.4.3. FTIR spectroscopy

FTIR spectra of the pure inhibitor molecules and the resulting solutions after MS immersion, both in 1 M HCl and SRB inoculated media are shown in Figure AI-6.

The spectra of all the pure CZ molecules show a group of bands between 1000 and 1500 cm^{-1} characteristics of the aromatic C-C stretching [151]. For all the five pure CZs, the C-H symmetric and asymmetric stretching due to the methyl and methylene groups were observed at around 2939 cm^{-1} [72]. A band at 1446.9 cm^{-1} due to the framework vibration of the aromatic rings [34] was also observed for the spectra of all the pure compounds. A band at 1599 cm^{-1} due to C-N stretching was also observed. C=C vibrations were observed for the molecules between 1590 cm^{-1} and 1610 cm^{-1} . All the molecules except EHCZDCA showed the N-H vibration band at around 3400 cm^{-1} . Meanwhile, the C=O vibration band for EHCZDCA was distinctly observed at 1685 cm^{-1} .

Upon MS immersion in the acidic medium (Figure AI-6 top), the peaks due to the aromatic rings have disappeared, though there is still the presence of C=C vibration bands at nearly the same position before the steel immersion. The N-H vibration band has disappeared completely in all the molecules, suggesting that the N-atom of the N-H group is involved in coordination with the metal. The difference between the FTIR spectral of the inhibitor molecules before and after MS immersion suggests the occurrence of chemical interactions between the inhibitor molecules and Fe (MS) [72].

The FTIR spectral of the corrosion products on MS surface inoculated with *D. vulgaris* in the presence of the inhibitor molecules (Figure AI-6 bottom) showed nearly the same features as the one obtained in the acidic medium. However, a distinct band was observed at 1000 cm^{-1} for all the molecules. This band is particularly conspicuous for CZ and THCZ, and may be attributed to Fe-S bond formed as a result of reduction of SO_4^{2-} to S^{2-} by *D. vulgaris* [174]. The marked differences between the spectral of the inhibitor molecules before and after steel immersion in the SRB-inhibitor containing medium also suggest the occurrence of distinctive chemical interactions between the inhibitor molecules and the steel.

4.1.5. Quantum chemical calculations

In an attempt to unravel the donor-acceptor interrelationships between the studied CZs and MS, and to correlate the inhibition potentials of the CZs to molecular structures and different substituents on the carbazole moiety, quantum chemical calculations [175], were executed on the CZs. In accordance to the Fukui's frontier orbital approximation, donor acceptor interactions take place between frontier molecular orbitals (HOMO and LUMO) of interacting/reacting species [31, 55]. A metal has a high propensity of accepting electrons from an electron donor, for instance an inhibitor molecule into its lowest unoccupied orbital [31]. On the other hand, a metal has the propensity to donate its HOMO electron to fitting vacant (LUMO) orbital of the inhibitor molecule [30, 103] for back-bonding.

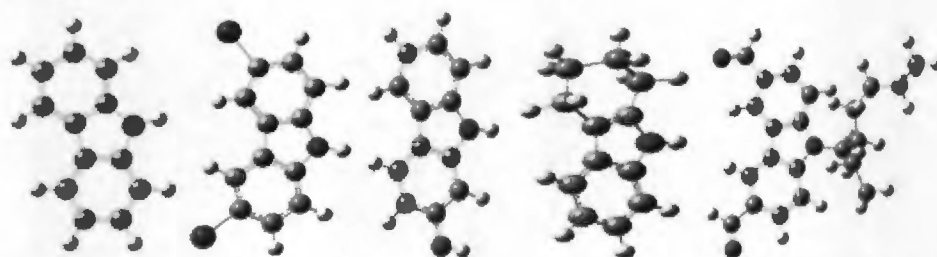
The optimized molecular structures, HOMO and LUMO electronic density distributions and electron density distributions for the electrophilic Fukui function (f^-) are presented in Figure 4.9. A close inspection of Figure 4.9 reveals that the HOMOs of all the molecules are mainly dominated by π bonding orbitals and delocalized over the entire aromatic carbazole rings in each molecule. In addition, the Br substituents (Br7 and Br15) in DBCZ are also involved in the HOMO distribution. In EHCZDCA, the HOMO is also spread to the ethylhexyl alkyl chain attached to the N1 atom of carbazole ring. The broadly distributed HOMO electron

density of the studied CZs is a feature of successful interactions of the molecules with electron defective metallic orbitals. The LUMO electron densities of all the molecules are well distributed over the carbazole rings. The observed HOMO and LUMO characteristics are indications that the studied compounds are susceptible to donor-acceptor interactions and might be responsible for the adsorption of the molecules on mild steel surface.

Local reactivity parameters employing the Fukui functions f^+ and f^- were explored to analyse the likelihood of the active atomic sites of an inhibitor molecule to electrophilic and nucleophilic attacks, respectively [106]. It is a well-known fact that the favoured site for electrophilic attack in a molecule is the atom that bears the highest value of f^- [72]. For this reason, the isosurface density of the Fukui function for electrophilic attack (f^-) has been presented in Figure 4.9. It is obvious that the electron density distributions of the f^- are centred mostly on the N-atom of the carbazole ring and the C=C π -electrons centres of the fused aromatic rings. This implies that these sites are the most susceptible sites for electrophilic attacks in the molecules. Moreover, the substituent Br-atoms in DBCZ, the O-atom of the OH group in HCZ and the C=O functional groups in EHCZDCA respectively are also prone to electrophilic attacks.

Some applicable quantum chemical parameters of the studied carbazoles both in the gas and aqueous phases are provided in Table 4.7. The energy of the HOMO orbital is a gauge of relative susceptibility of a molecule to donate electrons to electron deficient specie [20, 31, 103]. The results recorded in Table 4.7 prove that THCZ bears the maximum value of HOMO energy in the gas phase, which connotes highest propensity to donate electrons to an electron deficient site. It can therefore be inferred that THCZ has the highest propensity to adsorb onto mild steel surface and the observation is in good agreement with its elevated inhibition efficiency observed from the experiments. The LUMO energy quantifies the tendency of a molecule to accept electron(s) from electron rich specie. Consequently, molecules with low E_{LUMO} values have the propensity to accept electrons effortlessly [20, 31, 103].

Optimized structure



CZ

DBCZ

HCZ

THCZ

EHCZDCA

HOMO



CZ

DBCZ

HCZ

THCZ

EHCZDCA

LUMO



CZ

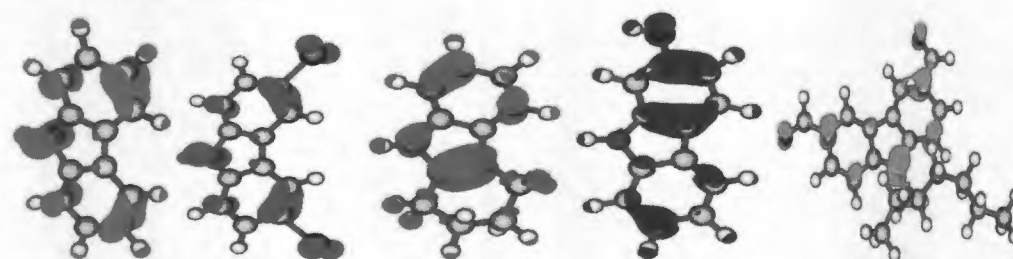
DBCZ

HCZ

THCZ

EHCZDCA

Electrophilic Fukui indices (f^-)



CZ

DBCZ

HCZ

THCZ

EHCZDCA

Figure 4.9. Optimized structure, HOMO, LUMO and the electrophilic Fukui function (f^- , isosurface value= 0.003) for the studied molecules.

Table 4.7. Selected quantum chemical parameters for the studied carbazoles.

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Dipole moment	η	σ	μ	ω	MV (Å ³)
Gas phase									
CZ	-5.76	-1.09	4.67	1.66	2.33	0.43	-3.43	2.52	184
DBCZ	-6.02	-1.62	4.40	4.40	2.20	0.46	-3.83	3.33	220
HCZ	-5.67	-0.97	4.70	2.89	2.35	0.43	-3.32	2.34	191
THCZ	-5.38	-0.38	4.00	2.54	2.50	0.40	-2.89	1.66	193
EHCZDCA	-6.35	-2.10	4.25	7.90	2.12	0.47	-4.23	4.21	374
Aqueous phase									
CZ	-5.84	-1.21	4.63	2.32	2.32	0.43	-3.53	2.69	-
DBCZ	-5.96	-1.56	4.41	2.20	2.20	0.45	-3.76	3.21	-
HCZ	-5.80	-1.08	4.72	2.36	2.36	0.42	-3.44	2.51	-
THCZ	-6.26	-2.22	4.04	2.02	2.02	0.50	-4.24	4.45	-
EHCZDCA	-5.51	-0.56	3.85	2.48	2.48	0.40	-3.04	1.86	-

EHCZDCA has a relatively low E_{HOMO} that affords it a better prospect of accepting charges in a favourable retro-donation formation during donor-acceptor activities with the metal. This very low value of E_{LUMO} of EHCZDCA might be the major reason for its relatively higher inhibition efficiency compared to CZ, DBCZ and HCZ.

The frontier molecular orbitals energy gap, ΔE ($\Delta E = E_{LUMO} - E_{HOMO}$) is mostly employed to distinguish the chemical reactivity and kinetic stability of inhibitor molecules [103]. Nwankwo *et al.* [168, 176] asserted that molecules with large value of ΔE are distinctly stable as they are known to possess low reactivity to chemical species whilst molecules with small value of ΔE have a high reactivity. The results outlined in Table 4.7 reveal EHCZDCA has the least ΔE value and consequently proves to be the most reactive compound. The high inhibition efficiency of EHCZDCA especially at 500 ppm compared to CZ, DBCZ and THCZ bears testimony to this observation.

Dipole moment is a signifier of the polarity of molecules [55, 103]. The lack of universal consensus on the relationship of dipole moment and corrosion inhibition efficiency has persisted [177, 178]. In the present study, the opinion that suggests that high dipole moment favours high inhibition efficiency was considered [179]. This analogy confers EHCZDCA with a relatively very high dipole moment as the most efficient inhibitor, which is in agreement with experimental inhibition efficiency.

Global (chemical) hardness (η) and softness (σ) provide molecular-based descriptions on reactivity and selectivity [103, 180]. Their alliance to corrosion inhibition is commonly expounded based on the Lewis theory of acid and bases and Pearson's concept of hard and soft acids and bases [55, 103]. The idea has it that a hard molecule will have a large ΔE value, while a soft molecule will have a small ΔE value. Inhibitor molecules will therefore adsorb onto metal surface at the region of the molecule where σ has the maximum value [103]. The trend across structures in the σ values as presented in Table 4.7, is such that $\text{EHCZDCA} > \text{DBCZ} > \text{CZ} \approx \text{HCZ} > \text{THCZ}$, which in support that EHCZDCA is the most reactive compound.

Global electronic chemical potential (μ) is usually presented as electronegativity (χ) in most previous studies [181, 182]. According to Wang *et al.* [181], electronegativity is ascribed to the negative of global electronic chemical potential. The values of μ communicated in Table 4.7 reveal that the trend of the μ values is $\text{THCZ} > \text{HCZ} > \text{CZ} > \text{DBCZ} > \text{EHCZDCA}$. This trend is in conflict with the experimental inhibition efficiency.

Another often used global reactivity index is electrophilicity index (ω). It is usually employed to predict the direction of a corrosion inhibition process [180]. A high electrophilicity value is a feature of a good electrophile while a small electrophilicity value connotes a good nucleophile. The observed trend across structures in the ω values as can be seen in Table 4.7, is such that $\text{EHCZDCA} > \text{DBCZ} > \text{CZ} > \text{HCZ} > \text{THCZ}$. This trend is in partial agreement with the experimental inhibition efficiencies.

Molecular volume (MV) describes the contact surface between the corrosion inhibitor molecule and metal surface [103]. The corrosion inhibition efficiency is often associated with the fraction of the surface engulfed by the adsorbed inhibitor molecule. The reasonably high value of MV for EHCZDCA in this thesis underpins its high inhibition efficiency compared to DBCZ, HCZ and CZ.

It is imperative to mention that quantum chemical parameters obtained in gas phase compare fairly well with data obtained in aqueous phase which supports the idea that the studied CZs are stable in water and therefore can be employed successfully to retard metal corrosion in aqueous media.

A careful inspection of the experimental inhibition efficiencies and quantum chemical parameters shows that there is no simple and uniform trend or relationship between inhibitive strengths of the studied compounds and singular quantum chemical descriptors. In this kind of situation, a more comprehensive investigation of possible correlations between the

inhibitive strengths and composite quantum chemical descriptors is often explored using the quantitative structure activity relationship (QSAR) analysis [183-185].

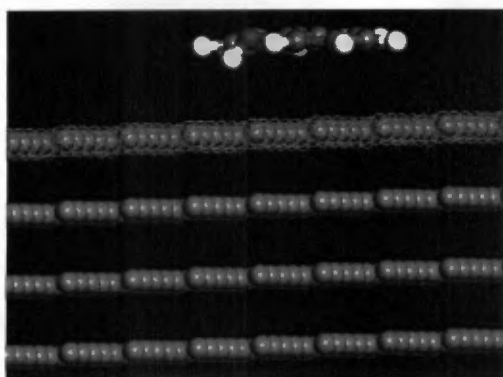
4.1.6. QSAR analyses

The QSAR analyses were carried out by taking different combinations of quantum chemical descriptors (in Table 4.7) and fitting them into empirical equations or models using the inhibition efficiency as the dependent variable. The suitability of the resulting models in describing the dependence of inhibition efficiencies of the studied compounds on a set of quantum chemical descriptors was judged based on the correlation coefficient (R^2) values, mean square error (MSE) and root mean square error (RMSE) values. The QSAR analyses were carried out with the aid of the XLSTAT software code used as a Microsoft Excel add-in [164]. The linear equations/models were generated based on the propositions of Lukovits *et al.* [165] and the results are listed in Table AI-1.

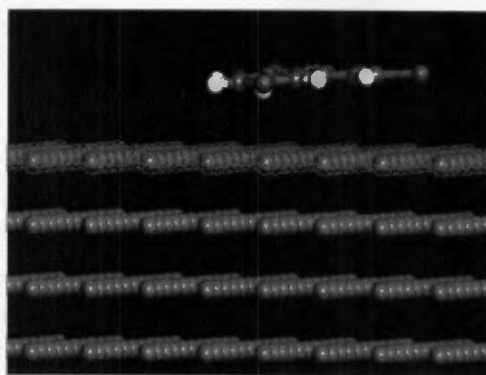
The results showed that a combination of three (3) quantum chemical parameters comprising the E_{HOMO} , E_{LUMO} and σ (softness) gave the best correlation with the inhibition efficiencies. The proposed QSAR equation ($\%IE_{\text{pred}} = -7326.397 - 998.129 * E_{\text{HOMO}} + 802.063 * E_{\text{LUMO}} + 5827.399 * \sigma$) suggests that for the studied compounds, a high inhibition efficiency depends on low E_{HOMO} , high E_{LUMO} and high σ .

4.1.7. Molecular dynamics simulation

The adsorption of the investigated inhibitor molecules (EHCZDCA, DBCZ, CZ, HCZ and THCZ) on MS surface was simulated by modelling the interactions between the inhibitor molecules and Fe(110) crystal surface. The most stable configurations of the simulated systems of Fe(110)/CZ and Fe(110)/DBCZ are shown in Figure 4.10, while the relevant energy indices of the systems are listed in Table 4.8. Similarly, the most stable configurations of Fe(110)/EHCZDCA, Fe(110)/HCZ and Fe(110)/THCZ are presented in Figure AI-7 (Appendix I). The results (in Figures 4.10 and AI-7) uncover that the moieties containing the aromatic rings and heteroatoms in the inhibitor molecules adsorbed on Fe(110) surface in an almost flat orientation, which afford excellent interactions of the inhibitor molecules with the metallic surface. The maximum values of adsorption and deformation energies were registered for the Fe(110)/EHCZDCA (Table 4.8), which recommends that EHCZDCA has the strongest interaction with Fe(110) surface.



Fe(110)/CZ



Fe(110)/DBCZ

Figure 4.10. The most stable configurations for the adsorption of CZ and DBCZ on Fe(110)/inhibitor systems.

Table 4.8. Energy parameters (kcal/mol) affiliated to the adsorption of the inhibitor molecules on Fe(110).

System	Adsorption energy	Rigid adsorption energy	Deformation energy
Fe(110)/CZ	-91.25	-91.65	0.40
Fe(110)/DBCZ	-109.89	-110.42	0.53
Fe(110)/THCZ	-93.86	-94.64	0.79
Fe(110)/HCZ	-95.43	-95.79	0.36
Fe(110)/EHCZDCA	-178.18	-185.07	6.89

4.1.8. Proposed mechanism of adsorption and inhibition

Corrosion inhibition authenticity of five carbazole derivatives (CZs) on MS corrosion and biocorrosion in 1 M HCl and microbial environments has been found to be as a result of the formation of protective film on the metal surface. The adsorption behaviour was found to be either physisorption, chemisorption or a combination of both. Based on the results procured from the electrochemical investigations, weight loss measurements, spectroscopy measurements, surface morphology, molecular dynamics simulation and quantum chemical calculations, the following clear-cut adsorption and inhibition mechanisms can be advocated for the studied inhibitor molecules.

(a) The investigated inhibitor molecules inhibit MS corrosion in 1 M HCl by adsorbing on the steel surface by forming protective layer. Their adsorption satisfactorily obeys Langmuir isotherm and occur mainly via physisorption.

(b) Molecular quantum chemical calculations revealed that the studied CZs may adsorb onto mild steel surface via chemisorption mechanism using the N-atom of the carbazole ring, the

pi-electron centres, and the other substituent heteroatoms (Br in DBCZ, O-H in HCZ, and C=O in EHCZDCA).

(c) SEM micrographs and EDX analyses also revealed that the studied compounds adsorbed on mild steel surface and form protective film that eventually shielded the surface from immediate attack of corrosive acid and SRB medium. FT-IR confirmed the possible formation of Fe--Inh complex.

(d) Molecular dynamic simulations strongly advocate that the studied molecules have strong interactions with Fe surface.

4.2. GROUP II: THCZCA, MTHCZ and MCZCA

Group II consists of three compounds as presented in Table 3.2. These compounds have similar backbone, but differ in the positions of methyl chain and other substituent groups. The hydroxyl (-OH) and carbonyl (C=O) functional groups are on positions 5 and 12 of the benzene ring in MCZCA and THCZCA respectively. The methyl (-CH₃) chain is attached to the first nitrogen atom of the pyrrole ring in MCZCA, and on position 10 in MTHCZ. Consequently, the effects of electronic and steric hindrance of the substituent carbonyl and hydroxyl groups, and methyl chain attached to different positions of the compounds were studied. The electrochemical measurements for this group were therefore executed within concentration range 300 ppm to 1000 ppm due to their poor inhibitory actions at lower concentrations.

The following sections of results and discussions pertaining to this set of compounds communicate the vital aspects of Group II.

4.2.1. Electrochemical studies

4.2.1.1. PDP studies

Polarization profiles for MS in 1 M HCl in the absence and presence of THCZCA, MTHCZ and MCZCA of various concentrations at 303 K are recorded in Figure 4.11. For the three mediums, the polarization profiles in Figure 4.11 display indistinguishable features with the 1 M HCl blank system. This characteristic feature suggests that the mechanism of inhibition is congruent for all the inhibitors studied in this thesis, and that addition of inhibitors does not remarkably alter the corrosion mechanism. Although both anodic and cathodic current densities can be seen to decrease in the presence of the studied inhibitors, the shifts in corrosion current densities are more visible for the cathodic than anodic curves between 800 ppm to 1000 ppm.

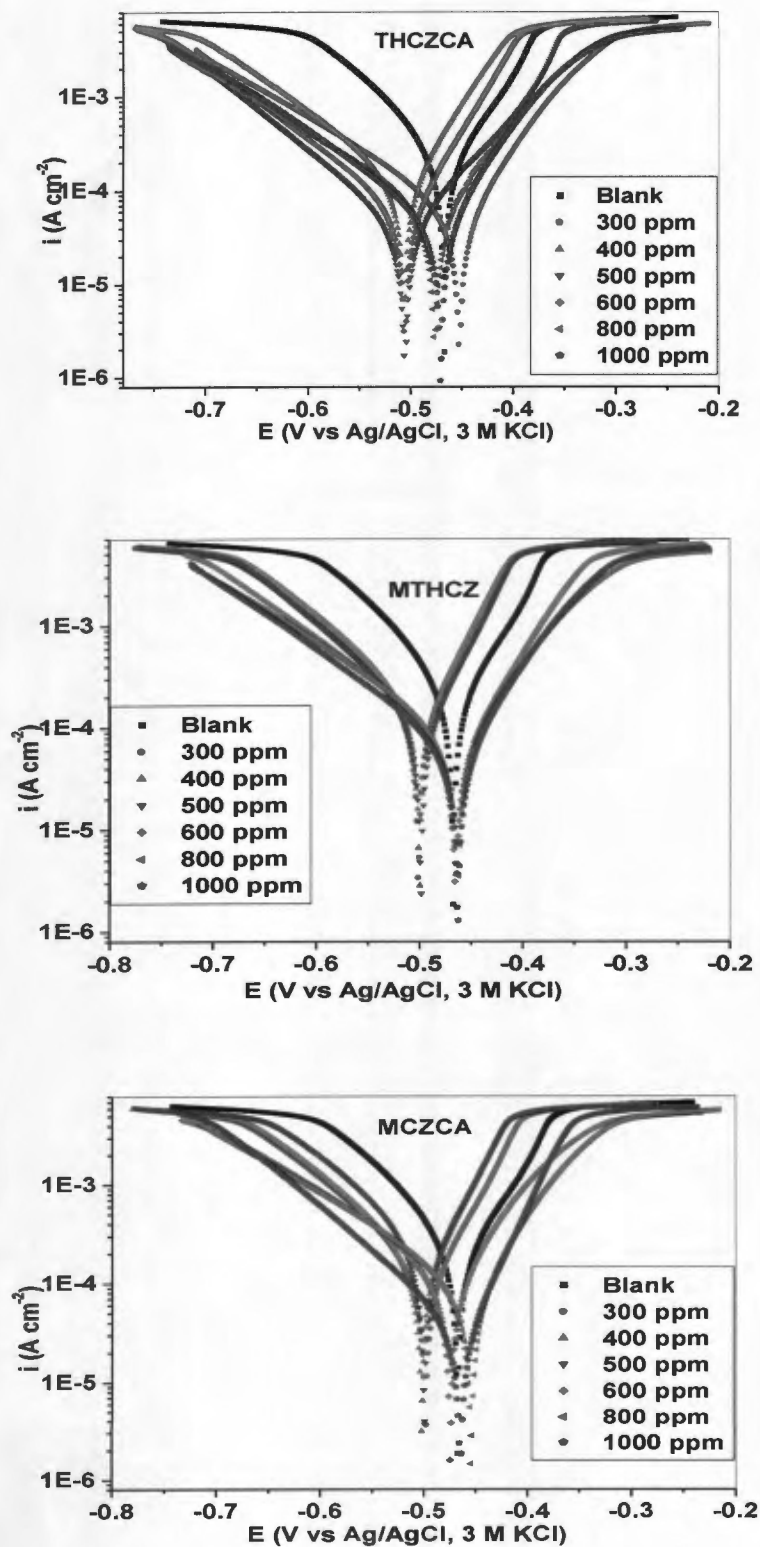


Figure 4.11. Polarization curves for MS in 1 M HCl without and with different concentrations of THCZCA, MTHCZ and MCZCA.

Table 4.9. Tafel polarization parameters for MS in 1 M HCl without and with different concentrations of THCZCA, MTHCZ and MCZCA.

Inhibitor	Conc (ppm)	β_a (mV/dec)	β_c (mV/dec)	$-E_{corr}$ (mV)	i_{corr} ($\mu A\ cm^{-2}$)	$\eta\%$
Blank	-	98.93	72.08	452.72	236.22	-
THCZCA	300	162.71	82.41	451.45	78.10	67
	400	48.70	80.31	505.66	68.44	71
	500	115.74	92.38	504.67	42.45	82
	600	55.68	79.43	504.89	38.11	84
	800	47.94	96.72	475.56	29.09	88
	1000	50.63	82.85	470.19	22.77	90
MTHCZ	300	105.95	60.57	500.23	135.15	43
	400	92.95	55.79	499.13	122.70	48
	500	100.83	55.34	497.94	98.69	58
	600	63.95	98.48	464.13	48.71	79
	800	57.23	94.83	462.04	39.98	83
	1000	51.22	96.22	462.34	31.10	87
MCZCA	300	129.44	70.98	497.66	193.82	18
	400	119.68	62.28	501.21	192.52	18
	500	93.03	60.97	498.85	181.33	23
	600	48.91	89.17	473.93	56.19	76
	800	52.14	91.22	453.43	46.25	80
	1000	117.33	53.83	463.98	42.30	82

At lower concentrations however, more pronounced effect on the cathodic arms of polarization curves is more obvious.

In addition, cathodic Tafel lines exhibit almost parallel displacements as concentration of the carbazoles increased. Such response conforms that hydrogen gas evolution is activation-controlled and introduction of inhibitors did not significantly alter the mechanism of the electrochemical process [186, 187]. The respective kinetic parameters derived from the polarizative plots such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), corrosion current density (I_{corr}) and the inhibition efficiency values $\eta\%$ are given in Table 4.9. The observed reduction in I_{corr} values recorded especially at high concentrations indicates that the CZs under study possess corrosion inhibition properties.

THCZCA and MTHCZ show significant $\eta\%$ than MCZCA at 300 ppm. A much improved $\eta\%$ could only be achieved for MCZCA at 600 ppm. Between 800 ppm to 1000 ppm, values of $\eta\%$ appear seemingly constant for THCZCA, MTHCZ and MCZCA suggesting that further increase in concentration may have no effect on the $\eta\%$. The maximum inhibition efficiency of 90% was obtained for THCZCA at 1000 ppm inhibitor

concentration advocating that THCZCA has greater inhibitive strength than MTHCZ and MCZCA.

4.2.1.2. EIS studies

The Nyquist and Bode plots in Figure 4.12 provide information on the impedance spectra for MS in 1 M HCl in the absence and presence of THCZCA at different concentrations. On the other hand, the Nyquist and Bode plots for MTHCZ and MCZCA are shown in Figures AII-1 and AII-2 (Appendix II) respectively.

The impedance behaviour of MS in HCl has noticeably changed following the addition of carbazole into the test solutions. The Nyquist plot for MS in the absence of inhibitor is marked by a high frequency capacitive semicircle [73, 188]. The impedance spectra recorded for the different concentrations of the inhibitors on the other hand, display similar shape at high frequency semicircle with radii hugely dependent on the type of carbazole and its concentration. Consequently the diameter of Nyquist plots increased on increasing the concentration of CZs suggesting strengthening of inhibitive film [73, 188]. The impedance spectra obtained in the present group of carbazoles clearly display a depressed semicircle with the centre under the real axis and such remarkable feature ascribed to surface roughness and inhomogeneity of solid electrodes [73, 188]. The Bode plots of phase angle against frequency reveal single peak that supports the idea that the decomposition of MS is characterized by single charge transfer process [73, 188] and that the process is marked by a single relaxation time constant. The observed gradual broadening of phase angle maxima at intermediate frequency in the presence of the studied CZs also supports surface coating of the MS by the inhibitor molecules.

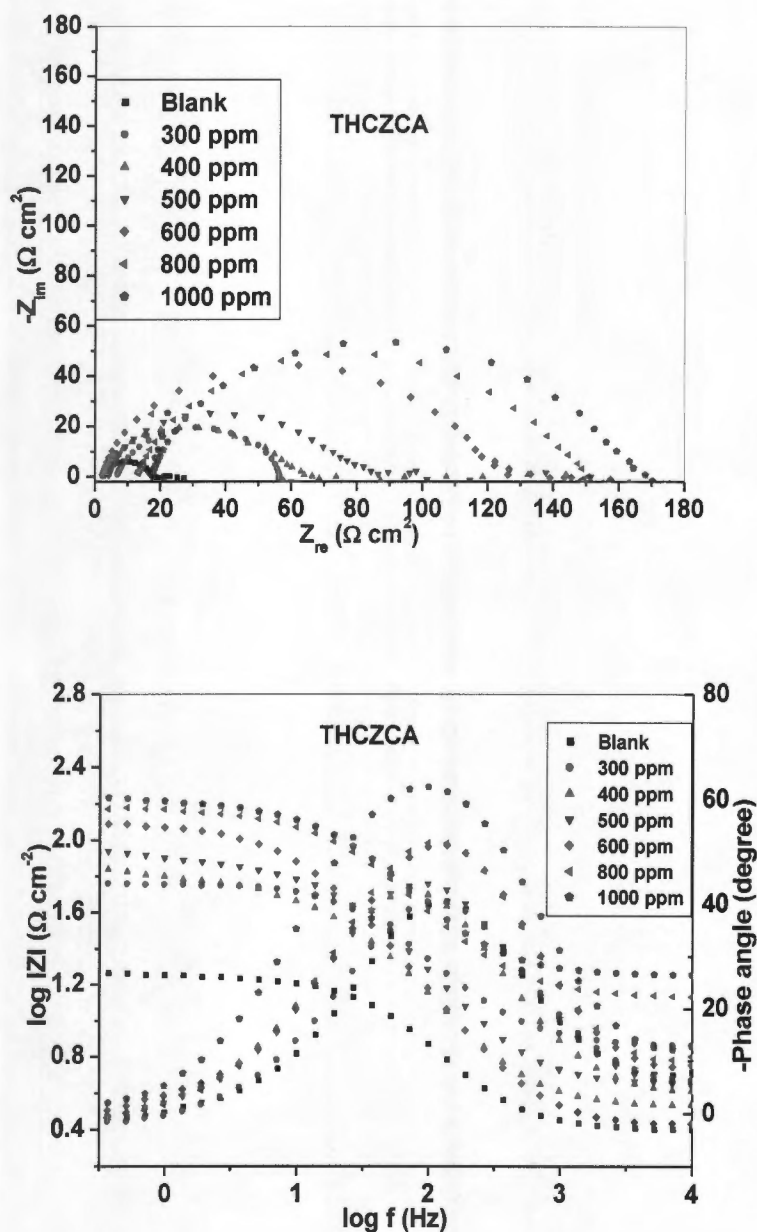


Figure 4.12. Nyquist and Bode plots for MS in 1 M HCl without and with different concentrations of THCZCA.

A simple equivalent circuit consisting of only one time constant is shown in Figure 4.4 and has been employed to model the experimental spectra, gave a satisfactory fit. The relevant electrochemical parameters procured from the fitting of the impedance spectra are presented in Table 4.10. On increasing inhibitor concentrations, the charge transfer

resistance, R_{ct} increased remarkably for all the CZs. Small R_{ct} values recorded for MCZCA especially at low concentrations suggest poor corrosion inhibition action compared to THCZCA and MTHCZ. Between 600 ppm to 1000 ppm, the R_{ct} values reflect insignificant change which resulted to $\eta\%$ values remaining almost unchanged for all the studied CZs.

The values of R_s and Y_0 do not form a definite trend with increasing concentration of the studied inhibitors. However, it can be observed that the values of the two are generally higher than the blank. The high R_s values especially for MTHCZ at 800 ppm, MCZCA at 600 ppm and THCZCA at 800 ppm to 1000 ppm reaffirm the relatively low conductivity media in the presence of the inhibitors. The magnitudes of n are predominantly lower for the inhibitor containing systems than the blank, implying that appreciable level of homogeneity of the MS surface was enhanced.

Table 4.10. Electrochemical impedance parameters obtained for MS in 1 M HCl without and with different concentrations of THCZCA, MTHCZ and MCZCA.

Inhibitor	Conc (ppm)	R_s ($\Omega \text{ cm}^{-2}$)	R_{ct} ($\Omega \text{ cm}^{-2}$)	Y_0 ($\mu\text{S s}^n \text{ cm}^{-2}$)	n	$\eta\%$
Blank	-	2.50	16.6	677	0.84	-
THCZCA	300	7.19	51.6	224	0.84	68
	400	3.14	71.4	486	0.78	77
	500	4.20	90.1	349	0.79	82
	600	2.57	130	264	0.86	87
	800	13.4	146	153	0.81	89
	1000	17.7	165	158	0.80	90
MTHCZ	300	4.70	28.4	594	0.76	42
	400	4.27	30.0	513	0.79	45
	500	3.36	37.8	505	0.80	56
	600	4.87	96.9	321	0.81	83
	800	14.8	122	211	0.79	86
	1000	7.01	179	182	0.80	91
MCZCA	300	3.59	19.5	629	0.78	15
	400	3.99	19.6	678	0.77	15
	500	3.74	20.7	644	0.80	20
	600	12.9	79.2	252	0.80	79
	800	8.09	84.8	207	0.83	80
	1000	4.75	89.2	348	0.82	81

Table 4.11. The slopes of the Bode impedance magnitude plots at intermediate frequencies (S) and the maximum phase angles (α) for MS in 1 M HCl solution in the absence and presence of 1000 ppm inhibitors.

Inhibitor	$-S$	$-\alpha$
Blank	0.30	40.47
THCZCA	0.64	63.39
MTHCZ	0.50	51.58
MCZCA	0.55	51.73

On close examination of Bode impedance modulus plots, an obvious linear segment at intermediate frequencies is apparent. Furthermore, the linearity of $\log|Z|$ vs $\log f$ plots at intermediate frequencies in the presence of the CZs is accompanied by higher slopes than the blank system as recorded in Table 4.11. The phase angle maxima observed for all the CZs was found to lie in the range of approximately -52 to -63 with slope values -0.50 to -0.64. These values of the phase angles and slopes taken at intermediate frequencies tend to approach -90 and -1. These observations are well-known features of pseudo-capacitive behaviour of electrode double layer [73, 188].

4.2.2. Adsorption isotherm

The adsorptions of THCZCA, MTHCZ and MCZCA were fitted to a series of non-identical isotherms including Freundlich, Langmuir and Flory-Huggins using the degree of surface coverage (θ) data obtained from EIS technique. The trials revealed that Freundlich adsorption model adequately supported the adsorption features of the studied CZs.

Figure 4.13 shows the Freundlich (Figure 4.13a) and Langmuir (Figure 4.13b) plots for the adsorption of THCZCA, MTHCZ and MCZCA on MS surface. Adsorption data derived from the plots are also reported in Table 4.12. The general equations for the Freundlich and Langmuir adsorption models employed are given in Equations 4.2 and 4.3 respectively.

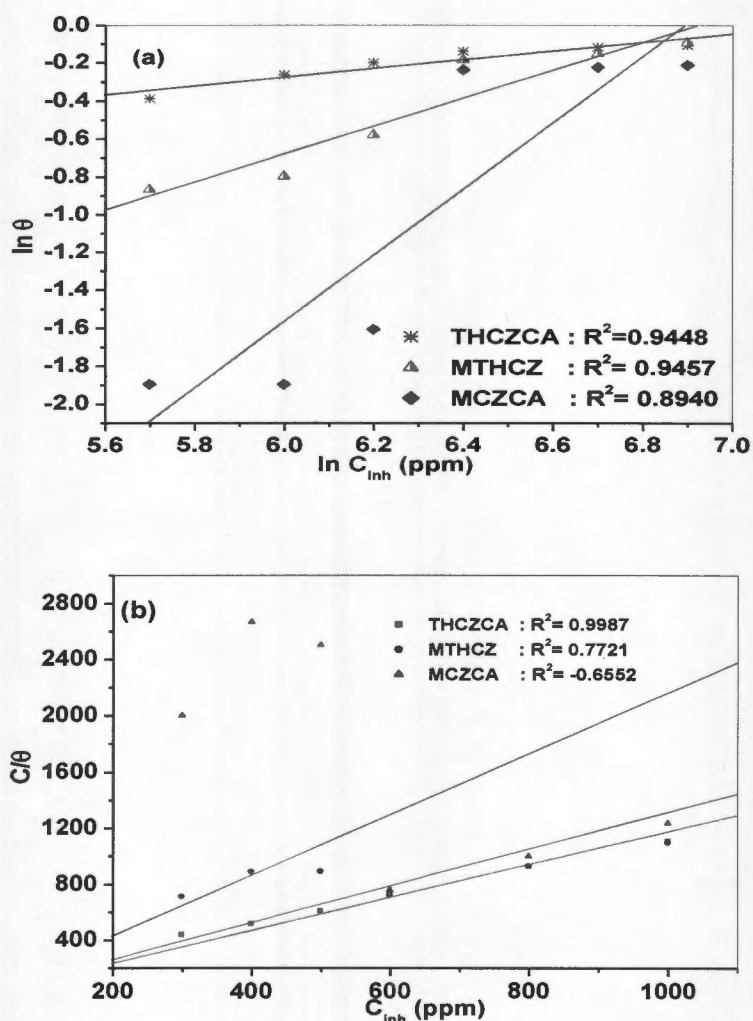


Figure 4.13. Representative adsorption isotherms for MS in 1 M HCl containing various concentrations of the studied CZs: (a) Freundlich (b) Langmuir.

Table 4.12. Freundlich and Langmuir parameters for the adsorption of CZs on MS surface obtained from Tafel parameters at 303 K.

Isotherm	Inhibitor	Slope	Intercept	K_{ads}	$-\Delta G^{\circ}_{ads}$ (kJ/mol)
Freundlich	THCZCA	1	6.518	10.40	16.02
	MTHCZ	1	6.763	10.22	15.97
	MCZCA	1	7.329	10.33	16.00
Langmuir	THCZCA	1.1778	-	-	-
	MTHCZ	1.3172	-	-	-
	MCZCA	2.1629	-	-	-

The linear regression coefficient obtained hovers around 0.8940 to 0.9457 and 0.6552 to 0.9987 for Freundlich and Langmuir adsorption isotherms respectively. Freundlich isotherm was therefore found to give the best fit even though an ideal Freundlich isotherm should give zero intercept. The deviation is usually ascribed to prospective interactions existing between the adsorbed molecules and MS surface [171]. The change in Gibb's free energy of adsorption (ΔG°_{ads}) was calculated from the Equation 4.4. The calculated ΔG°_{ads} values are presented in Table 4.12. The negative sign on ΔG°_{ads} denotes spontaneity of the adsorption process and the firmness of the adsorbed matrix on the MS surface [188]. The ΔG°_{ads} values obtained hover around -15.97 to -16.02 kJ.mol⁻¹ suggesting physisorption mechanism which involves charge transfer reactions between inhibitor compound and the MS surface [188].

4.2.3. Biocorrosion study (weight-loss measurements)

Figure 4.14 depicts the averaged weight loss after 9 days of incubation of MS coupons in *D. vulgaris* at 37 °C. In the absence of the studied CZs, WL data comprehensively supported the hypothesis that SRBs such as *D. vulgaris* causes extensive pitting which resulted in approximately 0.157 g.cm⁻² weight loss. Thus, the WL data in this work consistently suggested that the addition of these carbazoles significantly reduced MIC by *D. vulgaris* [136, 189].

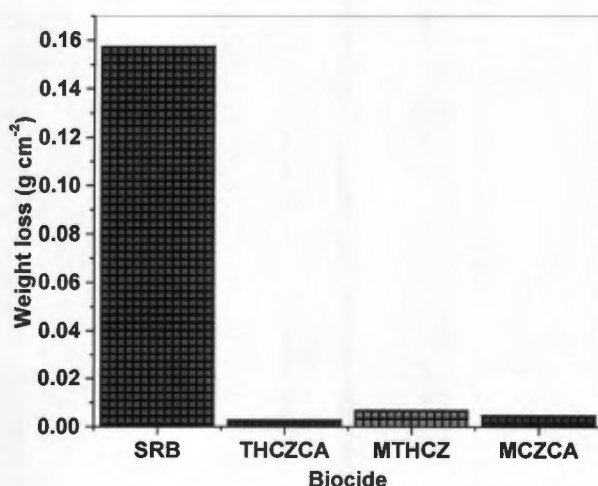


Figure 4.14. Weight loss measurements for MS exposed to SRB cultures after 9 days incubation with or without 100 ppm CZs at 310 K.

Table 4.13. The weight loss parameters obtained for mild steel exposed to SRB cultures after 9 days incubation with or without 100 ppm CZs.

Biocide	CR ($\text{g.cm}^{-2}.\text{d}^{-1}$)	$IE\%_{WL}$
SRB	0.018	-
THCZCA	0.00003	99.8
MTHCZ	0.00008	99.5
MCZCA	0.00005	99.7

The observed trend in WL values for MS exposed to pure and mixed SRB culture is such that $SRB > MTHCZ > MCZCA > THCZCA$. Corrosion rate (CR) was calculated using the Equation 3.3 and their individual standard deviation acquired from MS exposed to SRB cultures after 9 days incubation in the absence or presence of 100 ppm CZs are as follows: SRB ($0.018 \text{ g.cm}^{-2}.\text{d}^{-1} \pm 0.0002$), THCZCA ($0.00003 \text{ g.cm}^{-2}.\text{d}^{-1} \pm 0.000002$), MTHCZ ($0.00008 \text{ g.cm}^{-2}.\text{d}^{-1} \pm 0.00002$) and MCZCA ($0.00005 \text{ g.cm}^{-2}.\text{d}^{-1} \pm 0.00003$). The trend in corrosion rate is therefore such that $SRB > MTHCZ > MCZCA > THCZCA$. Accordingly, the inhibition efficiency due to WL ($IE\%_{WL}$) was calculated using the Equation 3.4 and presented as follows: THCZCA (99.8%), MCZCA (99.7%) and MTHCZ (99.5%). The protection efficiency of the CZs for MS in *D. vulgaris* follows the order $THCZCA > MCZCA > MTHCZ$. Above all, the three CZs studied proved to possess excellent protection efficiencies for MS corrosion in *D. vulgaris* dominated environment. The efficiency of these CZs can be attributed to their reasonable adsorptive strength as well as their inherent biocidal strengths.

4.2.4. SEM analysis

The SEM images obtained for acid treated MS surfaces with 100 ppm carbazoles are shown in Figure 4.15. Figure 4.15a (blank image) shows a harshly vandalized MS surface due to corrosive acid medium. However, a loosely localized protective film can be observed for MS surfaces (Figures 4.15b-4.15d) treated with 100 ppm of CZs. Analysis of *D. vulgaris* incubated MS reveals that in the absence of carbazoles, extensive localized pitting corrosion was recorded which in addition resulted to the highest averaged weight loss [189]. The loosely nature of the protective films and pitting cracks can be observed for the carbazole treated metal surfaces (Figures 4.16b and 4.16d) whereas Figure 4.16c reveals smooth and clear surface with traces of abrasion scratches. From the whole results obtained for SEM

micrographs in Figures 4.15a-4.15d and Figures 4.16a-4.16d, it can be deduced that the set of CZs discussed possess excellent film-forming ability and corroborate weight loss results.

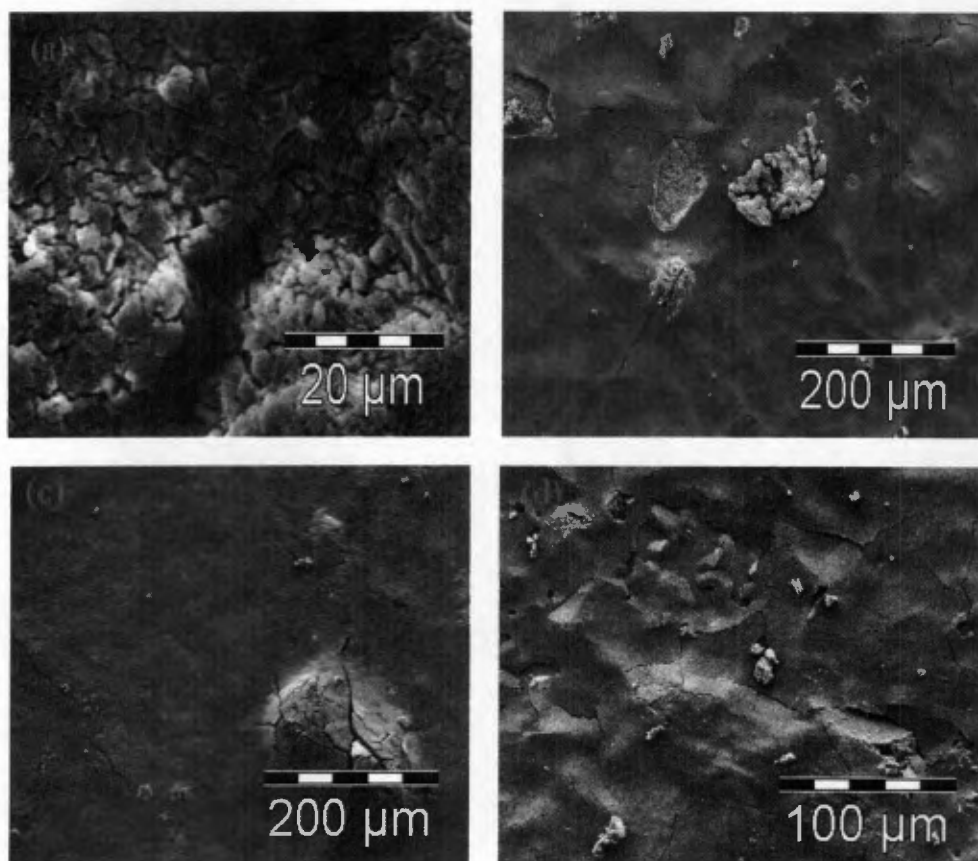


Figure 4.15. SEM images of MS surfaces immersed in 1 M HCl without and with 100 ppm of the studied inhibitors (a) blank (b) THCZCA (c) MTHCZ (d) MCZCA.

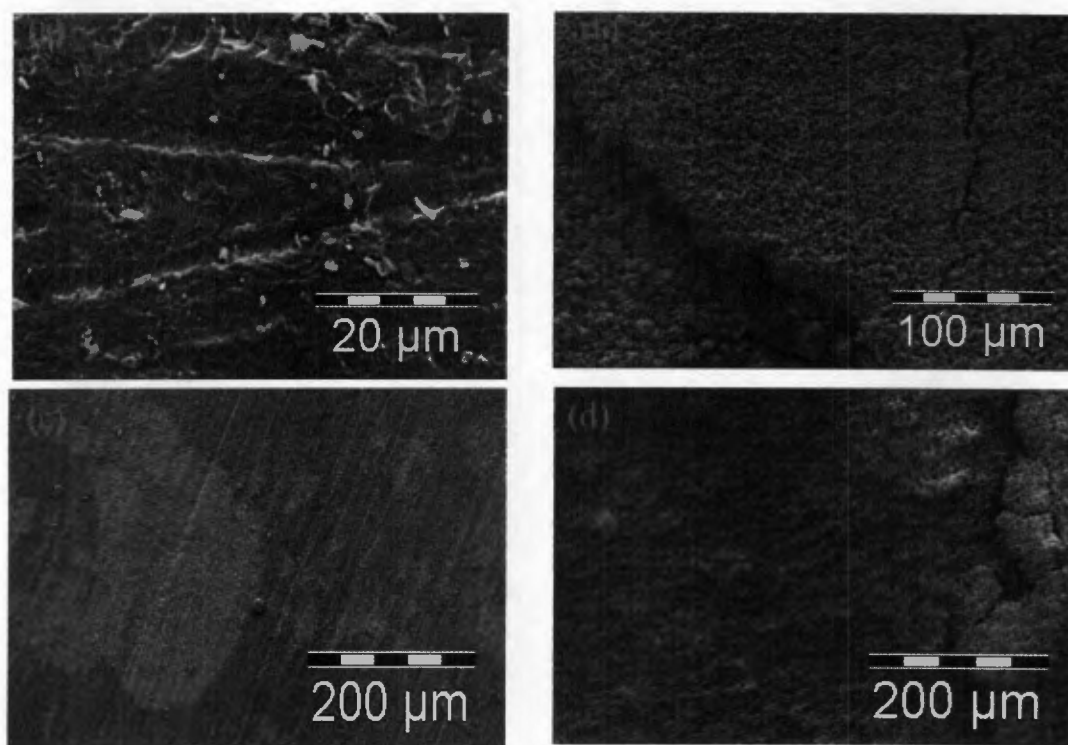


Figure 4.16. SEM images of MS surfaces immersed in SRB culture without and with 100 ppm of the studied inhibitors (a) blank (b) THCZCA (c) MTHCZ (d) MCZCA.

4.2.5. EDX study

The elemental analysis of corrosion products of MS exposed to abiotic and biotic conditions are shown in Table 4.14. Quantitative EDX analysis shows that the crystalline and amorphous layer obtained from coupons immersed in 1 M HCl with or without 100 ppm of CZs consist of mixtures of iron oxides and chlorides, in addition to carbon-based materials that may have accumulated from the inhibitor (CZs).

The characteristics of the resulting matrix in the presence of the SRB microbial consortium over 9 days incubation are also shown in Table 4.14. There is evidence to support the accumulation of sulphide-based compounds in the presence of SRB alone. The significant amount of products, for instance phosphate-based compounds observed in the SRB-incubated MS is primarily due to the formation of biofilm matrix. It has been established that the metabolic activities of the SRB consortium and associated biofilm enhance concentrations of phosphate-based compounds [186].

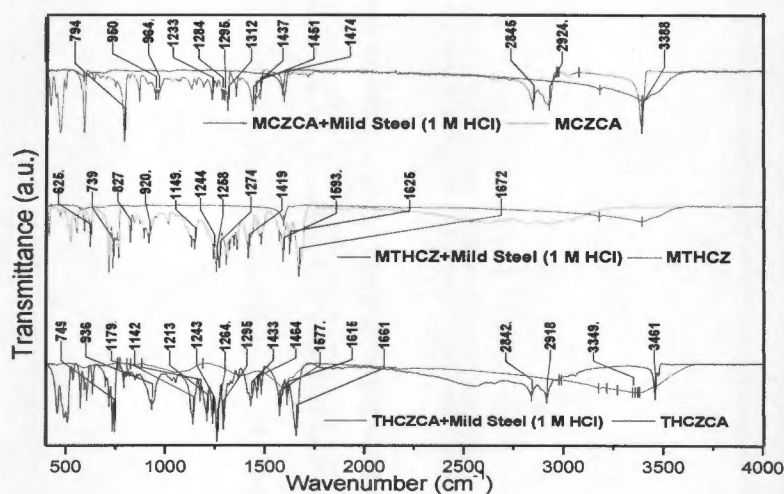
In general, the corrosion products for biotic and abiotic systems revealed remarkable dissimilarities in appearance, structure and composition (Figures 4.15-4.16 and Table 4.14).

Table 4.14. Atomic (in weight %) of elements obtained from EDX spectra of MS surface retrieved from the acidic and SRB corrosive media without and with 100 ppm of the inhibitors.

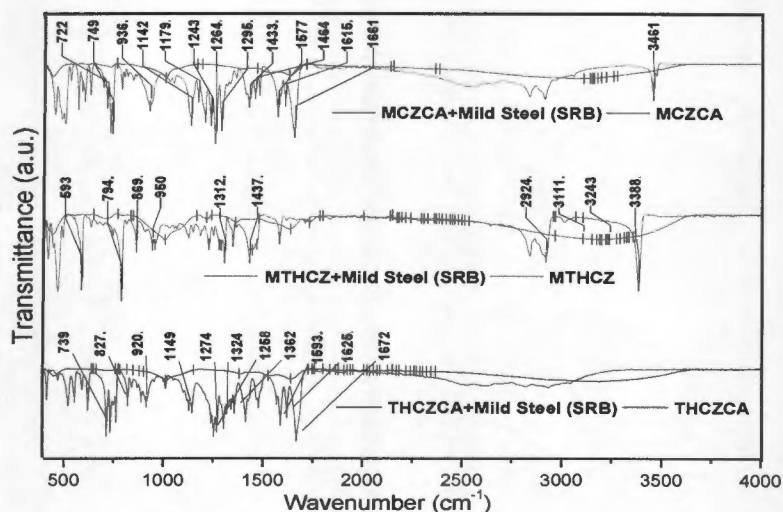
Inhibitors	C	Al	P	Cl	S	Ca	Mn	Fe	O
Acidic media									
1 M HCl Blank	6.86	-	-	34.6	-	-	-	34.55	23.99
THCZCA	8.66	0.08	-	13.62	-	-	-	42.37	35.27
MTHCZ	13.18	-	-	15.12	-	-	-	28.43	43.27
MCZCA	10.33	0.06	-	15.87	-	-	-	35.89	37.85
SRB Culture media									
SRB Blank	12.83	0.1	0.77	-	0.21	0.47	0.15	76.57	8.9
THCZCA	8.76	-	3.02	-	-	-	-	47.42	40.81
MTHCZ	8.13	0.08	0.28	-	-	-	-	53.68	37.55
MCZCA	12.68	-	2.74	-	-	-	-	36.73	47.85

4.2.6. FTIR spectroscopy

Figures 4.17a and 4.17b show the FTIR spectra of the unblended inhibitor molecules and the powdery corrosion products arising from MS immersion, in both 1 M HCl and *D. vulgaris* inoculated media.



(a)



(b)

Figure 4.17. FTIR spectra of the inhibitor molecules and their resulting surface powder after MS immersion in acidic medium (a) and SRB culture (b).

The spectra of all the pure CZ molecules display a group of distinctly bands between 500 and 1700 cm^{-1} characteristics of the aromatic C-C stretching [190]. The stretching bands around 2939 cm^{-1} could be attributed to C-H symmetric and asymmetric nodes of methyl and methylene groups [72]. A band at 1419-1447 cm^{-1} due to the framework vibration of the aromatic rings [191] was also observed for the spectra of all the pure CZs. Intense bands observed at 1599 cm^{-1} and between 1590-1672 cm^{-1} are due to C-N stretching and C=C

vibrations, respectively. The N-H vibration bands occurred around 3388 cm^{-1} and 3461 cm^{-1} for MTHCZ and THCZCA. In addition, the pure THCZCA and MCZCA molecules showed the C=O vibration band at around 1672 cm^{-1} and 1661 cm^{-1} .

The FTIR spectra obtained after MS immersion in 1 M HCl (Figure 4.17a) displayed that the peaks due to the aromatic rings stretching, C-N stretching, C=C vibrations, and C-H symmetric and asymmetric stretching have all disappeared completely in all the molecules. The disappearance of the N-H vibration bands and the subsequent appearance of low intensity bands around 2918 cm^{-1} for THCZCA and MTHCZ confirm coordination via the N1 atom with the metal [72].

Upon MS inoculation with *D. vulgaris* in the presence of the inhibitor molecules (Figure 4.17b), the FTIR spectra of the corrosion products on MS surface revealed similar features as the ones obtained in the acidic medium. Moreover, a distinctive broad band was observed at 1000 cm^{-1} for all the molecules which can be attributed to Fe-S bond formed as a result of reduction of SO_4^{2-} to S^{2-} by *D. vulgaris* [174]. The marked spectral differences observed for the inhibitor molecules before and after steel immersion in the SRB-inhibitor containing medium offers compelling evidence that chemical interactions between the inhibitor molecules and the steel occurred.

4.2.7. Quantum chemical calculations

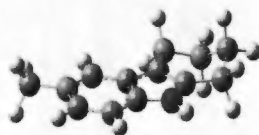
Figure 4.18 shows the optimized molecular structures, HOMO and LUMO electronic density distributions and calculated Mulliken atomic charges distribution of the three CZ derivatives. The HOMO and LUMO of the three CZ molecules are mostly dominated by π bonding orbitals and delocalized over the entire aromatic carbazole rings in each molecule. This characteristic uniqueness could offer favourable conditions for donor-acceptor interactions and might be responsible for the adherence of the molecules on MS surface. However, the methyl alkyl chain in MTHCZ is not involved in the HOMO-LUMO distribution. The central N-atom of the carbazole moiety in THCZCA is excluded from LUMO. In addition, the O-atom of the OH group in THCZCA and MCZCA is not included in the HOMO.

In order to authenticate the local reactivity of the studied carbazole derivatives, the Mulliken atomic distribution of each one of the atoms (excluding H-atoms) in the neutral molecules have been numerically quantified and presented in Figure 4.18. The partial charges on the atoms have been used severally in previous studies as a reliable quantum chemical tool in unpacking the behaviour of corrosion inhibitors [108].

Optimized structure



THCZCA

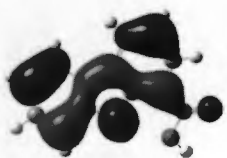


MTHCZ



MCZCA

HOMO



THCZCA

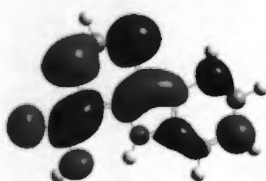


MTHCZ



MCZCA

LUMO



THCZCA

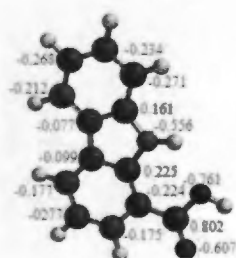


MTHCZ

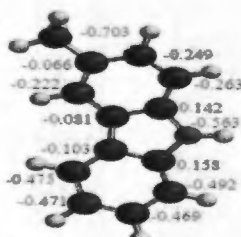


MCZCA

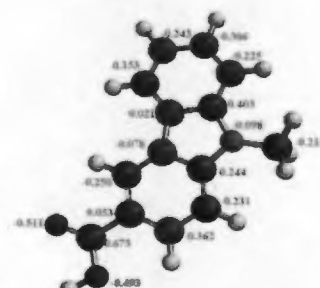
Mulliken atomic charge distribution



THCZCA



MTHCZ



MCZCA

Figure 4.18. Optimized structure, HOMO, LUMO and Mulliken charge distribution (excluding H-atoms) for the studied molecules.

Murulana *et al.* [103] added that a high negative atomic charge on inhibitor molecules enhances their electron donating ability. In line with this construct, it can be concluded that the most reactive centres in the molecules include: for THCZCA, N(1), O(15) and O(16); for

MTHCZ, N(1), C(3), C(4), C(5), C(6) and C(14); for MCZCA, O(15) and O(16). Based on this result, it can be concluded that MTHCZ possesses many active sites for adsorption onto MS surface.

Some other quantum chemical parameters relevant to this study are presented in Table AII-1 (Appendix II) and include the E_{HOMO} , E_{LUMO} , ΔE and ω , etc. According to Khaled [192], E_{HOMO} is usually linked to the electron donating ability of a molecule. A high E_{HOMO} value implies a greater tendency to donate electrons to favourable empty low energy molecular orbitals [193]. In addition, molecules with high E_{HOMO} value will therefore have high likelihood to adsorb onto the MS surface, resulting to improved inhibition efficiency. From the Table AII-1, this would mean that the E_{HOMO} values for the studied CZs follow the order MTHCZ > MCZCA > THCZCA. Based on established certitude regarding these quantum chemical parameters and their relationships to inhibition efficiency as described extensively in Groups I and II, the obtained values of the E_{LUMO} , ΔE , σ , η and ω recommend that THCZCA is the better inhibitor. That is, the order in inhibition efficiency is such that THCZCA > MCZCA > MTHCZ. In this form, trends in inhibition efficiencies for electrochemical and weight loss are fairly corroborated. All the calculated parameters in gas and aqueous phases tally except for MCZCA with an improved dipole moment in aqueous phase.

4.2.8. MD simulations

Figure 4.19 and Table 4.15 show the most consistent adsorption configurations of THCZCA, MTHCZ and MCZCA on Fe(110) surface in the presence of 50 water molecules as well as their corresponding outputs and descriptors, respectively. A close inspection of Figure 4.19 reveals the aspect of molecular structure that supports the idea that it is plausible for the three CZs to adsorb on iron surface in almost flat and parallel orientation on the Fe(110) surface through the following scheme:

(a) Sharing the electrons of nitrogen and oxygen atoms with iron to form coordination bond between Fe-N, Fe-O, and π -electrons interactions of the ring structures of carbazole molecule and iron atom.

These interactions enable the molecules to form coordination bond with iron [109]. From Table 4.15, the maximum values of adsorption and deformation energies were recorded for the Fe(110)/MCZCA system which suggests that MCZCA has the strongest interaction with Fe(110) surface.

Table 4.15 shows also (dE_{ad}/D_{H_2O}) that indicates the energy, in kcal mol^{-1} , of substrate–adsorbate configurations where one of the adsorbate units has been displaced. A close inspection of Table 4.15 shows that the adsorption energies of the inhibitor compounds under consideration follow the trend: $MCZCA > THCZCA > MTHCZ$ which correlates fairly with the experimental inhibition efficiency values. In all the three configurations, higher adsorption energies greater than that of water molecules were recorded.

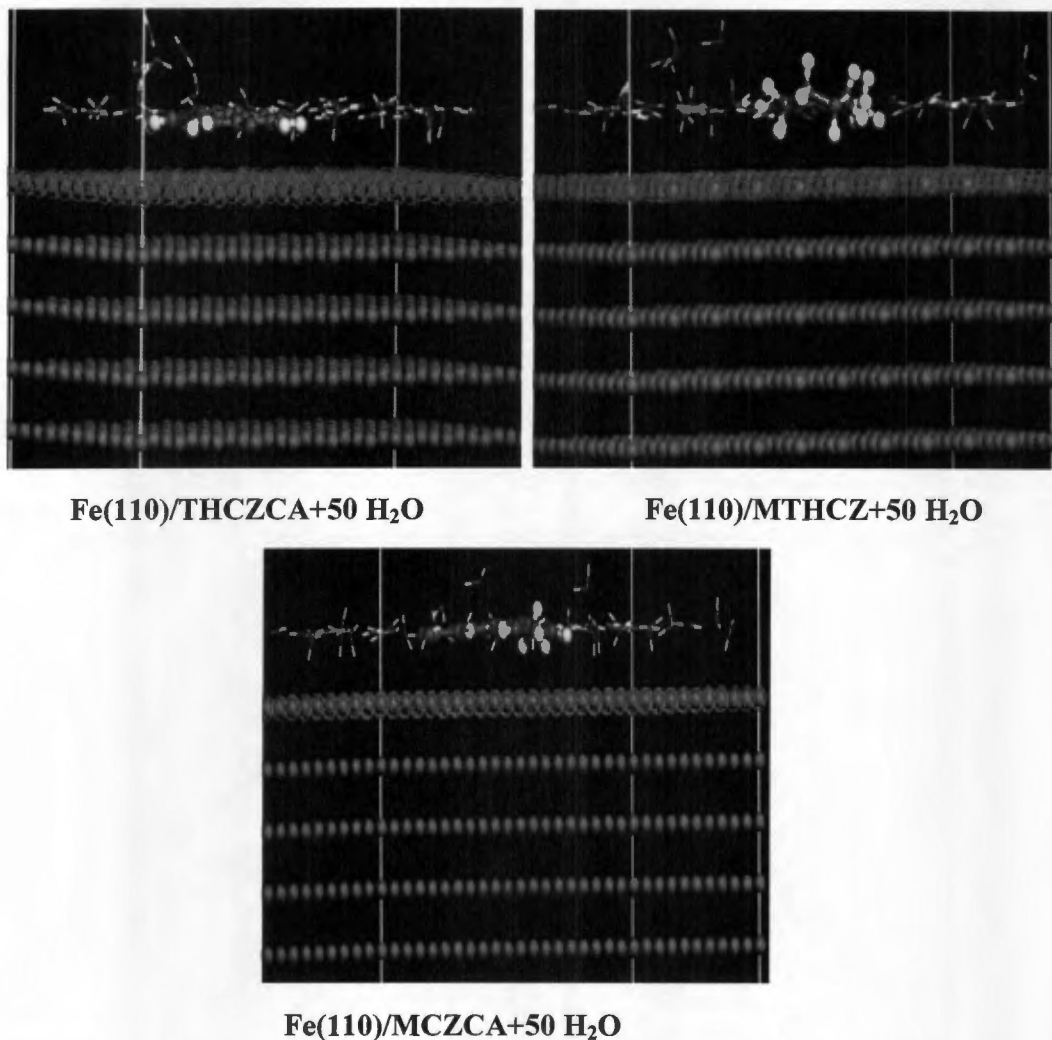


Figure 4.19. Side view of the lowest energy configurations of the Fe(110)/inhibitor systems in the presence of 50 molecules of water.

Table 4.15. Energy parameters (kcal/mol) associated with the adsorption of the inhibitor molecules on Fe(110) in the presence of 50 molecules of water.

System	Adsorption energy	Rigid adsorption energy	Deformation energy	H ₂ O:dE _{ad} /DH ₂ O	Inhibitor: dE _{ad} /dN _i
Fe(110)/ THCZCA+50 H ₂ O	-841.80	-867.95	26.15	-16.45	-135.93
Fe(110)/ MTHCZ+50 H ₂ O	-836.74	-863.29	26.55	-11.19	-109.12
Fe(110)/ MCZCA+50 H ₂ O	-867.75	-892.89	25.14	-13.67	-146.15

This further guarantees the prospect of gradual displacement of water medium from the metal surface leading to appearance of a coherent monolayer which shielded the iron from the devastating effect of aqueous corrosion.

4.2.9. Inhibition activity of the studied inhibitors and carboxyl reactivity

Since the three inhibitors studied in the present work only differ in the presence and positions of the carboxyl and methyl groups, it becomes imperative to explore potential correlations between the trends of inhibition efficiency and the reactivity of methyl and carboxyl groups. The reactivity of carboxyl group is as a result of the electronegativity of oxygen atoms and the resulting polarization of the carbon-oxygen double bond. The results obtained for the $\eta\%$ of the studied inhibitors underpin that the introduction of methyl group markedly reduces the inhibition efficiency of MCZCA.

4.3. GROUP III: DBPCZ and CZPD

GROUP III consists of two carbazole derivatives as shown in Table 3.3. The two differ with the presence of a phenyl ring and aliphatic diol chain attached directly to the N-atom of the carbazole ring. There is also the presence of bromine atoms at either side of the benzene rings in DBPCZ. The effects of these attachments on the adsorption characteristics and anticorrosion properties of these compounds were probed.

4.3.1. Electrochemical studies

4.3.1.1. PDP studies

Tafel plots were acquired for MS in 1 M HCl in the absence and presence of various concentrations of DBPCZ and CZPD and the results are recorded in Figure 4.20. It can be observed that the curves shifted towards lower current density region in the presence of the

inhibitors compared to the blank acid medium. This finding supports the idea that the investigated carbazoles decrease the corrosion current and consequently decrease the corrosion rate. The polarization curves exhibit shifts in potential towards more cathodic regions than the acid blank although the direction of the shift varies with concentrations of the inhibitors. For instance, DBPCZ displays clear cathodic effect and CZPD displays both cathodic and anodic effects with the former dominating at 500-1000 ppm. As a result, it can be inferred that the two inhibitors decrease corrosion rate with increasing concentrations of the inhibitors. Both cathodic and anodic Tafel lines display almost parallel displacements as concentration of the carbazoles increased. This behaviour supports the idea that the release of hydrogen gas is activation-controlled and addition of inhibitors did not remarkably alter the mechanism of the electrochemical process [187].

Tafel parameters acquired from Figure 4.20 are recorded in Table 4.16. The shift in corrosion potential (E_{corr}) in the presence of the inhibitor and the blank altogether is lower than the threshold value of 85 mV for DBPCZ and CZPD. This recommends that the studied compounds are of a mixed-type inhibitor category. Another common feature of DBPCZ and CZPD is the shift in E_{corr} towards more cathodic regions at all the concentrations compared to the blank. A substantial decrease in corrosion current density, I_{corr} was achieved above 500 ppm with a resultant tangible inhibition efficiency recorded for the group. This is supported by the fact that high concentration of inhibitor is often accompanied by increase in both surface coverage and inhibition efficiency.

The $\eta\%$ of DBPCZ and CZPD increases slowly between 300 ppm to 400 ppm. Further substantial increase was recorded at 500 ppm. At 1000 ppm, $\eta\%$ of DBPCZ is at 81 % and that of CZPD stands at 87 %. This suggests that further improvement in $\eta\%$ may be possible beyond 1000 ppm for the two compounds. Based on the maximum value of $\eta\%$ recorded for each compound within the concentration range (300-1000 ppm), it can be adduced that CZPD performed better than DBPCZ.

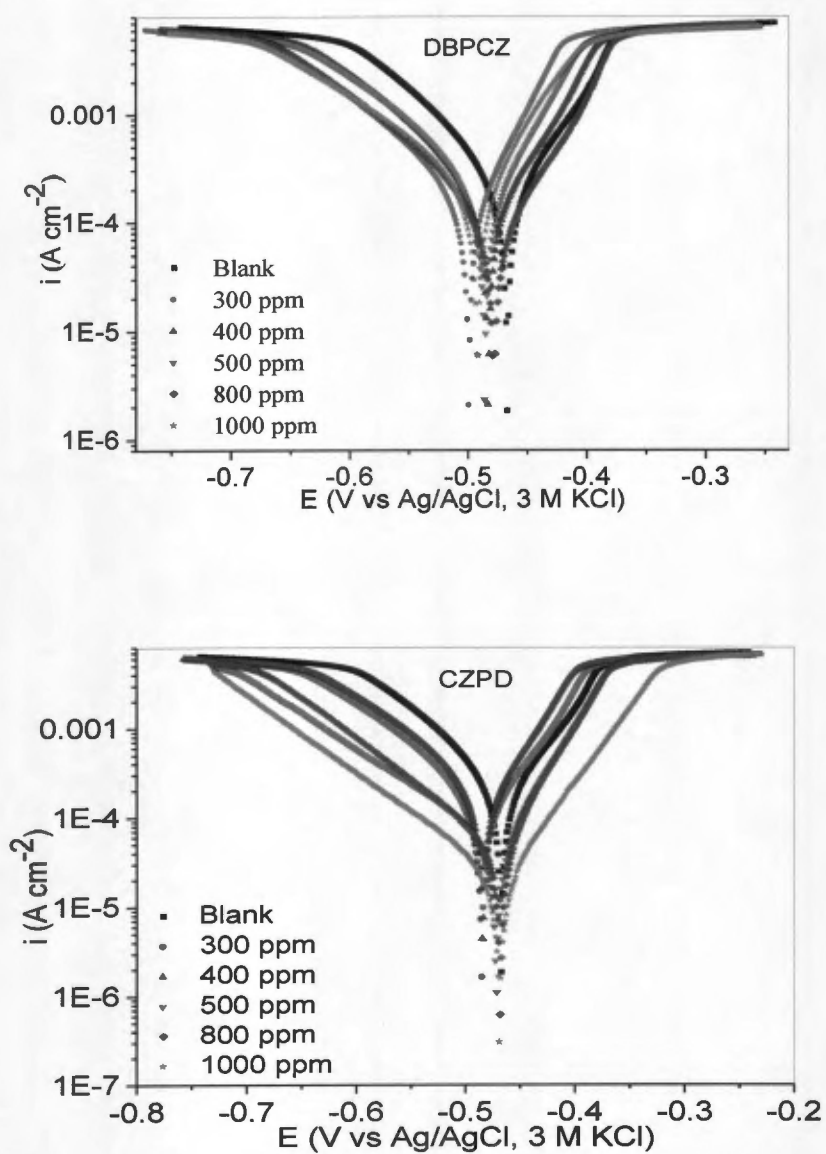


Figure 4.20. Polarization curves for MS in 1 M HCl without and with different concentrations of DBPCZ and CZPD.

Table 4.16. Tafel parameters and percentage inhibition efficiency for MS corrosion in 1 M HCl solution in absence and presence of different concentrations of DBPCZ and CZPD.

Inhibitor	Conc (ppm)	b_a (mV/dec)	b_c (mV/dec)	$-E_{\text{corr}}$ (mV)	i_{corr} ($\mu\text{A cm}^{-2}$)	$\eta\%$
Blank	-	98.93	72.08	452.72	236.22	-
DBPCZ	300	61.32	108.12	485.32	199	16
	400	126.79	74.02	477.75	162	32
	500	49.76	80.97	491.4	119	50
	800	51.65	122.47	461.27	65	73
	1000	56.20	96.06	460.89	45	81
CZPD	300	131.37	84.26	510.94	176	25
	400	116.63	62.22	497.72	168	29
	500	147.30	65.77	471.06	98	58
	800	131.73	62.18	467.63	92	61
	1000	122.44	68.92	468.12	31	87

4.3.1.2. EIS measurements

The Nyquist and Bode plots in Figures 4.21 and 4.22 supply information on the impedance spectra for MS in 1 M HCl in the absence and presence of DBPCZ and CZPD at different concentrations. The impedance behaviour of MS in HCl has remarkably changed following the addition of carbazole into the test solutions. The impedance spectra recorded for the different concentrations of the inhibitors on the other hand, display similar shape at high frequency semicircle with radii hugely dependent on the type of carbazole and its concentration. Consequently the diameter of Nyquist plots increased on increasing the concentration of CZs suggesting strengthening of inhibitive film [73, 188]. The impedance spectra obtained in the present group of CZs clearly show a depressed semicircle with the centre under the real axis with such remarkable feature ascribed to surface roughness and inhomogeneity of solid electrodes [73, 188]. The Bode plots of phase angle against frequency reveal single peak that suggests that the decomposition of MS is marked by single charge transfer process [73, 188]. The observed gradual broadening of phase angle maxima at intermediate frequency in the presence of the studied CZs also connotes surface covering of the MS by the inhibitor molecules.

The relevant electrochemical parameters procured from the fitting of the impedance spectra are presented in Table 4.17. On increasing inhibitor concentration, the charge transfer resistance, R_{ct} increased remarkably for all the CZs. Small R_{ct} values recorded for the two inhibitors especially at low concentrations suggest poor film-forming action. Reasonable $\eta\%$

could only be achieved at 500 ppm. Between 800 ppm to 1000 ppm, the R_{ct} values remain nearly the same with the corresponding $\eta\%$ for DBPCZ. Similar feature can be observed for CZPD between 500 ppm to 800 ppm. However, further tangible increase was recorded at 1000 ppm.

The values of R_s and Y_0 do not follow a definite trend with increasing concentrations of the studied inhibitors. Nevertheless, it can be spotted that the values of the R_s are generally higher than the blank. The high R_s values reassured the relatively low conductivity media in the presence of the inhibitors. The magnitudes of n in general are lower for the inhibitor containing systems than the blank, suggesting that appreciable level of homogeneity of the MS surface was enhanced.

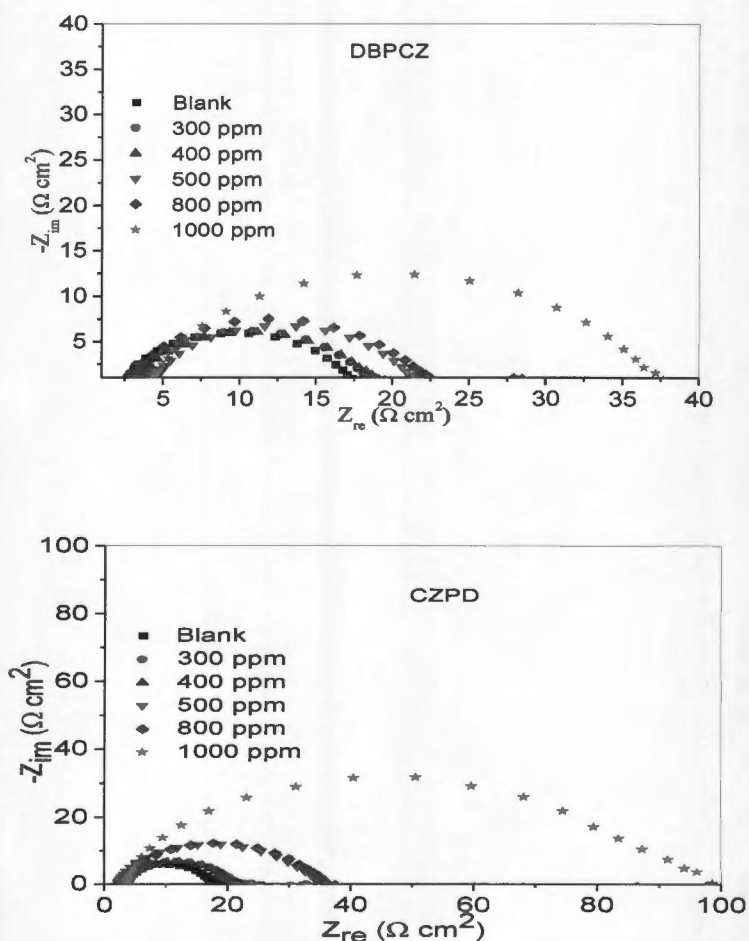


Figure 4.21. Nyquist plots for MS in 1 M HCl without and with different concentrations of DBPCZ and CZPD.

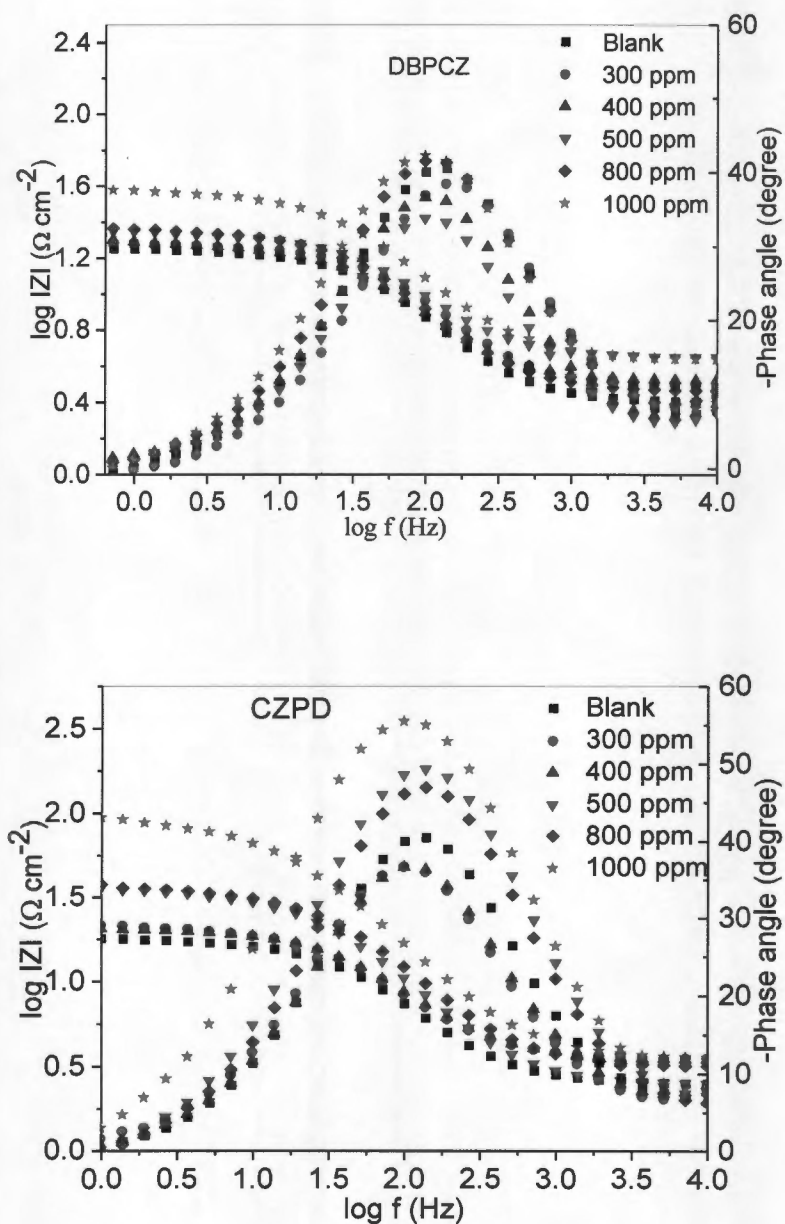


Figure 4.22. Bode plots for MS in 1 M HCl without and with different concentrations of DBPCZ and CZPD.

In the presence of the studied inhibitors at both minimum and maximum concentrations, the linearity of $\log|Z|$ vs $\log f$ plots at intermediate frequencies displayed higher slopes than the blank system as recorded in Table 4.17. The values of the phase angles and slopes taken at intermediate frequencies gradually tend to approach -90 and -1 which is an important feature of pseudo-capacitive behaviour of electrode double layer [73, 188].

Table 4.17. Electrochemical impedance parameters, slopes of the Bode impedance magnitude plots at intermediate frequencies (S) and the maximum phase angles (α) obtained for MS in 1 M HCl in absence and presence of different concentration of DBPCZ and CZPD.

Inhibitor	Conc (ppm)	R_s ($\Omega \text{ cm}^{-2}$)	R_{ct} ($\Omega \text{ cm}^{-2}$)	Y_0 ($\mu\text{S s}^n \text{ cm}^{-2}$)	n	C_{dl}	$\eta\%$	$-S$	$-\alpha$
Blank	-	2.50	16.6	677	0.84	79.96	-	0.30	40.47
DBPCZ	300	4.30	20	815	0.78		17	0.59	33.76
	400	2.77	23	811	0.80		27		
	500	4.21	36	478	0.81		54		
	800	7.05	70	295	0.81		76		
	1000	7.42	81	256	0.82		79		
CZPD	300	4.14	22	497	0.80		24	0.49	36.72
	400	3.19	22	616	0.80		26		
	500	2.48	37	466	0.84		55		
	800	3.15	38	431	0.83		56		
	1000	3.50	109	322	0.82		85		

4.3.2. Adsorption isotherms

The adsorption of DBPCZ, and CZPD have been fitted to various adsorption isotherms. In the end, the Freundlich isotherm gave better fit. The representative adsorption isotherm of the Freundlich for the compounds is presented in Figure 4.23 while the relevant interpretations regarding Freundlich adsorption isotherm are already given in Group I. The plots of the Freundlich isotherm appear linear with R^2 values of almost unity. The thermodynamic parameters for the adsorption process are given in Table 4.18. The values of $\Delta G^\circ_{\text{ads}}$ for the group assert strong chemisorption mechanisms [184, 194-196].

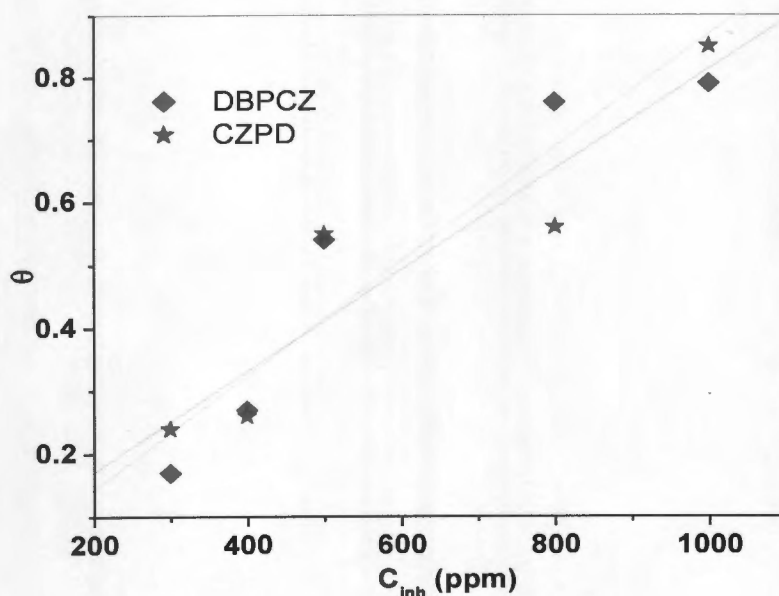


Figure 4.23. Freundlich adsorption isotherms for MS in 1 M HCl containing various concentrations of the studied DBPCZ and CZPD.

Table 4.18. Freundlich parameters for the adsorption of DBPCZ or CZPD on mild steel surface obtained from Tafel parameters at 303 K.

Inhibitor	Slope $\times 10^{-4}$	Intercept	R^2	$K_{ads} (\times 10^6)$	$-\Delta G_{ads}^{\circ}$ (kJ/mol)
DBPCZ	9.09	0.039	0.94	10.2	50.8
CZPD	8.03	0.010	0.93	24.1	52.9

4.3.3. Biocorrosion study (weight-loss measurements)

Figure 4.24 reveals the averaged weight loss after 9 days of incubation of MS coupons in *D. vulgaris* at 37 °C. As already described in Groups I and II, in the absence of the studied CZs, WL data obtained in pure *D. vulgaris* resulted to larger weight loss. The WL in the presence of DBPCZ and CZPD suggested that their addition reasonably reduced MIC by *D. vulgaris* with DBPCZ recording the least WL. The WL values are consistent with the corresponding trend in corrosion rate, C_R , in such a manner that SRB > CZPD > DBPCZ.

The trend in IE%_{WL} (Table 4.19) therefore reaffirms that DBPCZ possesses superior inhibitive action against MS corrosion in *D. vulgaris* dominated environment. However, a comparison of this group with others such as Groups I and II reveals that the present group possesses weaker activities.

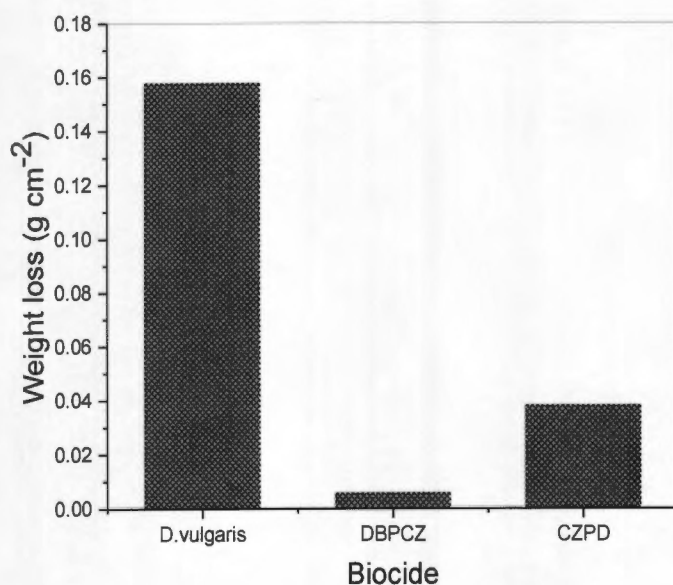


Figure 4.24. Weight loss measurements for MS exposed to SRB cultures after 9 days incubation with or without 100 ppm DBPCZ and CZPD at 310 K.

Table 4.19. The weight loss parameters obtained for MS exposed to SRB cultures after 9 days incubation with or without 100 ppm DBPCZ and CZPD.

Biocide	CR (g.cm ⁻² .d ⁻¹)	IE% _{WL}
<i>D. vulgaris</i>	0.018	-
DBPCZ	0.0057	68.3
CZPD	0.0068	62.2

4.3.4. Surface morphology studies

4.3.4.1. SEM study

Figures 4.25 and 4.26 are SEM micrographs of MS surfaces immersed in 1 M HCl and or SRB culture without and with 100 ppm of DBPCZ and CZPD. As described earlier in Groups I and II, MS surface in 1 M HCl solution reveals extensively corroded and damaged surface ascribed to the free acid corrosion of MS whilst the MS for the SRB control reveals extensive localized pitting corrosion.

The addition of inhibitors in both media reveals MS surfaces with loosely held deposits of the studied inhibitors that protected the surfaces from aggressive attack. This finding supports the idea that the CZs inhibit MS corrosion in 1 M HCl and *D. vulgaris* infested medium by forming a protective film.

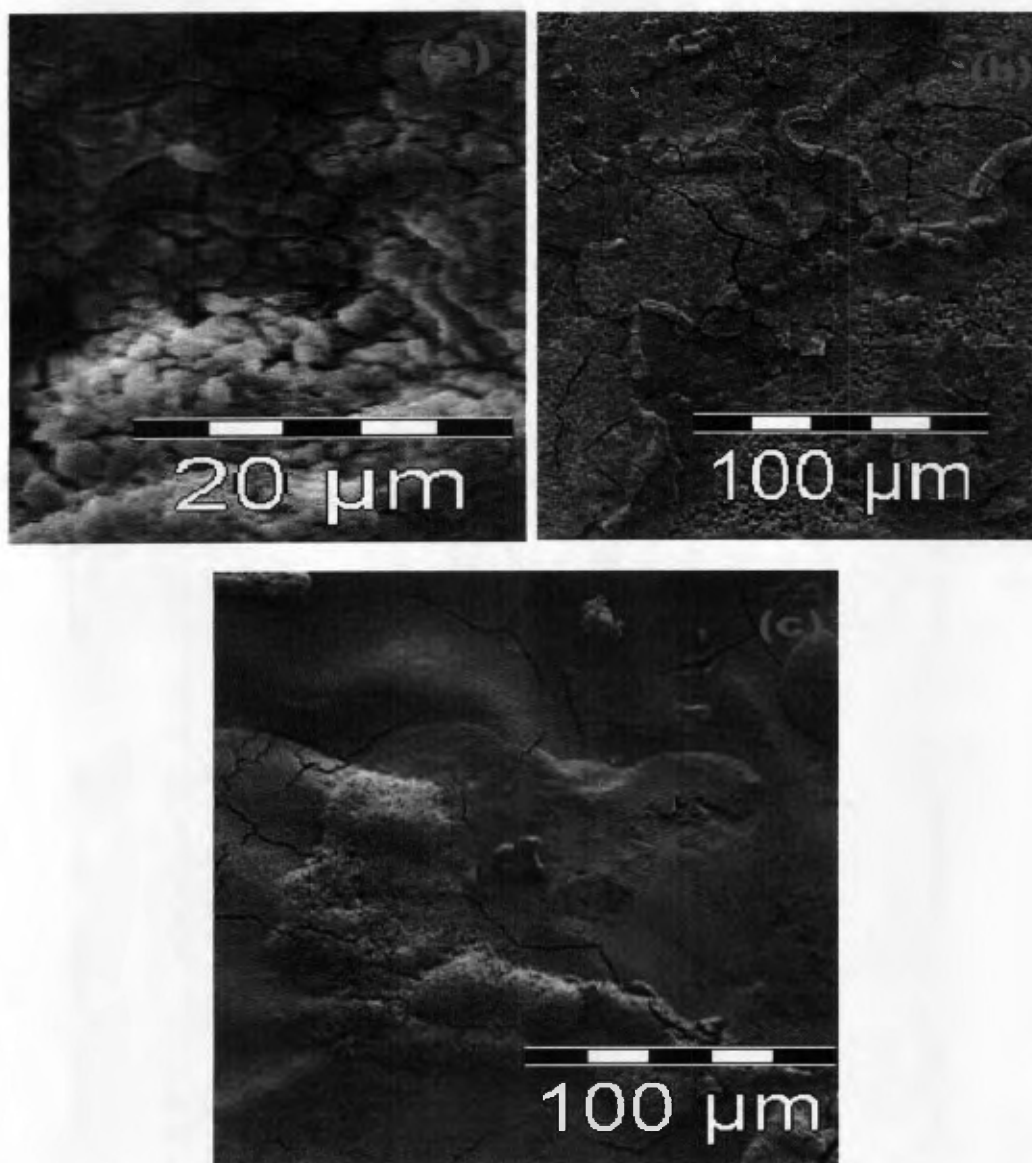


Figure 4.25. SEM images of MS surfaces immersed in 1 M HCl without and with 100 ppm of the studied inhibitors (a) blank (b) DBPCZ (c) CZPD.

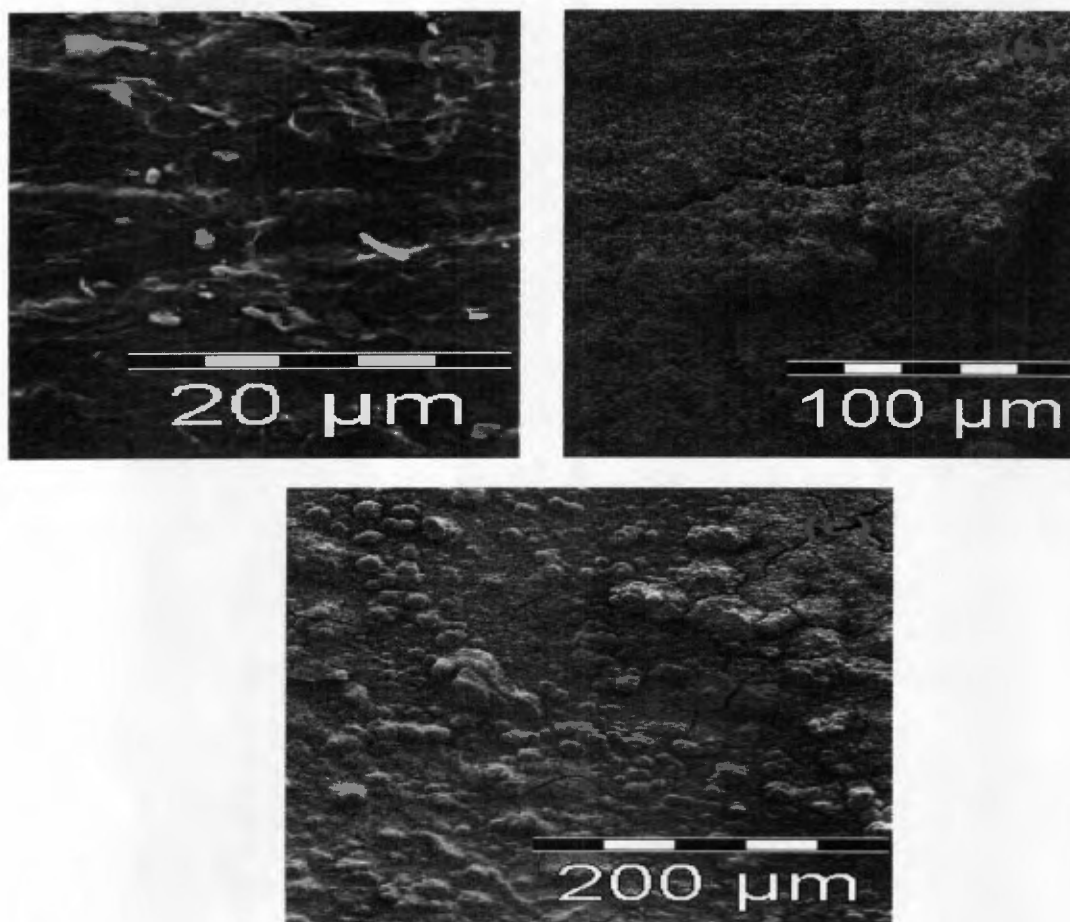


Figure 4.26. SEM images of MS surfaces immersed in SRB culture without and with 100 ppm of the studied inhibitors (a) blank (b) DBPCZ (c) CZPD.

4.3.4.2. EDX study

The results from elemental analysis are shown in Table AIII-1 (Appendix III). Comprehensive description of EDX results can be found in groups I and II. Above all, the deposits found on MS surfaces treated with 100 ppm of inhibitors showed that these aggregates are mainly dominated by carbon, chlorine, iron oxide crystals and traces of other elements such as calcium, sulphur, phosphorous and aluminium.

4.3.4.3. FTIR spectroscopy

The FTIR spectra of DBPCZ and CZPD are presented in Figure AIII-1 (Appendix III). The spectra of the pure DBPCZ and CZPD molecules display a group of unique bands between 500 cm^{-1} to 1725 cm^{-1} similar to Groups I and II. Detailed interpretations of these bands have been given in Groups I and II.

However, these peaks after MS immersion in 1 M HCl were found to weaken in intensity. There is in addition, the appearance of a broad peak for DBPCZ+MS+1 M HCl, CZPD and CZPD+MS+1 M HCl systems between 3300-3420 cm^{-1} due to O-H functional group in CZPD moiety and solution effect on DBPCZ+MS+1 M HCl system. The presence of O-H functional group ensured the adhesion of the inhibitor molecules on MS surfaces [197]. DBPCZ+MS+SRB and CZPD+MS+SRB systems on the other hand display a distinct broad band at 1000 cm^{-1} characteristic feature of Fe-S bond.

4.3.5. Quantum chemical calculations

Having discussed extensively the interrelationships of similar quantum chemical indices to corrosion inhibition in Groups I and II, herein, effort has been made to highlight their observable trends on present group of carbazoles. The optimized molecular structures, HOMO and LUMO electronic density distributions of the neutral species and electron density distributions for the electrophilic Fukui function (f^-) are given in Figure 4.27. Their applicable quantum chemical parameters in the gas phase are listed in Table AIII-2 (Appendix III).

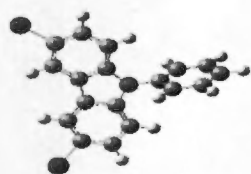
A close observation of Figure 4.27 reveals that both HOMO and LUMO of DBPCZ and CZPD are delocalized over the entire aromatic carbazole rings in each molecule with little or no involvement of the phenyl in DBPCZ and the hydroxyl groups (-OH4 and -OH5) in CZPD. In addition, the bromine atoms (Br20 and Br21) of DBPCZ are poor centres for LUMO interactions. The electron density distributions of the f^- disclosed that the N-atom of the carbazole ring and the C=C π -electrons centres of the fused aromatic rings are the most susceptible sites for electrophilic attacks in both molecules. The substituent Br atoms in DBPCZ and the O-atom of the OH group in CZPD respectively are also probable sites for electrophilic attacks.

Based on the obtained quantum chemical parameters and their respective relationships to corrosion inhibition, the following insights can be made; that is, the values of the quantum chemical parameters in relation to their characteristic effects that have already been described in Groups I and II compounds are as follows:

- ✚ HOMO: CZPD > DBPCZ.
- ✚ LUMO, ΔE , higher dipole moment, MP, MV and log P, σ , η , μ and higher ω : DBPCZ > CZPD.

That is, the high HOMO value favours CZPD over DBPCZ, whereas other quantum chemical parameters favour CZPD. The former corroborates inhibition efficiency obtained from electrochemical method whereas the latter corroborates WL inhibition efficiency.

Optimized structure

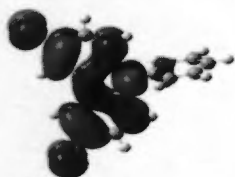


DBPCZ

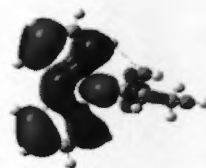


CZPD

HOMO

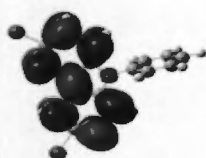


DBPCZ

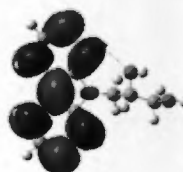


CZPD

LUMO

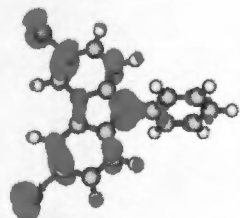


DBPCZ

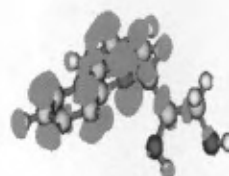


CZPD

Electrophilic Fukui indices (f^-)



DBPCZ



CZPD

Figure 4.27. Optimized structure, HOMO, LUMO and electrophilic Fukui function (f^-) for the studied molecules (at isosurface value =0.002).

4.3.6. Molecular dynamics simulation

The equilibrium configurations of the simulated systems are shown in Figure 4.28, while the relevant energy parameters of the systems are listed in Table 4.20. The results recorded in Figure 4.28 revealed that the moieties containing the aromatic rings and heteroatoms in DBPCZ molecules adsorbed on Fe(110) surface in almost flat orientation whereas that of CZPD is slightly slant. This finding alongside the highest magnitudes of adsorption and deformation energies recorded for the Fe(110)/DBPCZ system ensure optimum interactions of the inhibitor molecules with the metallic surface.

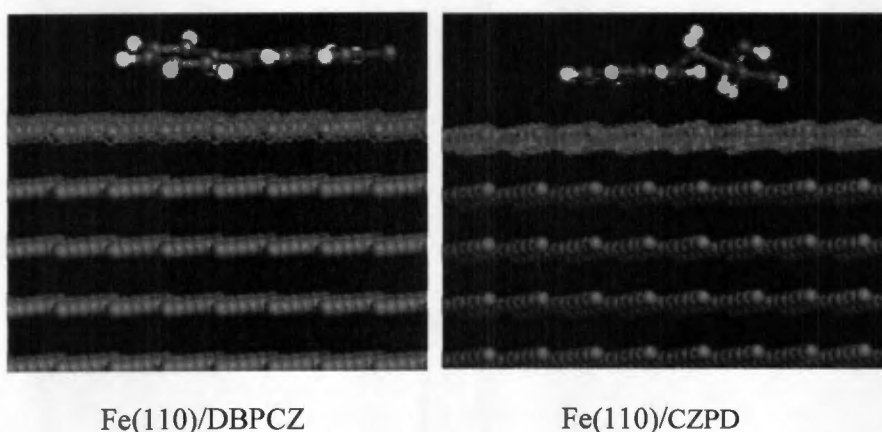


Figure 4.28. The most stable configurations for the adsorption of DBPCZ and CZPD on Fe(110)/inhibitor systems.

Table 4.20. Energy parameters (kcal/mol) affiliated to the adsorption of the inhibitor molecules on Fe(110).

System	Adsorption energy	Rigid adsorption energy	Deformation energy
Fe(110)/CZPD	-119.85	-121.04	1.63
Fe(110)/DBPCZ	-141.24	-148.24	7.00

4.4. GROUP IV: HTHCZ, CZAA and DMCZ

The group IV consists of three compounds with a common carbazole backbone as listed in Table 3.4 and differ with two methyl chains attached to positions 3 and 6 of the benzene ring in DMCZ; a hydroxyl and amide groups at positions 14 and 15 in HTHCZ and a carboxyl group in CZAA. Understanding the effect of these substituents on MS corrosion in 1

M HCl and two species of corrosive SRBs (*D. vulgaris* and *D. multivorans*) was made possible by comparing their adsorption and anticorrosion behaviours.

On the other hand, CZAA and HTHCZ share some similarity offered by the presence of a hydroxyl group attached to positions 14 and 15 respectively.

4.4.1. Electrochemical studies

4.4.1.1. PDP studies

The polarization curves for MS in 1 M HCl in the absence and presence of different concentrations of HTHCZ, CZAA and DMCZ are presented in Figure 4.29. The electrochemical corrosion parameters and inhibition efficiencies are listed in Table 4.21. It is evident from the polarization curves that the increase in the inhibitor concentrations of HTHCZ, CZAA and DMCZ reduces the corrosion current density, I_{corr} . The curves clearly exhibit dissimilar patterns. In relation to the Tafel curve for the blank system, the curves for HTHCZ appear at more apparent cathodic points at lower concentrations (300-500 ppm), after which there is a more obvious anodic and cathodic shift at higher concentrations (800 to 1000 ppm). The Tafel curves for CZAA and DMCZ however appear generally at more cathodic potentials than anodic at 800 to 1000 ppm whereas there is little or no shift in anodic potentials for both at lower concentrations. These revelations and the shift in E_{corr} upon addition of the studied inhibitors when compared to the blank with less than 85 mV evince that the studied carbazoles act as mixed-type inhibitors [73, 188]. In general, the more pronounced effect on inhibition efficiency observed at high concentrations of inhibitors support the idea that the geometric blocking of the active sites on the MS surface was successful.

The maximum shift of approximately 44 mV obtained for the inhibited systems imply that the addition of the studied inhibitors does not, or, perhaps slightly perturbed the MS electrode surface. The values of the Tafel slopes, b_a and b_c appear to fluctuate with concentrations of the inhibitors, however without a straightforward precise trend. A careful study of the effect of concentrations of the inhibitors on the Tafel slope values reveals more apparent variation for b_c than b_a . These findings suggest that the inhibitive strengths of the studied compounds are more prominent on the cathodic reaction than its anodic counterpart.

The values of the I_{corr} diminish with increasing concentrations of the inhibitors with its attendant increase in $\eta\%$.

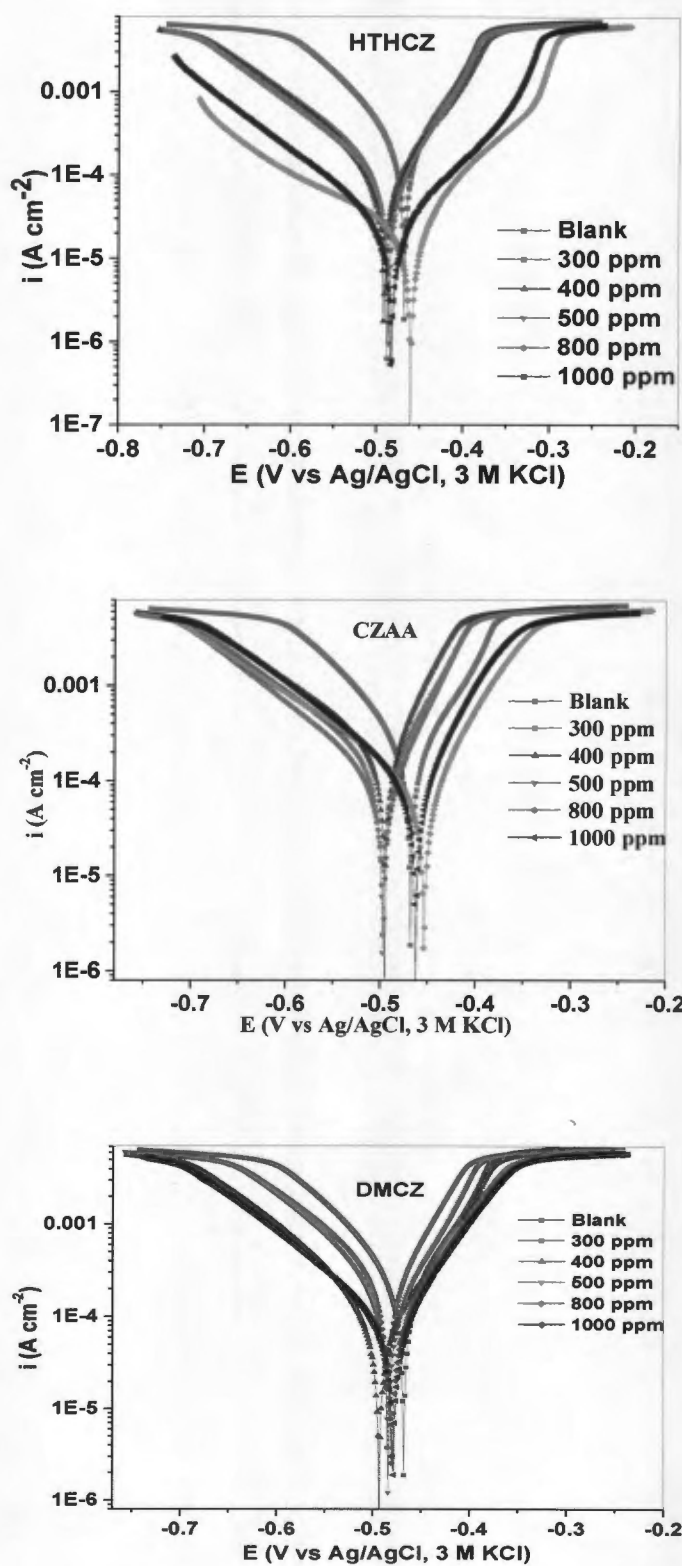


Figure 4.29. Polarization curves for MS in absence and presence of different concentrations of HTHCZ, CZAA and DMCZ.

Table 4.21. Tafel parameters and percentage inhibition efficiency for MS in 1 M HCl solution in absence and presence of different concentrations of HTHCZ, CZAA and DMCZ.

Inhibitor	Conc (ppm)	b_a (mV/dec)	b_c (mV/dec)	$-E_{corr}$ (mV)	i_{corr} ($\mu A\ cm^{-2}$)	$\eta\%$
Blank	-	98.93	72.08	452.72	236	-
HTHCZ	300	151.21	85.79	487.19	165	30
	400	143.40	85.47	491.60	140	41
	500	139.30	71.79	485.16	112	52
	800	76.14	164.41	459.57	17	93
	1000	111.65	77.36	482.43	13	94
CZAA	300	147.04	67.03	495.63	157	33
	400	50.61	104.85	494.73	148	37
	500	133.27	63.02	496.43	144	39
	800	58.08	142.02	452.63	76	68
	1000	50.24	79.52	461.82	54	77
DMCZ	300	56.28	107.78	483.89	197	16
	400	140.37	93.09	493.06	183	22
	500	107.20	67.10	483.24	167	30
	800	61.16	90.21	479.71	61	74
	1000	65.49	93.53	478.47	59	75

This recommends that the studied compounds retard MS corrosion in the acid solution via the formation of adsorbed film of the inhibitor molecules on the steel surface. The $\eta\%$ for HTHCZ increases with increasing concentration of the inhibitor from 30 % at 300 ppm up to 93 % at 800 ppm. At 800 ppm, further increment in concentration could not yield any significant difference in the value of $\eta\%$.

The $\eta\%$ for CZAA increases from 33 % at 300 ppm to 77 % at 1000 ppm. The values of $\eta\%$ between 300 ppm to 500 ppm seem very close. It is apparent that appreciable increase in $\eta\%$ can be achieved at 1000 ppm and even beyond. The $\eta\%$ for DMCZ starts with the lowest $\eta\%$ at 300 ppm and shows no significant improvement until at 800 ppm. At 1000 ppm, no outstanding increase in $\eta\%$ could be achieved.

The general trend in performance of these inhibitors adjudged from the values of $\eta\%$ within the concentration range 800 ppm to 1000 ppm in this work is such that HTHCZ > CZAA > DMCZ.

4.4.1.2. EIS measurements

Figure 4.30 provides details of the Nyquist and Bode plots for HTHCZ whilst those of the remaining two are presented in Figures AIV-2 and AIV-3 (Appendix IV).

The Nyquist plot for HTHCZ is marked by distinctly larger diameter compared to CZAA and DMCZ. Moreover, the diameter of the Nyquist semicircles was found to increase with increasing inhibitor concentration in all the three compounds. This improvement supports the strengthening of inhibitive film on MS surface. In addition, the Nyquist plots obtained are generally larger than the blank. A single depressed semicircles corresponding to one time constant in the Bode plots was obtained proving that the dissolution of MS electrode in the investigated electrolytes is marked by a single charge transfer mechanism.

More so, the formation of the protective film of the inhibitor molecules was confirmed in the broadening of single time constant maximum in the Bode phase plots of the inhibitor-containing systems.

Parameters on the electrochemical reactions that were procured from the fitting and simulation of the impedance spectra are listed in Table 4.22. The values of R_s and Y_0 do not form a definite trend with increasing concentration of the studied inhibitors. However, it can be seen that the values of R_s are generally higher than the blank except for HTHCZ at 1000 ppm. The high R_s values confirm the relatively low conductivity media in the presence of the inhibitors.

The R_{ct} values increase with increasing concentrations with resultant increase in $\eta\%$ values. HTHCZ attained a maximum value at 800 ppm after which further increase in concentration did not reveal noticeable improvement in the value of R_{ct} . CZAA and DMCZ could only record perceptible improvement in $\eta\%$ values at 800 ppm. Above all, the trend of the values of $\eta\%$ recorded from the EIS is similar to that of the Tafel analyses. The magnitudes of n are predominantly lower for the inhibitor containing systems implying higher degree of homogeneity of the MS surface than the blank.

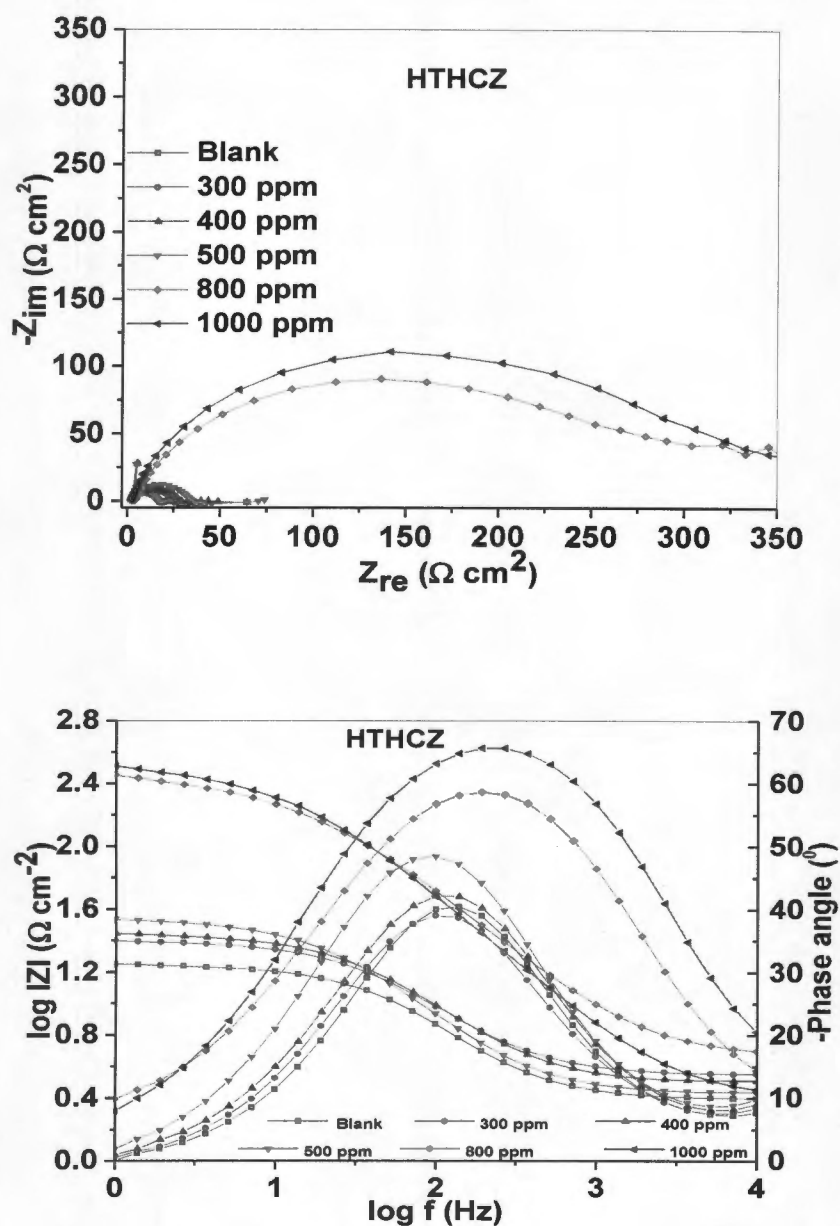


Figure 4.30. Nyquist and Bode plots for MS in 1 M HCl without and with different concentrations of HTHCZ.

The values of α and S recorded for the studied compounds at minimum and maximum concentrations recommend pseudo capacitive behaviour and verify the formation of adsorbed film of the inhibitors on the MS surface that subsequently protected the surface from direct impact of the acid.

Table 4.22. Electrochemical impedance parameters, minimum and maximum slopes (S) of the Bode impedance magnitude plots at intermediate frequencies and the corresponding maximum phase angles (α) obtained for MS in 1 M HCl in absence and presence of different concentration of HTHCZ, CZAA and DMCZ.

Inhibitor	Conc (ppm)	R_s ($\Omega \text{ cm}^{-2}$)	R_{ct} ($\Omega \text{ cm}^{-2}$)	Y_0 ($\mu\text{S s}^n \text{ cm}^{-2}$)	n	$\eta\%$	$-S$	$-\alpha$
Blank	-	2.50	16.6	677	0.84	-	0.30	40.47
HTHCZ	300	3.48	23	632	0.81	29	0.40	39.07
	400	3.10	28	656	0.80	40		
	500	2.65	35	627	0.83	53		
	800	4.36	351	156	0.76	95		
	1000	2.45	391	115	0.81	96	0.53	65.67
CZAA	300	3.50	25	657	0.78	32	0.46	38.03
	400	3.95	25	434	0.80	33		
	500	4.19	26	536	0.76	37		
	800	4.64	50	300	0.83	67		
	1000	7.02	78	309	0.80	79	0.66	44.09
DMCZ	300	4.56	20	888	0.77	17	0.44	32.21
	400	5.09	20	706	0.78	18		
	500	3.92	23	998	0.77	27		
	800	6.49	63	336	0.78	74		
	1000	8.13	69	482	0.72	76	0.52	54.58

4.4.2. Adsorption isotherms

The adsorption parameters of HTHCZ, CZAA, and DMCZ were fitted to series of adsorption isotherms with the Freundlich isotherm being preferred. The representative adsorption isotherm of the Freundlich for the compounds is shown in Figure 4.31 whilst the relevant interpretations relating to Freundlich adsorption isotherm are already given in Group I. The plots of the Freundlich isotherm appear linear with R^2 values of almost unity. The parameters on the thermodynamic adsorption process are given in Table 4.23. The values of $\Delta G^\circ_{\text{ads}}$ for the group suggest strong chemisorption mechanisms [186, 194-196].

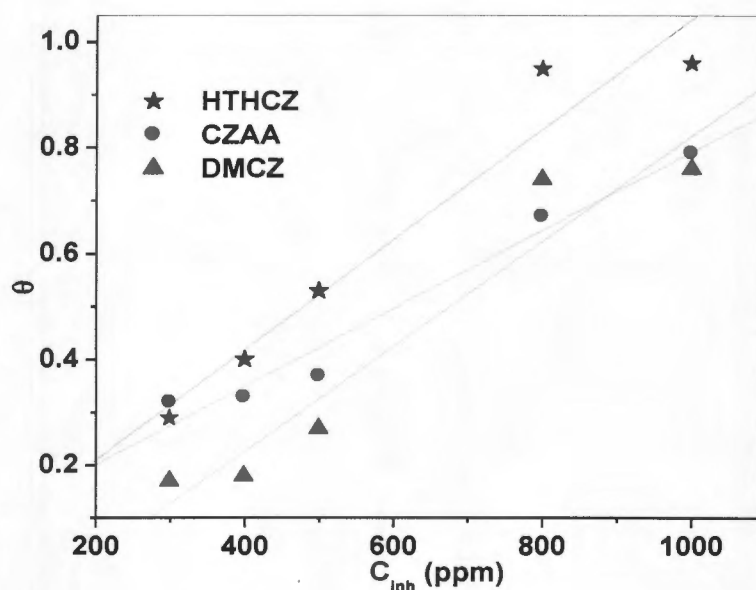


Figure 4.31. Freundlich adsorption isotherm plots of for mild steel in the presence of HTHCZ, CZAA and DMCZ.

Table 4.23. Freundlich parameters for the adsorption of CZs on mild steel surface obtained from EIS parameters at 303 K.

Inhibitor	Slope	Intercept	R^2	$K_{ads} (x10^6)$	$-\Delta G^{\circ}_{ads}$ (kJ/mol)
HTHCZ	0.001	0.001	0.97	229	58.6
CZAA	7.382×10^{-4}	0.053	0.98	4247	66.0
DMCZ	9.941×10^{-4}	0.172	0.97	1134	62.6

4.4.3. Biocorrosion study (weight-loss measurements)

Figure 4.32 reveals the averaged weight loss after 9 days of incubation of MS coupons in *D. vulgaris* and *D. multivorans* at 37 °C. *Desulfococcus multivorans* (*D. multivorans*) is another specie of SRBs recruited for the present group. Comparing the WL values obtained in pure *D. vulgaris* and *D. multivorans* shows that the latter resulted to a more significant weight loss. In the presence of the studied CZs, their inhibitive actions varied. For instance, HTHCZ proved to be the most efficient inhibitor in the presence of both SRBs than CZAA and DMCZ. That is, the presence of HTHCZ reasonably reduced MIC by *D. vulgaris* and *D. multivorans*. This was later reaffirmed from the WL parameters of Table 4.24. In *D. multivorans* medium, CZAA revealed stronger inhibitory action than in *D. vulgaris*.

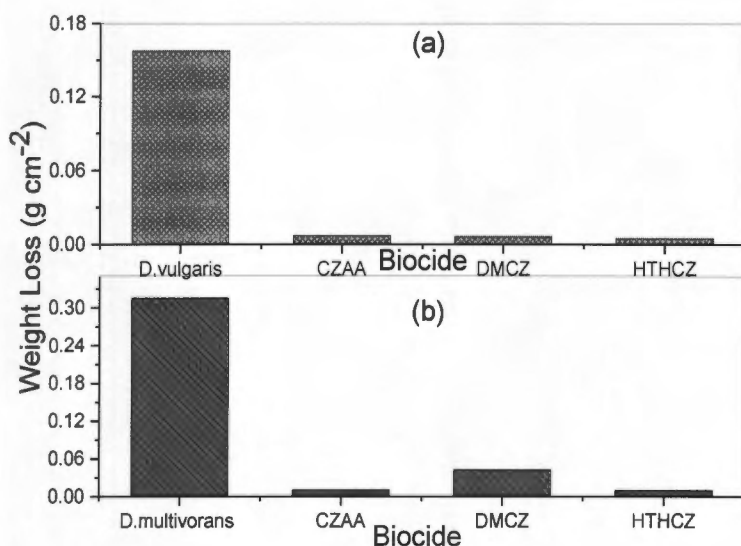


Figure 4.32. Weight loss measurements for MS exposed to SRB cultures after 9 days incubation with or without 100 ppm carbazoles at 310 K (a) In *D. vulgaris* (b) In *D. multivorans*.

Table 4.24. The weight loss parameters obtained for MS exposed to SRB cultures after 9 days incubation with or without 100 ppm CZs.

Biocide	CR (g.cm ⁻² .d ⁻¹)	IE% _{WL}
<i>D. vulgaris</i>		
<i>D. vulgaris</i>	0.018	-
CZAA	0.007	61.1
DMCZ	0.0066	63.3
HTHCZ	0.005	72.2
<i>D. multivorans</i>		
<i>D. multivorans</i>	0.3152	-
CZAA	0.0101	96.8
DMCZ	0.042	86.7
HTHCZ	0.0098	96.9

4.4.4. Surface morphology studies

4.4.4.1. SEM study

Figures 4.33, 4.34, and 4.35 are SEM micrographs of MS surfaces immersed in 1 M HCl, *D. vulgaris* and *D. multivorans* culture medium without and with 100 ppm of CZAA. The remaining images of DMCZ and HTHCZ in different medium are shown in Appendix AIV as Figures AIV-4, AIV-5 and AIV-6. In order to avoid repeating most of the

observations given in Groups I and II, certain highlights of the noticeable changes between MS coupons inoculated with *D. vulgaris* and *D. multivorans* culture medium are hereby discussed. There is evidence to support the formation of protective films of the inhibitors in the presence of 1 M HCl.

In both the SRB controls however, there is observable pitting corrosion, with *D. multivorans* blank recording the highest. This finding corroborates the WL data. In the presence of 100 ppm of the studied compounds, loosely-held carbonaceous layers were found on the surfaces of MS except for HTHCZ in *D. vulgaris* medium that reveals clearer surface with sparsely distributed Fe_2O_3 crystals.

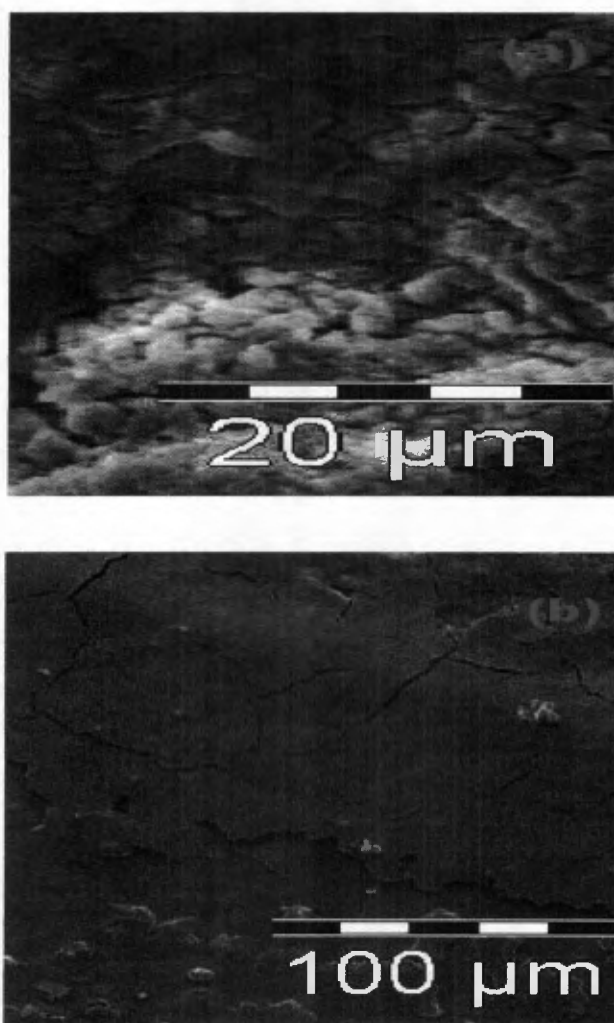


Figure 4.33. SEM images of MS surfaces immersed in 1 M HCl without and with 100 ppm of the studied inhibitors (a) blank (b) CZAA.

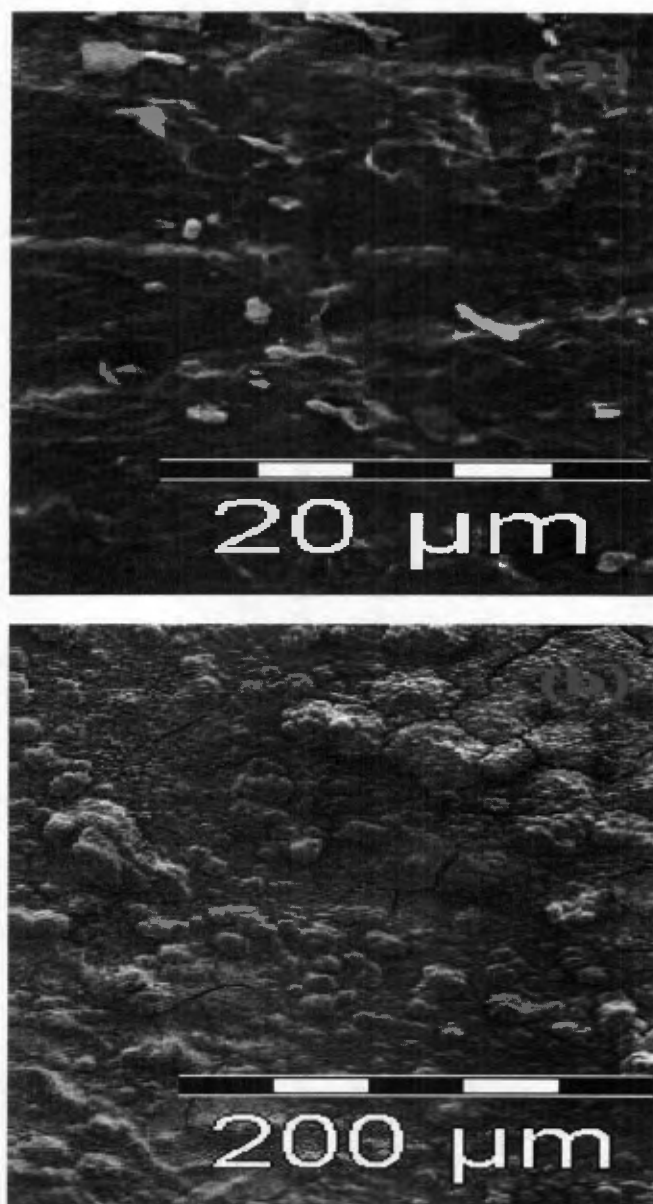


Figure 4.34. SEM images of MS surfaces immersed in *D. vulgaris* culture without and with 100 ppm of the studied inhibitors (a) blank (b) CZAA.

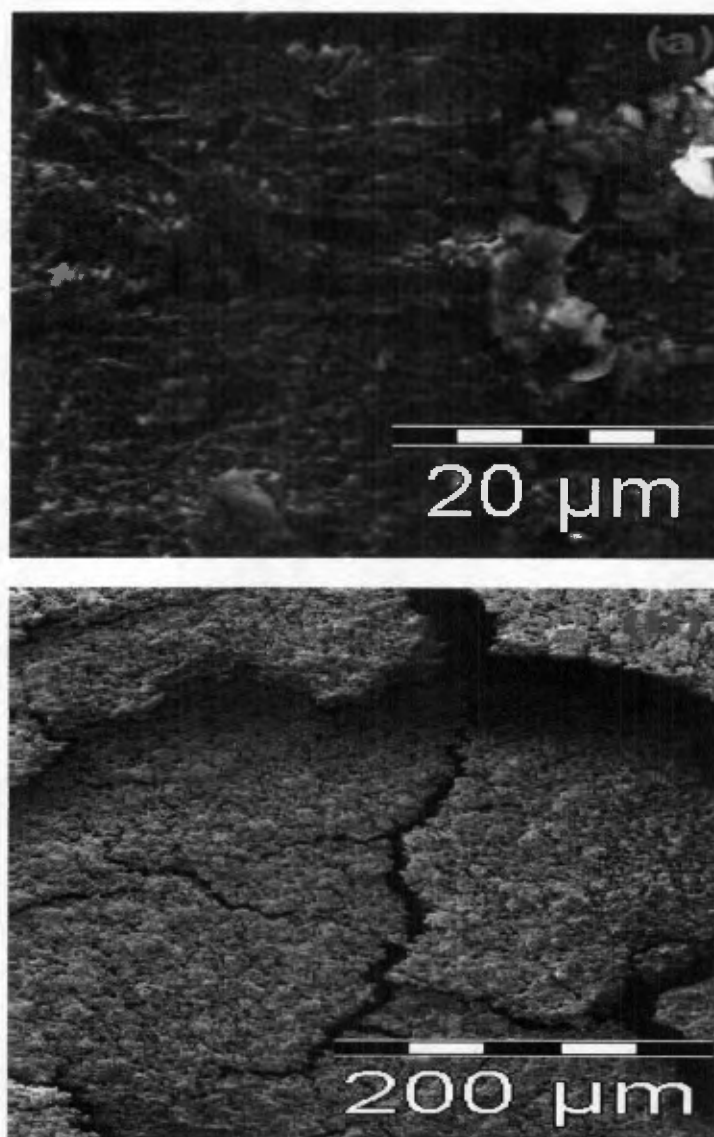


Figure 4.35. SEM images of MS surfaces immersed in *D. multivorans* culture without and with 100 ppm of the studied inhibitors (a) blank (b) CZAA.

4.4.4.2. EDX study

Table 4.25 is the list of percentage atomic contents of elements obtained from EDX spectra with or without 100 ppm of inhibitors in various studied media. Quantitative EDX analysis showed that these aggregates are hugely dominated by carbon-based materials and oxide films. The presence of phosphorous was confirmed for all MS exposed to SRB cultures whereas steel coupons immersed in 1 M HCl revealed varying percentage weights of chloride-based materials.

Table 4.25. EDX elemental constituents (in weight %) of mild steel surface retrieved from the acidic and SRB corrosive media without and with 100 ppm of the inhibitors.

Inhibitors	C	Al	Mg	Na	P	Cl	S	Ca	Mn	Fe	O
Acidic media											
1 M HCl Blank	6.86	-	-	-	-	34.6	-	-	-	34.55	23.99
CZAA	6.38	-	-	-	-	4.13	-	-	-	56.34	33.15
DMCZ	6.36	-	-	-	-	8.51	-	-	-	53	32.13
HTHCZ	8.59	-	-	-	-	25.74	-	-	-	33.26	32.41
<i>D. vulgaris</i> Culture media											
<i>D. vulgaris</i> Blank	12.83	0.1	-	-	0.77	-	0.21	0.47	0.15	76.57	8.9
CZAA	15.17	-	-	-	-	-	-	-	-	34.53	50.3
DMCZ	12.34	-	-	0.12	5.03	-	-	-	-	33.49	49.01
HTHCZ	5.2	0.06	-	-	0.13	-	-	-	-	62.61	32
<i>D. multivorans</i> Culture media											
<i>D. multivorans</i> Blank	7.7	0.1	-	-	0.08	-	0.2	-	-	89.93	1.99
CZAA	8.25	0.11	-	-	1.84	-	-	0.11	0.3	50.38	39.01
DMCZ	10.95	-	0.2	-	5.6	-	-	-	-	36.32	46.94
HTHCZ	11.58	0.14	0.27	-	1.76	-	-	0.61	0.16	40.23	45.24

4.4.4.3. FTIR spectroscopy

The IR spectra of pure CZAA, DMCZ and HTHCZ molecules alongside their corresponding powdery products in 1 M HCl, *D. vulgaris* and *D. multivorans* media are presented in Figure AIV-7 (Appendix IV).

The spectra of the pure CZAA, DMCZ and HTHCZ molecules display a group of unique bands between 500 cm^{-1} to 1725 cm^{-1} equivalent to Groups I, II and III. Rigorous interpretations of these bands have been given in Groups I and II. In addition, DMCZ molecule shows characteristic absorption band at 3417 cm^{-1} due to N-H group whereas HTHCZ shows group of bands at 3320 cm^{-1} and 3460 cm^{-1} due to NH_2 and O-H groups respectively [198].

The peak shift from 1626 to 1600 cm^{-1} observed for DMCZ+MS+1 M HCl and HTHCZ+MS+1 M HCl may be due to the formation of MS--Inh complex. In addition, broad band at 3380 cm^{-1} observed for both systems can be attributed to the presence of a superficial adsorbed water of an O-H group from the test solution [13].

In the presence of *D. vulgaris* medium, broad bands can be noticed except for the CZAA+MS+ *D. vulgaris* system that appears slightly broad.

The IR spectra of products after incubation with *D. multivorans* show medium absorption bands with reduced intensity between 540 cm^{-1} to 1680 cm^{-1} that suggest an improved formation of MS--Inh complex.

4.4.5. Quantum chemical calculations

Figure 4.36 shows the optimized structure, HOMO, LUMO and Mulliken charge distribution for CZAA, DMCZ and HTHCZ molecules. Their associated quantum chemical parameters in the gas phase are presented in Table 4.26.

In addition to the similar delocalized HOMO and LUMO observed in previous groups, there is also involvement of the O-atom (OH17) in HTHCZ HOMO-LUMO interaction. The -NH₂ group attached to the C14 atom in HTHCZ is not involved in HOMO distribution. The HOMO and LUMO of DMCZ is also slightly extended to the methyl alkyl chains attached to the C3 and C6 atoms of carbazole ring. Both the O-atoms attached to the C14 atom in CZAA are not involved in the HOMO-LUMO interaction. The Mulliken atomic distribution revealed the preferred sites in the neutral molecules with electron donating ability. The following sites with -0.350 charges or more are selected:

CZAA: C4, C11, C14, O16 and O17

DMCZ: NH1, C4, C6, C10, C12 and C15

HTHCZ: C13, N15 and NH₂16

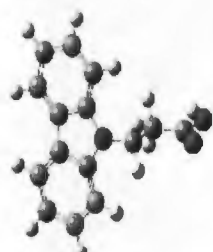
From Table 4.26, the following insights can be made in relation to the relevance of the recorded quantum chemical parameters to their respective favoured inhibitors:

- ✚ HOMO and log P: DMCZ
- ✚ Highest dipole moment and MV: CZAA
- ✚ LUMO, ΔE , σ , η , μ and highest ω : HTHCZ.

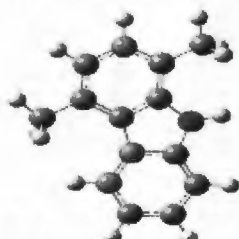
Hydrophobicity, log P is the measure of the solubility of inhibitor molecule. A high log P value connotes reduced solubility in water which from corrosion studies point of view implies reduced probability of formation of the oxide/hydroxide layer that marks corroded surface [199].

Consequently the trend in inhibition efficiency is such that HTHCZ > CZAA > DMCZ, which suggests that HTHCZ is a better corrosion inhibitor. This trend undoubtedly corroborate electrochemical and weight loss inhibition efficiencies.

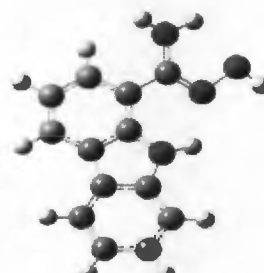
Optimized structure



CZAA



DMCZ



HTHCZ

HOMO



CZAA

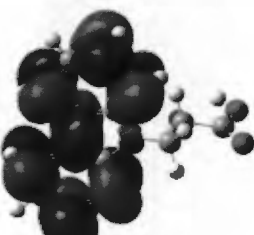


DMCZ

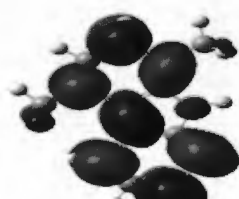


HTHCZ

LUMO



CZAA

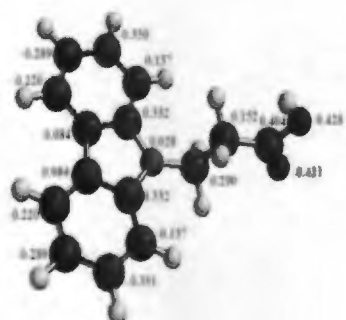


DMCZ

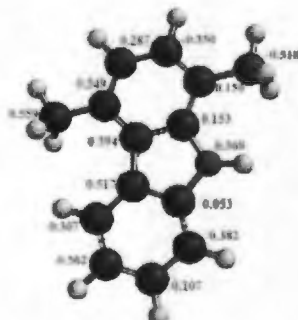


HTHCZ

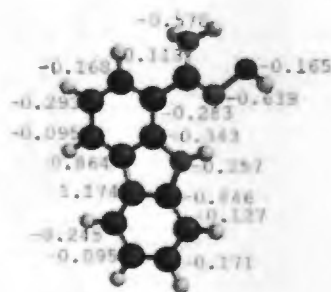
Mulliken atomic charge distribution



CZAA



DMCZ



HTHCZ

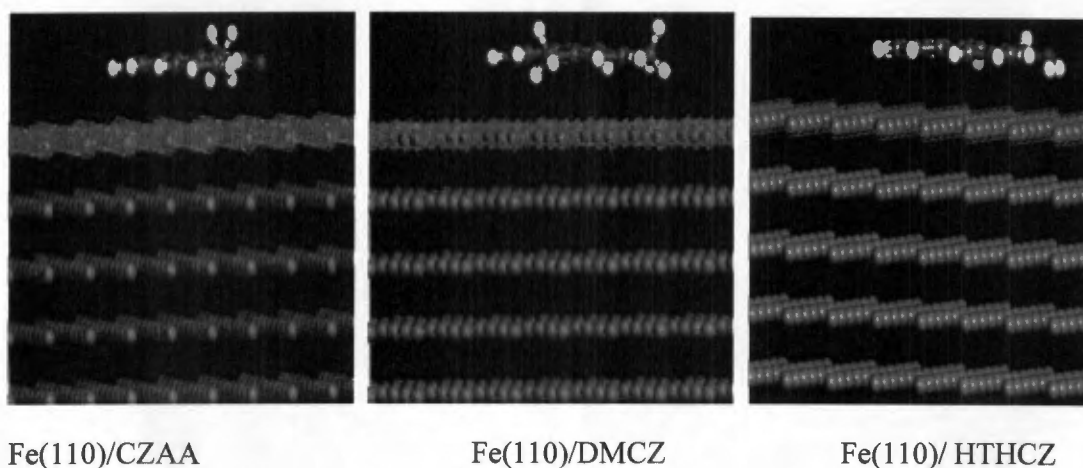
Figure 4.36. Optimized structure, HOMO, LUMO and Mulliken charge distribution (excluding H-atoms) for the studied molecules.

Table 4.26. Selected quantum chemical parameters for the studied carbazoles.

Inhibitor	E_{HOMO} eV	E_{LUMO} eV	ΔE	Dipole moment	logP	MV $\text{\AA}^3$	η	σ	μ	ω
CZAA	-5.833	-1.270	4.563	3.1888	2.42	250	2.282	0.438	-3.552	2.764
DMCZ	-5.584	-0.908	4.676	1.6509	3.60	220	2.338	0.428	-3.246	2.254
HTHCZ	-5.704	-1.427	4.277	1.5794	1.94	226	2.139	0.468	-3.566	2.973

4.4.6. MD simulation

The equilibrium configurations of the simulated systems are shown in Figure 4.37, while the relevant energy parameters of the systems are listed in Table 4.27. The results recorded in Figure 4.37 revealed that the three inhibitor molecules adsorbed on Fe(110) surface in almost flat orientation. This finding coupled with the highest magnitudes of adsorption and deformation energies obtained for the Fe(110)/CZAA system ensure optimum interactions of the inhibitor molecules with the metallic surface.

**Figure 4.37.** The most stable configurations for the adsorption of CZAA, DMCZ and HTHCZ on Fe(110)/inhibitor systems.**Table 4.27.** Energy parameters (kcal/mol) affiliated to the adsorption of the inhibitor molecules on Fe(110).

System	Adsorption energy	Rigid adsorption energy	Deformation energy
Fe(110)/DMCZ	-110.42	-111.13	0.71
Fe(110)/CZAA	-122.05	-129.30	7.25
Fe(110)/HTHCZ	-111.23	-110.71	-0.51

4.5. GROUP V: 9-ECZ, 3-ECZ, ENCZ and CZE

The group V consists of four compounds with a common carbazole backbone as listed in Table 3.5. They differ in the nature of substituent groups attached to different positions of the parent carbazole ring. This set of carbazole can also be distinguished with respect to the presence or absence of an ethyl chain attached to different positions of the carbazole. In addition, the effect of the presence of a nitro group at position 5 in ENCZ provides additional bases for the comparative analysis of the anticorrosion behaviours of the group.

4.5.1. Electrochemical studies

4.5.1.1. PDP studies

The representative polarization curves for MS in 1 M HCl in the absence and presence of different concentrations of the GROUP V compounds are presented in Figure 4.38 for 9-ECZ and CZE. The polarization curves for ENCZ and 3-ECZ show similar features and so are presented in Figure AV-1 (Appendix V). The electrochemical corrosion parameters and inhibition efficiency are listed in Table 4.28. The curves distinctly parade reduced current density in the presence of the studied inhibitors compared to the blank, suggesting that the compounds reduce the corrosion current density with a concomitant reduction of the corrosion rate.

In relation to the Tafel curve for the blank system, all the curves appear at more apparent cathodic regions than the anodic counterpart. This effect is even more conspicuous at elevated concentrations. These findings coupled with the shift in E_{corr} with less than 85 mV upon addition of the studied inhibitors portray that the studied carbazoles act as mixed-type inhibitors [73, 188]. The largest shift in E_{corr} of about 22 mV obtained for the inhibited systems alludes that the addition of the studied inhibitors does not, or, maybe slightly changed the MS electrode surface. The values of the Tafel slopes, β_a and β_c appear to fluctuate with concentrations of the inhibitors, however without a coherent exact order. A closer look at Table 4.28 reveals that β_a and β_c values for 3-ECZ are generally lower than the blank. For the other three inhibitors, the effect on β_c is more definite than β_a . These findings corroborate the more inhibitive actions of the studied compounds on the cathodic reaction than its anodic counterpart.

The observable recognizable effect on inhibition efficiency recorded at high concentrations of inhibitors support the idea that the geometric blocking of the active sites on the MS surface was attained.

The values of the I_{corr} decrease with increasing concentrations of the inhibitors which consequently increase $\eta\%$ values. This feature recommends that the studied compounds retard MS corrosion in the acid via the formation of adsorbed film of the inhibitor molecules on the steel surface.

The $\eta\%$ for 9-ECZ increases with increasing concentration of the inhibitor from 76 % at 300 ppm up to 87 % at 1000 ppm. Between 400 ppm to 1000 ppm, further increment in concentration could not yield any substantial difference in the value of $\eta\%$. Similar trend can be observed for ENCZ, CZE and 3-ECZ between 400 ppm to 1000 ppm.

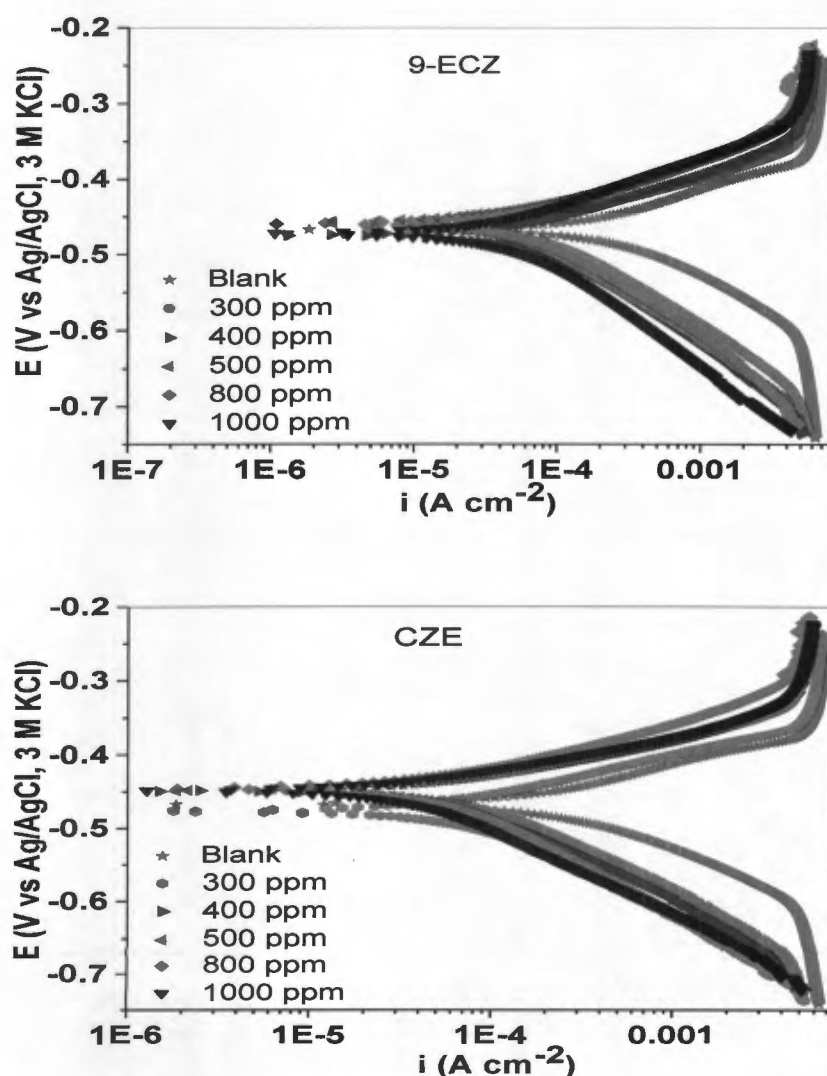


Figure 4.38. Polarization curves for mild steel in absence and presence of different concentrations of 9-ECZ and CZE.

Table 4.28. Tafel polarization parameters for MS in 1 M HCl solution in absence and presence of different concentrations of 9-ECZ, ENCZ, CZE and 3-ECZ.

Inhibitor	Conc (ppm)	β_a (mV/dec)	β_c (mV/dec)	$-E_{corr}$ (mV)	i_{corr} ($\mu A\ cm^{-2}$)	$\eta\%$
Blank	-	98.93	72.08	452.72	236	-
9-ECZ	300	52.69	94.45	464.32	57	76
	400	54.55	84.72	474.35	41	83
	500	52.50	97.69	457.30	32	86
	800	46.11	78.61	459.11	31	87
	1000	86.32	66.07	472.59	30	87
ENCZ	300	70.26	215.75	390.01	95	60
	400	61.56	137.14	408.56	50	79
	500	48.19	95.30	398.98	43	82
	800	54.98	112.38	423.67	39	83
	1000	81.53	46.35	445.50	35	85
CZE	300	146.95	74.95	476.08	120	49
	400	46.17	88.22	448.51	39	83
	500	47.91	73.00	448.27	37	84
	800	56.08	102.64	445.56	36	85
	1000	112.97	48.38	448.94	33	86
3-ECZ	300	40.58	28.42	474.79	39	83
	400	38.93	17.83	464.92	22	91
	500	22.94	23.06	459.66	15	94
	800	24.98	14.70	452.18	9	96
	1000	30.64	22.58	457.39	6	97

The general trend in performance of these inhibitors adjudged from their individual average values of $\eta\%$ within the concentration range 300 ppm to 1000 ppm is such that 3-ECZ > 9-ECZ > ENCZ > CZE.

4.5.1.2. EIS measurements

Figures 4.39 and 4.40 supply details of the Nyquist and Bode plots for 9-ECZ and CZE whilst those of the remaining two are presented in Figures AV-2 and AV-3 (Appendix V) respectively.

The Nyquist plots are marked by distinctly larger diameter compared to the blank. Moreso, the diameter of the Nyquist semicircles was found to increase with increasing inhibitor

concentration for all the four inhibitors. This improvement recommends the strengthening of inhibitive film on MS surface.

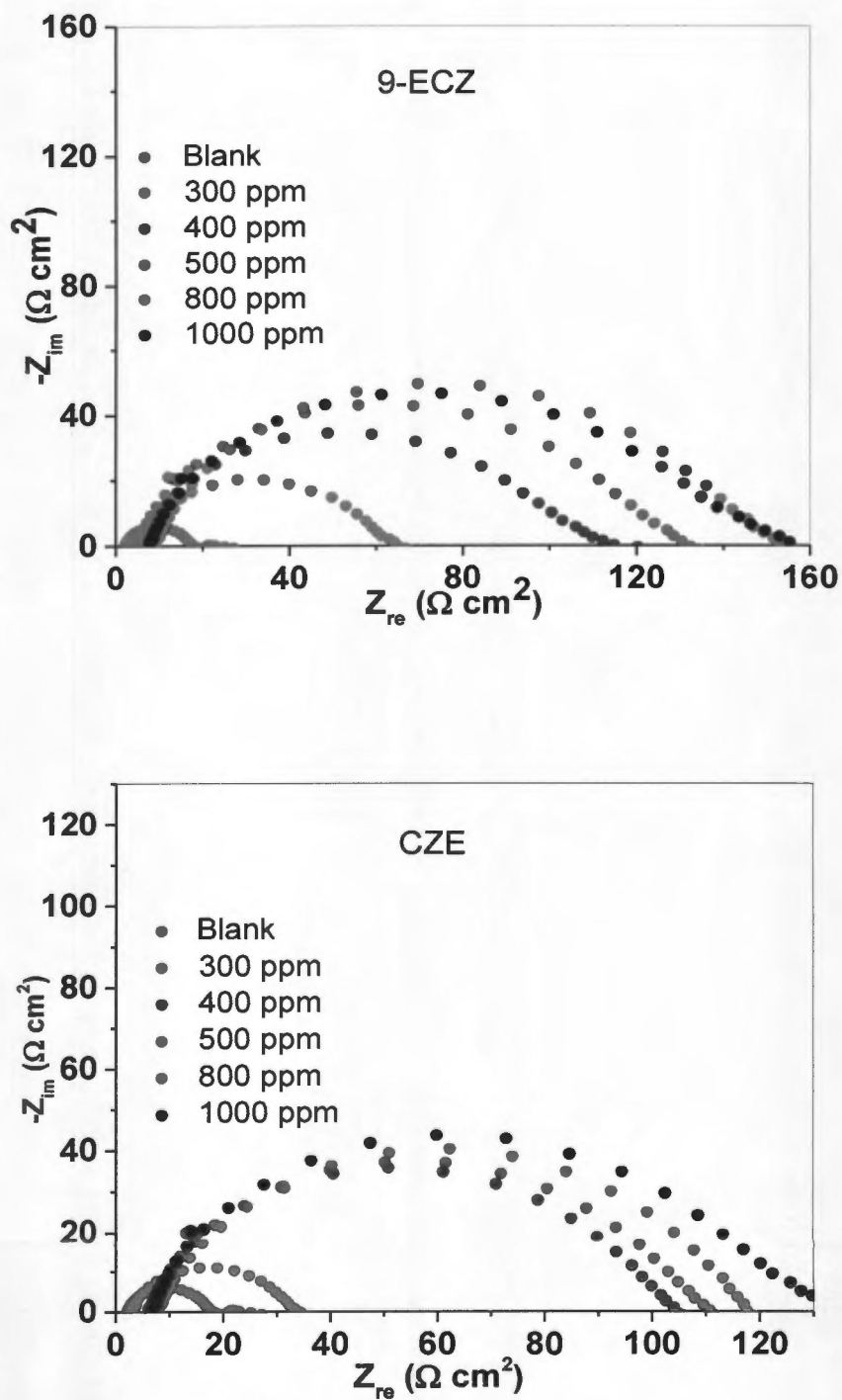


Figure 4.39. Nyquist plots for MS in 1 M HCl without and with different concentrations of 9-ECZ and CZE.

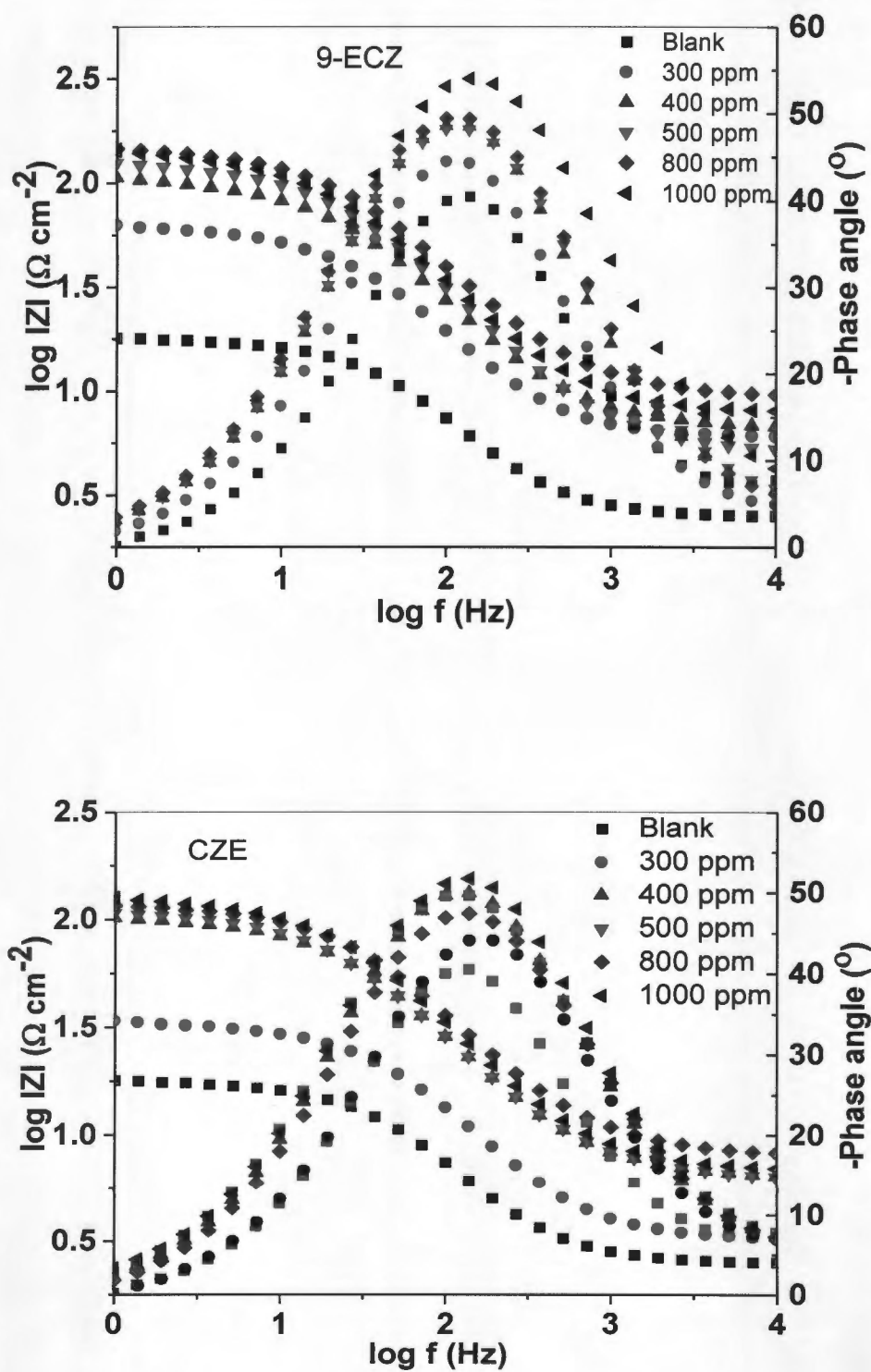


Figure 4.40. Bode plots for MS in 1 M HCl without and with different concentrations of 9-ECZ and CZE.

A single depressed semicircles corresponding to one time constant in the Bode plots was obtained providing evidence that the dissolution of MS electrode in the studied electrolytes is characterized by a single charge transfer mechanism. In addition, the formation of the protective film of the inhibitor molecules was confirmed in the broadening of single time constant maximum in the Bode phase plots of the inhibitor-containing systems.

Table 4.29. Electrochemical impedance parameters, minimum and maximum slopes (S) of the Bode impedance magnitude plots at intermediate frequencies and the corresponding maximum phase angles (α) obtained for MS in 1 M HCl in absence and presence of different concentration of 9-ECZ, ENCZ, CZE and 3-ECZ.

Inhibitor	Conc (ppm)	R_s ($\Omega \text{ cm}^{-2}$)	R_{ct} ($\Omega \text{ cm}^{-2}$)	Y_0 ($\mu\text{S s}^{-1} \text{ cm}^{-2}$)	n	$\eta\%$	$-\alpha$	$-S$
Blank	-	2.50	17	677	0.84	-	40	0.30
9-ECZ	300	6.0	64	309	0.81	73	44	0.57
	400	6.59	115	247	0.79	85		
	500	5.10	133	173	0.81	87		
	800	9.37	152	156	0.80	89		
	1000	7.80	158	196	0.79	89	54	0.74
ENCZ	300	26.0	42	134	0.76	60	26	0.63
	400	23.5	74	110	0.77	77		
	500	32.4	90	64.6	0.81	81		
	800	36.7	106	74.9	0.82	84		
	1000	37.3	141	85.7	0.80	88	31	0.99
CZE	300	3.25	33	390	0.82	48	44	0.53
	400	6.36	105	186	0.82	84		
	500	6.28	111	199	0.81	85		
	800	8.12	117	154	0.81	85		
	1000	6.82	134	165	0.81	87	52	0.69
3-ECZ	300	21.1	105	127	0.83	84	39	0.78
	400	19.4	140	131	0.80	88		
	500	19.9	171	99.5	0.82	90		
	800	34.0	270	88.9	0.78	94		
	1000	12.7	483	67.3	0.78	96	55	0.84

Parameters on the electrochemical reactions that were acquired from the fitting and simulation of the impedance spectra are listed in Table 4.29. The values of R_s and Y_0 do not maintain a precise order with increasing concentration of the studied inhibitors. Notwithstanding, it can be seen that the values of R_s are generally higher than the blank with

the highest R_s recorded for ENCZ and 3-ECZ. The high R_s values reassert the relatively low conductivity media in the presence of the inhibitors.

The R_{ct} values increase with increasing concentrations with resultant increase in $\eta\%$ values. 9-ECZ reached a maximum value at 800 ppm after which further increase in concentration did not reveal noticeable improvement in the value of R_{ct} . The remaining three do not show any significant increase in $\eta\%$ at 1000 ppm. 3-ECZ recorded the highest $\eta\%$ at 1000 ppm. Above all, the trend of the values of $\eta\%$ recorded for the EIS corroborates with that of the Tafel analyses. The magnitudes of n are generally lower for the inhibitor containing systems than the blank validating that appreciable level of homogeneity of the MS surface was enhanced.

The magnitudes of α and S recorded for the studied inhibitors at minimum and maximum concentrations recommend pseudo capacitive behaviour and verify the formation of adsorbed film of the inhibitor molecules on the MS surface that subsequently protected the surface from direct impact of the acid.

4.5.2. Adsorption isotherms

The representative adsorption isotherms of the Langmuir and Freundlich isotherms for the inhibitors are shown in Figure 4.41. The adsorption of 9-ECZ, ENCZ, CZE, and 3-ECZ were found to prefer the Langmuir adsorption isotherm.

A close look at all the plots suggests that they are linear with R^2 values of almost unity for the Langmuir. The parameters on the thermodynamic adsorption process are given as follows: 9-ECZ ($K_{ads} = 27.69 \times 10^2$; $\Delta G^\circ_{ads} = -30.08$ kJ/mol), ENCZ ($K_{ads} = 14.66 \times 10^2$; $\Delta G^\circ_{ads} = -28.48$ kJ/mol), CZE ($K_{ads} = 9.81 \times 10^2$; $\Delta G^\circ_{ads} = -27.47$ kJ/mol) and 3-ECZ ($K_{ads} = 30.58 \times 10^2$; $\Delta G^\circ_{ads} = -30.33$ kJ/mol). The values of ΔG°_{ads} suggest competitive physical and chemical adsorption mechanisms. The values of ΔG°_{ads} were obtained using the already described Equation 4.4 in Group I.

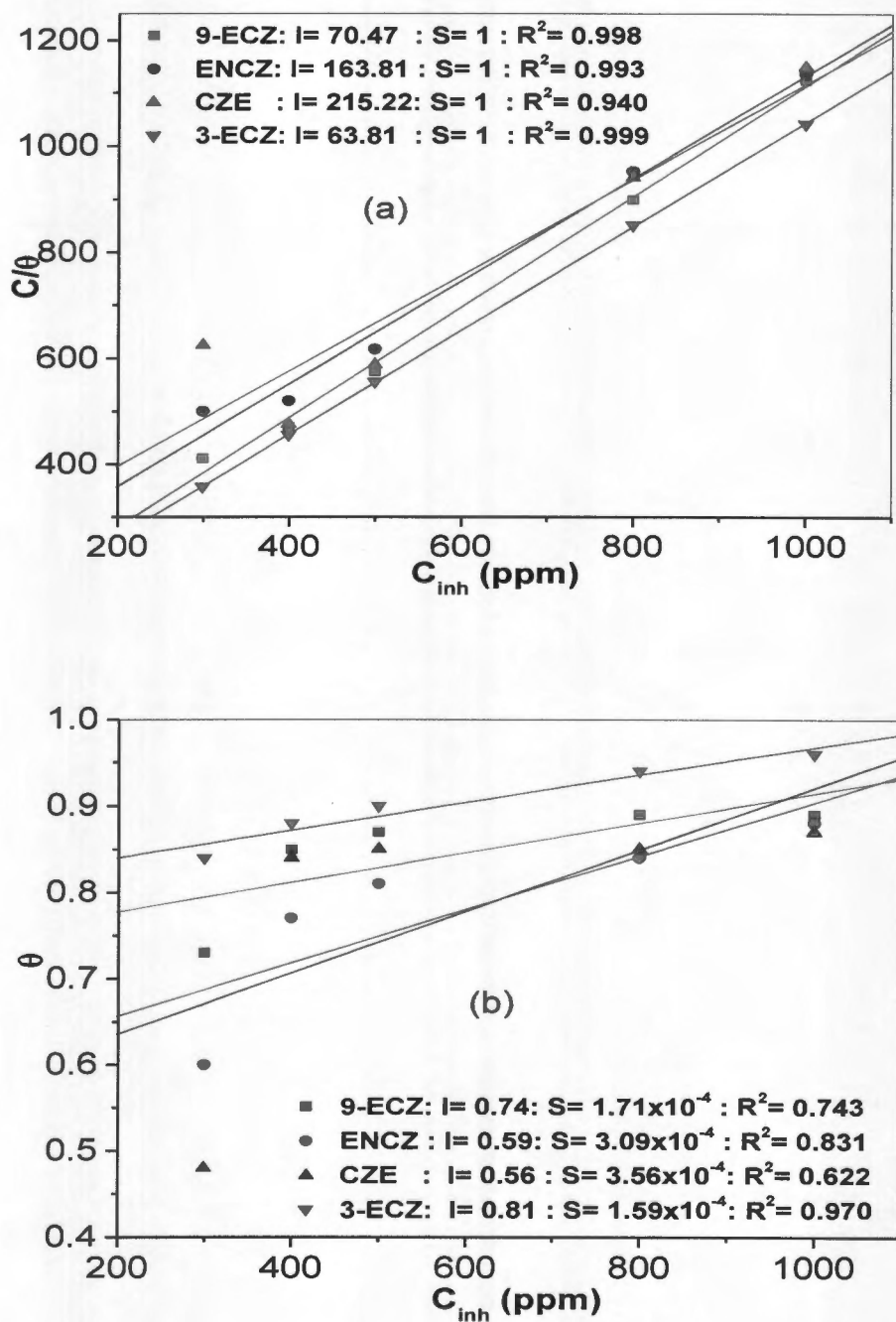


Figure 4.41. Langmuir (a) and Freundlich (b) adsorption isotherm plots of for mild steel in the presence of 9-ECZ, ENCZ, CZE and 3-ECZ.

4.5.3. Biocorrosion study (weight-loss measurements)

Table 4.30 presents the averaged weight loss after 5 and 9 days of incubation of MS coupons exposed to *D. vulgaris* medium with or without 100 ppm of 9-ECZ, ENCZ, CZE and 3-ECZ. It should be noted that the averaged WL values of MS obtained after 5 days differ from that obtained after 9 days inoculation.

Table 4.30. The weight loss parameters obtained for mild steel exposed to SRB cultures after 5 and 9 days incubation with or without 100 ppm CZs.

Biocide	Weight loss (g.cm ⁻²)	C_R (g.cm ⁻² .d ⁻¹)	IE% _{WL}
After 5 days			
<i>D. vulgaris</i>	0.1293	0.026±0.003	-
9-ECZ	0.1038	0.021±0.0029	19±3
ENCZ	0.0097	1.94x10 ⁻³ ±0.00275	93±8
CZE	0.0101	2.02x10 ⁻³ ±0.00293	92±2
3-ECZ	0.0021	4.2x10 ⁻⁴ ±0.0025	98±17
After 9 days			
<i>D. vulgaris</i>	0.1576	0.018±0.0004	-
9-ECZ	0.0939	0.0104±0.000372	42±7
ENCZ	0.0106	1.7x10 ⁻³ ±0.00038	91±5
CZE	0.0164	1.8x10 ⁻³ ±0.000330	90±17
3-ECZ	0.008	8.8x10 ⁻⁴ ±0.000351	95±12

From Table 4.30, the corrosion damage on MS in un-inoculated *D. vulgaris* medium increased after 5 days reaffirming the corrosiveness of this particular SRB specie and their metabolic activities up to 9 days period. In the presence of 100 ppm of the studied inhibitors however, there is significant reduction in WL values. For instance, a closer scrutiny of the trend in inhibition efficiency (IE%_{WL}) suggests that 3-ECZ > ENCZ > CZE > 9-ECZ after both periods (5 and 9 days) of incubation. That is, the corrosion damage in the presence of 9-ECZ was more severe than in 3-ECZ. Overall, there is reduction in IE%_{WL} after 9 days for all the studied inhibitors except for 9-ECZ system which can be ascribed to reduction in *D. vulgaris* activities due to carbon source starvation [189]. The slight improvement in IE%_{WL}

for the 9-ECZ system from 19 % to 42 % after 9 days may account for reduction in sulphide concentration due to dead cells as well as the subsequent accumulation of extracellular polymeric substances on MS surface [173, 189].

4.5.4. Surface morphology studies

4.5.4.1. SEM study

Figures 4.42 and 4.43 represent SEM micrographs of MS surfaces immersed in 1 M HCl and *D. vulgaris* medium without and with 100 ppm of 9-ECZ respectively. The remaining SEM images are presented in Figures AV-4 and AV-5 (Appendix 5).

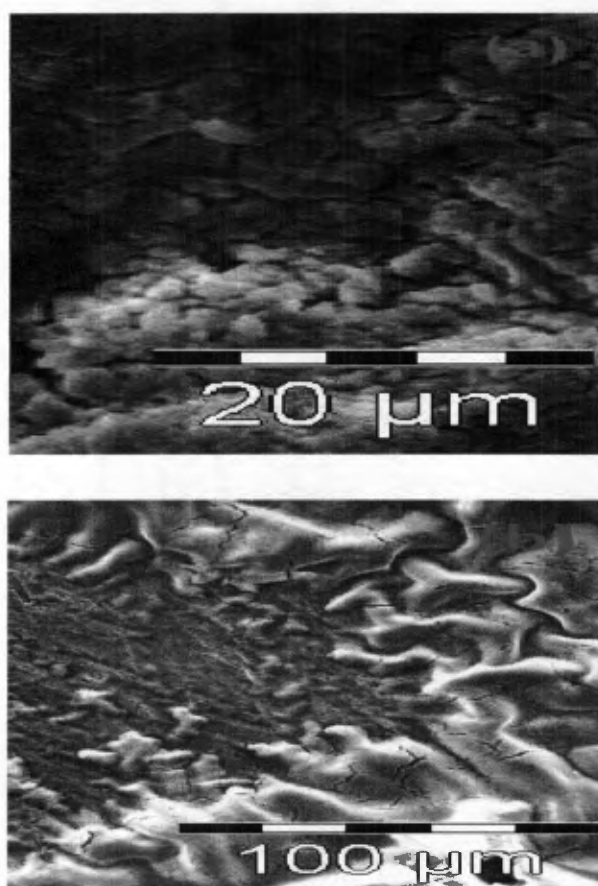


Figure 4.42. SEM images of MS surfaces immersed in 1 M HCl without and with 100 ppm of the studied inhibitors (a) blank (b) 9-ECZ.

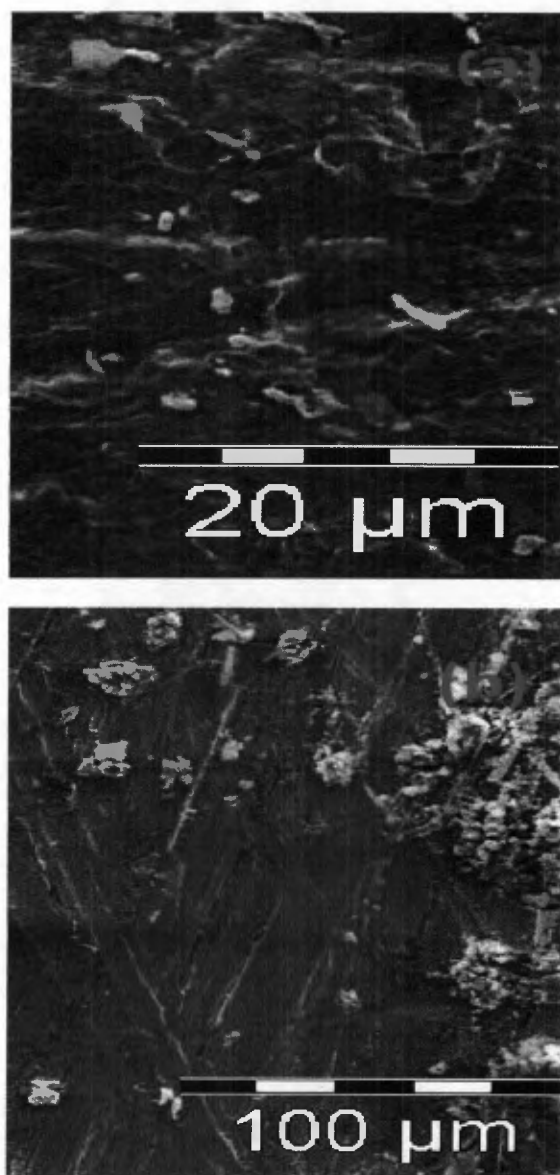


Figure 4.43. SEM images of MS surfaces immersed in *D. vulgaris* culture without and with 100 ppm of the studied inhibitors obtained after 9 days incubation (a) blank (b) 9-ECZ.

Less severely corroded surfaces were obtained for MS surfaces exposed to 1 M HCl in the presence of the studied inhibitors than the blank. The degree of their surface protective film differed with ENCZ recording the least with a smoother surface. In addition, SEM image of 9-ECZ treated with 1 M HCl shows MS surface with strongly-held protective film that connotes better inhibitory action.

For MS incubated in *D. vulgaris* with 100 ppm of CZs, less corroded surface was also obtained compared to the blank. For 3-ECZ (Figure AV-5e) however, the protective film

appears to be strongly delocalized on the entire surface which further confirms the inhibition action and adsorption of inhibitor on MS surface.

4.5.4.2. EDX study

Table 4.31 is the record of percentage atomic contents of MS retrieved from acidic and SRB corrosive media without and with 100 ppm of the inhibitors. The dominance of chloride- and iron-based materials marked the MS coupons immersed in 1 M HCl.

On the other hand, coupons immersed in the SRB consortium reveal varying percentages of sulphur and phosphorous that corroborates the presence of the sulphate-reducing bacteria, *D. vulgaris*. In addition, it has been established that the metabolic actions of the SRB consortium and associated biofilm induce higher concentrations of sulphide and phosphate-based that collectively aggravate corrosion process [190].

It is imperative to highlight the significant reduction in iron content for MS recovered from 3-ECZ in comparison with its corresponding high carbon content. This finding confirms that MS surface was covered with protective film of inhibitor molecules. This suggests that 3-ECZ exhibits better protective action.

Table 4.31. EDX elemental constituents (in weight %) of MS surface retrieved from the acidic and SRB corrosive media without and with 100 ppm of the inhibitors: the MS for SRB were obtained after 9 days incubation.

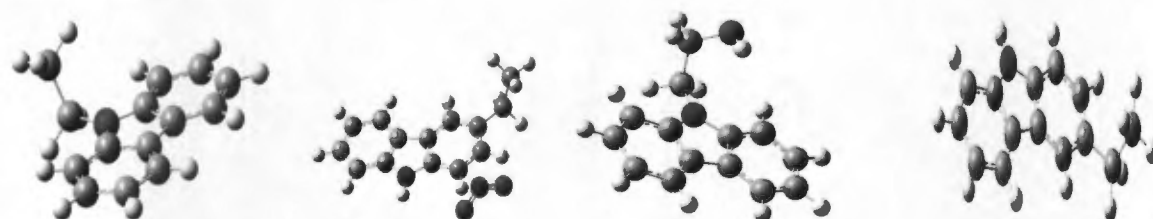
Inhibitors	Fe	Mn	Ca	K	Cl	S	P	Al	Na	Si	O	C
Acidic media												
1 M HCl Blank	34.55	-	-	-	34.6	-	-	-	-	-	23.99	6.86
9-ECZ	48.53	-	-	-	13.46	-	-	-	-	-	29.62	8.39
ENCZ	48.02	-	-	0.25	26.6	-	-	-	0.39	-	24.73	-
CZE	58.01	-	-	-	6.97	-	-	-	-	-	35.02	-
3-ECZ	52.43	-	-	-	12.07	-	-	-	-	-	35.49	-
SRB Culture media												
SRB Blank	76.57	0.15	0.47	-	-	0.21	0.77	0.1	-	-	8.9	12.83
9-ECZ	61.89	-	-	-	-	-	-	-	-	-	18.57	19.54
ENCZ	30.03	-	-	-	-	0.16	0.18	-	-	0.14	5.29	64.21
CZE	50.31	-	-	-	-	2.31	0.4	-	-	-	26.26	20.72
3-ECZ	9.11	-	-	-	-	0.18	-	-	-	0.23	5.45	85.04

4.5.5. Quantum chemical calculations

Figure 4.44 displays the optimized molecular structures, HOMO and LUMO electronic density distributions of the studied 9-ECZ, ENCZ, CZE and 3-ECZ. As was observed for the previous molecules in Groups I to IV, the HOMO of the four CZ molecules are mainly influenced by π bonding orbitals and distributed over the entire aromatic carbazole

rings in each molecule. In addition, similar observations can be made in LUMO density distributions except for ENCZ and 3-ECZ. The entire aromatic carbazole rings and ethyl alkyl chain in ENCZ; the C14 atom in CZE and the unsubstituted benzene ring in 3-ECZ are all not involved in the LUMO distribution. The observed distributions are likely going to offer conducive environments for donor-acceptor interactions and might be accountable for the adherence of the molecules on MS surface.

Optimised structure



9-ECZ

ENCZ

CZE

3-ECZ

HOMO



9-ECZ

ENCZ

CZE

3-ECZ

LUMO



9-ECZ

ENCZ

CZE

3-ECZ

Figure 4.44. Optimized structures, HOMO and LUMO for the studied molecules.

Table 4.32. Selected quantum chemical parameters for the studied 9-ECZ, ENCZ, CZE and 3-ECZ.

Inhibitor	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	Dipole moment	η	σ	μ	ω
Gas Phase								
9-ECZ	-5.59	-1.06	4.53	2.01	2.27	0.44	-3.33	2.44
ENCZ	-5.74	-2.45	3.29	1.72	1.65	0.61	-4.10	5.09
CZE	-5.74	-1.19	4.55	1.32	2.28	0.44	-3.47	2.64
3-ECZ	-5.63	-1.05	4.58	1.51	2.29	0.44	-3.34	2.44
Aqueous Phase								
9-ECZ	-5.71	-1.22	4.49	2.84	2.25	0.44	-3.47	2.68
ENCZ	-5.83	-2.47	3.36	2.95	1.68	0.60	-4.15	5.13
CZE	-5.77	-1.25	4.52	2.01	2.26	0.44	-3.51	2.73
3-ECZ	-5.73	-1.18	4.55	2.15	2.28	0.44	-3.46	2.63

The calculated quantum chemical descriptors in both gas and aqueous phases are listed in Table 4.32. Based on the results in Table 4.32, the following insights can be made in relation to the relevance of the recorded quantum chemical parameters to their respective most favourable inhibitory action:

In gas phase

- ✚ LUMO, ΔE, η, σ and ω: ENCZ
- ✚ HOMO, dipole moment and μ: 9-ECZ

In aqueous phase

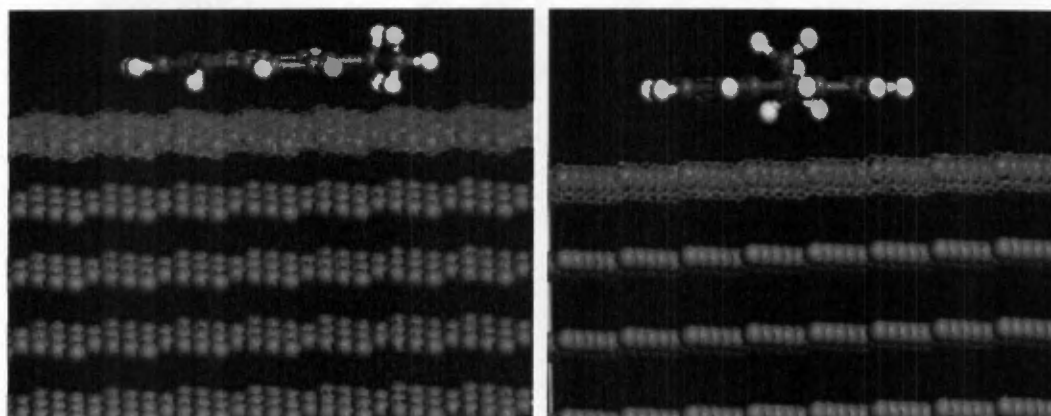
- ✚ HOMO: 9-ECZ
- ✚ LUMO, ΔE, dipole moment, η, σ and ω: ENCZ
- ✚ μ: 3-ECZ

Consequently, the trend in inhibition efficiency for both phases is such that ENCZ > 9-ECZ > CZE > 3-ECZ. This reaffirms that there is little or no solvent effect on the reported inhibitors. In conclusion, this trend does not corroborate the experimental inhibition efficiencies.

4.5.6. Molecular dynamics simulation

The equilibrium configurations of the simulated Fe(110)/9-ECZ and Fe(110)/ENCZ systems are shown in Figure 4.45, while that of Fe(110)/CZE and Fe(110)/3-ECZ are shown in Figure AV-6. The results presented in Figures 4.45 and AV-6 revealed that all the reported inhibitor molecules adsorbed on Fe(110) surface in near flat orientation. From Table 4.33, it

is evident that CZE which possesses the highest magnitudes of adsorption and deformation energies exhibited the strongest interaction and by extension highest inhibition efficiency.



Fe(110)/9-ECZ

Fe(110)/ENCZ

Figure 4.45. The most stable configurations for the adsorption of 9-ECZ and ENCZ on Fe(110)/inhibitor systems.

Table 4.33. Energy parameters (kcal/mol) affiliated to the adsorption of the inhibitor molecules on Fe(110).

System	Adsorption energy	Rigid adsorption energy	Deformation energy
Fe(110)/9-ECZ	-104.93	-106.07	1.14
Fe(110)/CZE	-136.61	-141.59	4.98
Fe(110)/ENCZ	-108.24	-109.82	1.58
Fe(110)/3-ECZ	-107.83	-110.20	2.37

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The corrosion inhibition actions and adsorption strengths of sixteen (16) carbazole derivatives were explored for MS in 1 M HCl solution and sulphate reducing bacterial (SRB) consortium using electrochemical, weight loss, Fourier transform infrared, energy dispersive X-ray, scanning electron microscopy, quantum chemical, molecular dynamics simulations, and quantitative structure activity relationship techniques. The sixteen compounds were divided into five groups (Groups I - V), and the following conclusions were made.

(1) All the investigated carbazoles displayed substantial protection efficiency for MS in 1 M HCl solution with the following corrosion inhibition trends obtained from their respective maximum concentrations:

GROUP I: THCZ > EHCZDCA > HCZ > DBCZ > CZ

GROUP II: THCZCA > MTHCZ > MCZCA

GROUP III: CZPD > DBCPCZ

GROUP IV: HTHCZ > CZAA > DMCZ

GROUP V: ECZ > 9-ECZ > ENCZ > CZE.

The electrochemical results showed that all the compounds inhibit the acid (1 M HCl) induced corrosion and their inhibition efficiencies increase with increase in concentration. Potentiodynamic polarization suggests mixed-type corrosion inhibitors with profound cathodic effects at elevated concentrations.

(2) All the investigated compounds except the Group III compounds and 9-ECZ of Group V showed considerable protection strengths for MS incubated in SRBs consortium with the following inhibition trends:

GROUP I: CZ > EHCZDCA > DBCZ > THCZ > HCZ

GROUP II: THCZCA > MCZCA > MTHCZ

GROUP III: DBPCZ > CZPD (both recorded %IE_{WL} less than 70%).

GROUP IV: In the presence of *D. vulgaris* specie: HTHCZ > DMCZ > CZAA

In the presence of *D. multivorans* specie: HTHCZ > CZAA > DMCZ

GROUP V: 3-ECZ > ENCZ > CZE > 9-ECZ.

(3) The corrosion inhibitive strengths of these compounds in the SRB media suggest a combination of biocidal effect of CZs on the bacteria that are responsible for corrosion in the SRB media and the observed protection of the steel surface by adsorbed molecules of the tested CZs. Overall, the presented carbazoles demonstrated higher resistance to pitting corrosion compared to blank SRB media.

(4) The inhibition actions of these carbazoles were attributable to the adsorption of their molecules on mild steel surface. Their adsorption mechanisms differ according to groups: Groups I and V compounds obey the Langmuir isotherm with competitive physical and chemical adsorption mechanisms; Groups III and IV obey the Freundlich isotherm with strong chemisorption mechanisms while Group II compounds adheres to the Freundlich isotherm via physisorption mechanisms.

(5) SEM micrographs obtained for MS in SRB and 1 M HCl media revealed that the studied CZs got adsorbed on the metal surface forming highly cohesive protective layer that prevents further aggressive effect of the acid and SRB media.

(6) EDX elemental constituents of MS surface retrieved from 1 M HCl and SRB corrosive media without and with 100 ppm of the inhibitors were consistent with the studied corrosive media.

(7) The FT-IR spectra in both media reaffirmed the occurrence of chemical interactions between the inhibitor molecules and the steel.

(8) Molecular quantum chemical calculations revealed that the pi-electron centres and the other substituent heteroatoms of the carbazole ring were involved during Fe-inhibitor interactions. The E_{LUMO} , energy gap (ΔE), electrophilicity index (ω), chemical hardness (η) and softness (σ) are strongly related to corrosion inhibition efficiencies of the studied carbazole molecules. The results also strongly suggest that these quantum chemical parameters correlate with inhibition efficiencies of these carbazole derivatives for MS under microbiologically-influenced corrosion.

(9) The proposed QSAR equation for Group I compounds reasserts that indeed a high inhibition efficiency depends on low E_{HOMO} , high E_{LUMO} and high σ .

(10) The results of the MD simulations on the groups showed that these class of carbazoles adsorb on the Fe(110) surface in flat/planar orientations and the trend of the predicted adsorption energies is in fair rapport with the experimental inhibition efficiency values.

5.2. Recommendations and future studies

5.2.1. Industrial and academic recommendations

The carbazole derivatives investigated in this thesis have been found to be efficient corrosion inhibitors for mild steel corrosion in hydrochloric acid and sulphate reducing

bacteria media. The two corrosive environments abound in many industrial components such as biochemical reactors, effluent treatment plants, water treatment plants, and fossil-fired power stations. In the face of stiff environmental regulations, depleting natural resources and need to cut cost, it has become imperative to make effective use of corrosion inhibitors. In this regards, these compounds can be employed as additives to paints and coating materials to improve their corrosion protection properties. This study therefore recommends that consideration be given to other possible corrosive environments that machineries and industrial components may be exposed to in future corrosion studies.

The use of diverse surface morphology techniques provides sufficient support to the weight loss method employed for the mild steel exposed to SRBs. Reasonable correlation was also found between some chemical quantum parameters with the weight loss inhibition efficiencies (%IE_{WL}) of the studied carbazoles for mild steel incubated in SRB media. Consequently, this study recommends that researches on microbiologically influenced corrosion be reinforced with possible theoretical studies.

5.2.2. Possible future studies

The weight loss technique has limitation as it can only furnish averaged corrosion rates data without giving details of the time-resolved trend of corrosion. This study therefore suggests that weight loss method be complimented with electrochemical frequency modulation (EFM) technique that has the potential to instantaneously display Tafel parameters without extensive polarization for all future MIC studies.

The toxicity of some carbazole derivatives has also been raised in some past studies with particular emphasis on their solubility. The present study proposes future studies that will deal with the biodegradability as well as the solubility of the compounds in various solvents.

Since biocidal action of these carbazoles cannot be ruled out in the studied SRB medium, research study focusing on the mechanism by which carbazoles render the SRB incapacitated as biocides will make an interesting research focus in future.

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APPENDIX I: SUPPLEMENTARY FIGURES GROUP I

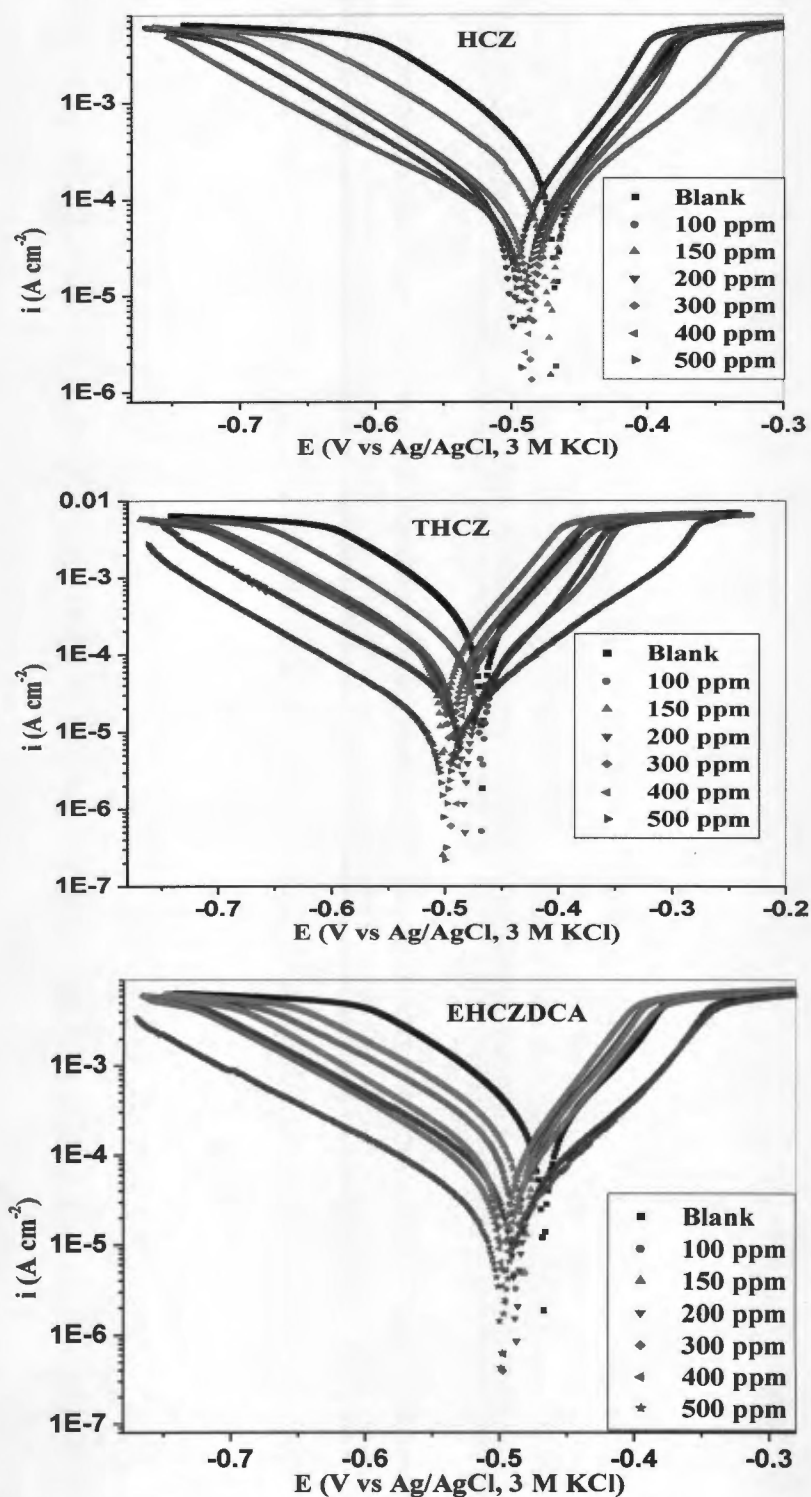


Figure AI-1. Tafel plots for MS in 1 M HCl without and with various concentrations of HCZ, THCZ and EHCZDCA.

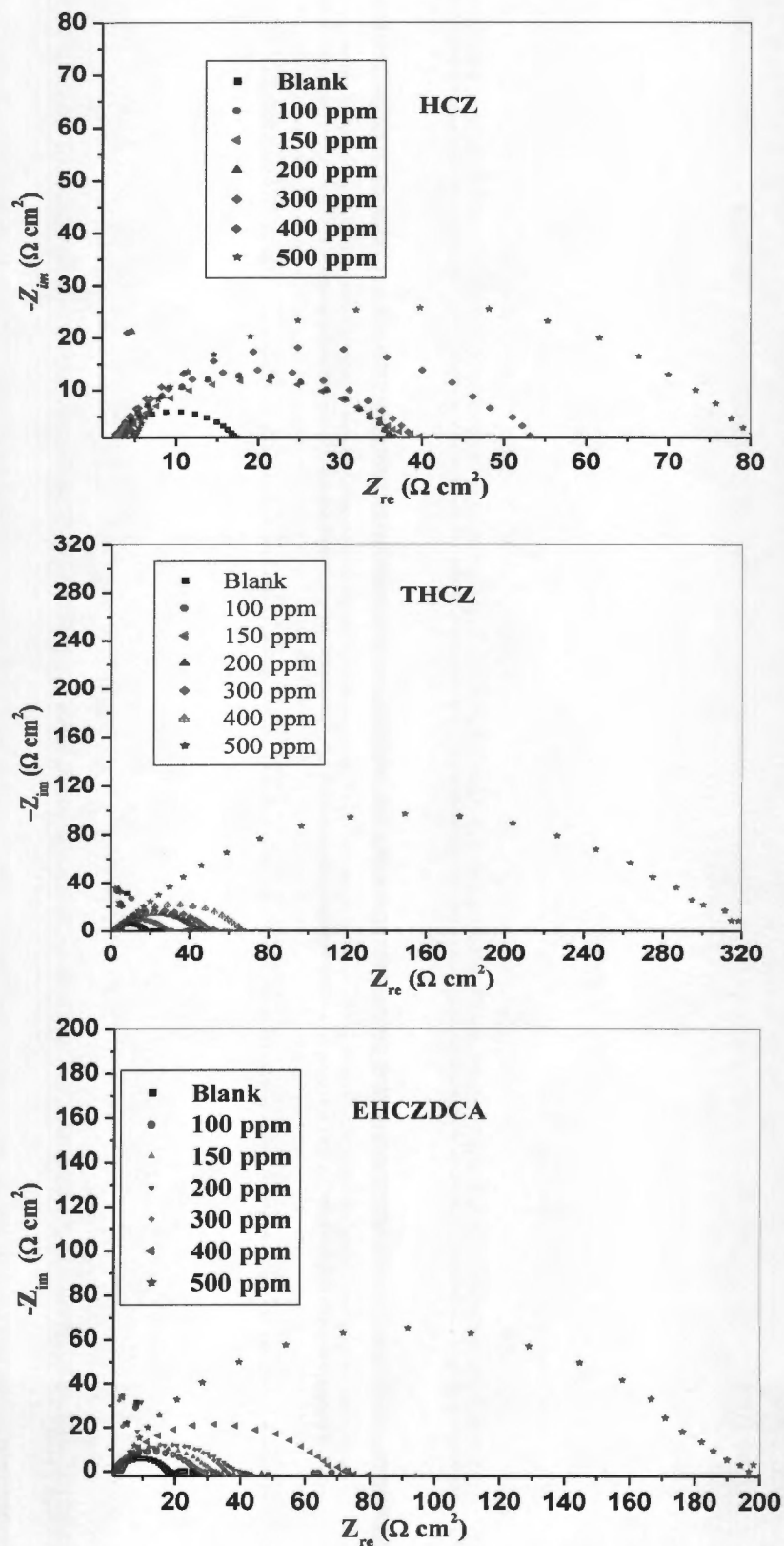


Figure AI-2. Nyquist plots for MS in 1 M HCl without and with various concentrations of HCZ, THCZ and EHCZDCA.

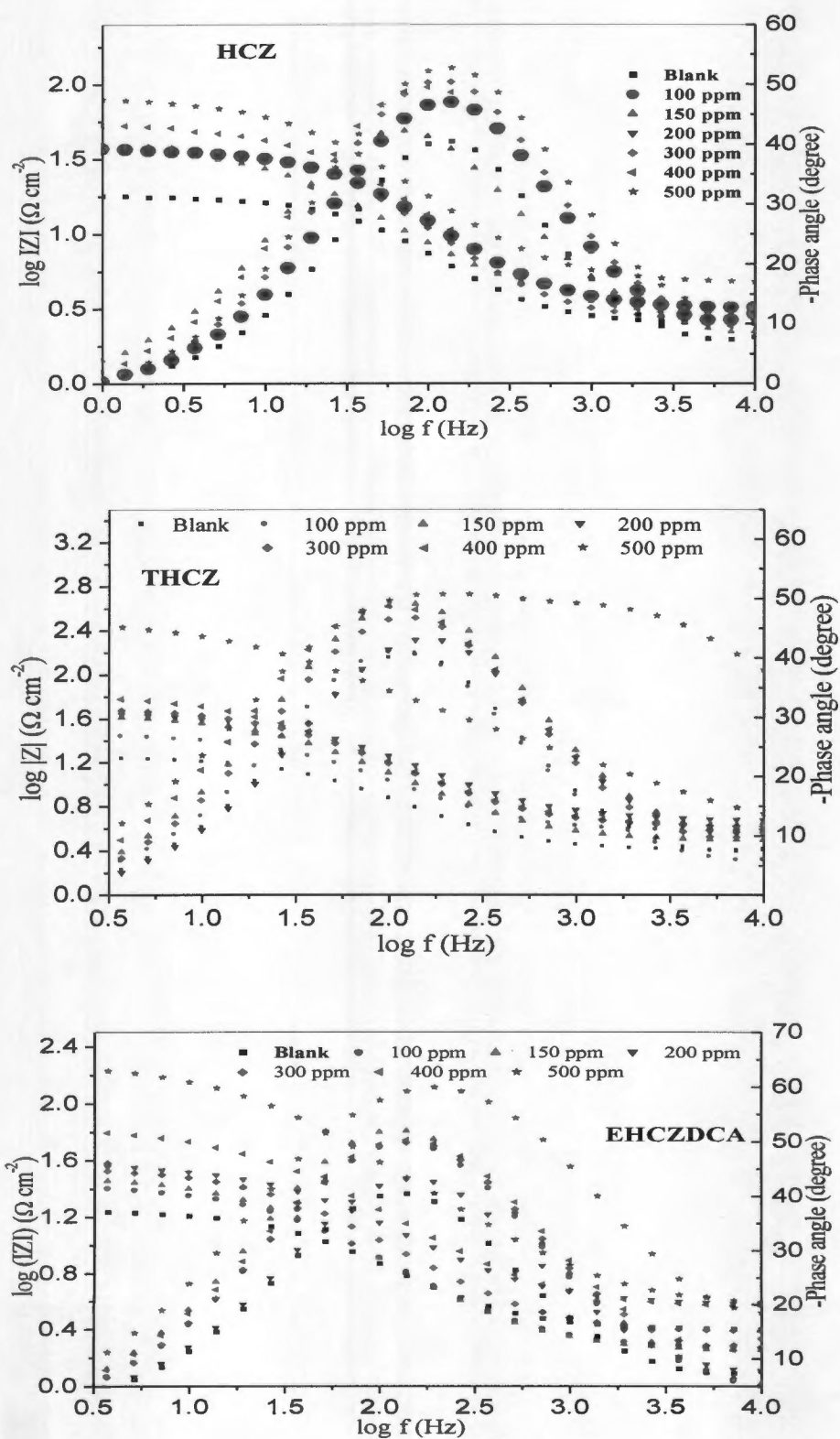


Figure AI-3. Bode plots for MS in 1 M HCl without and with various concentrations of HCZ, THCZ and EHCZDCA.

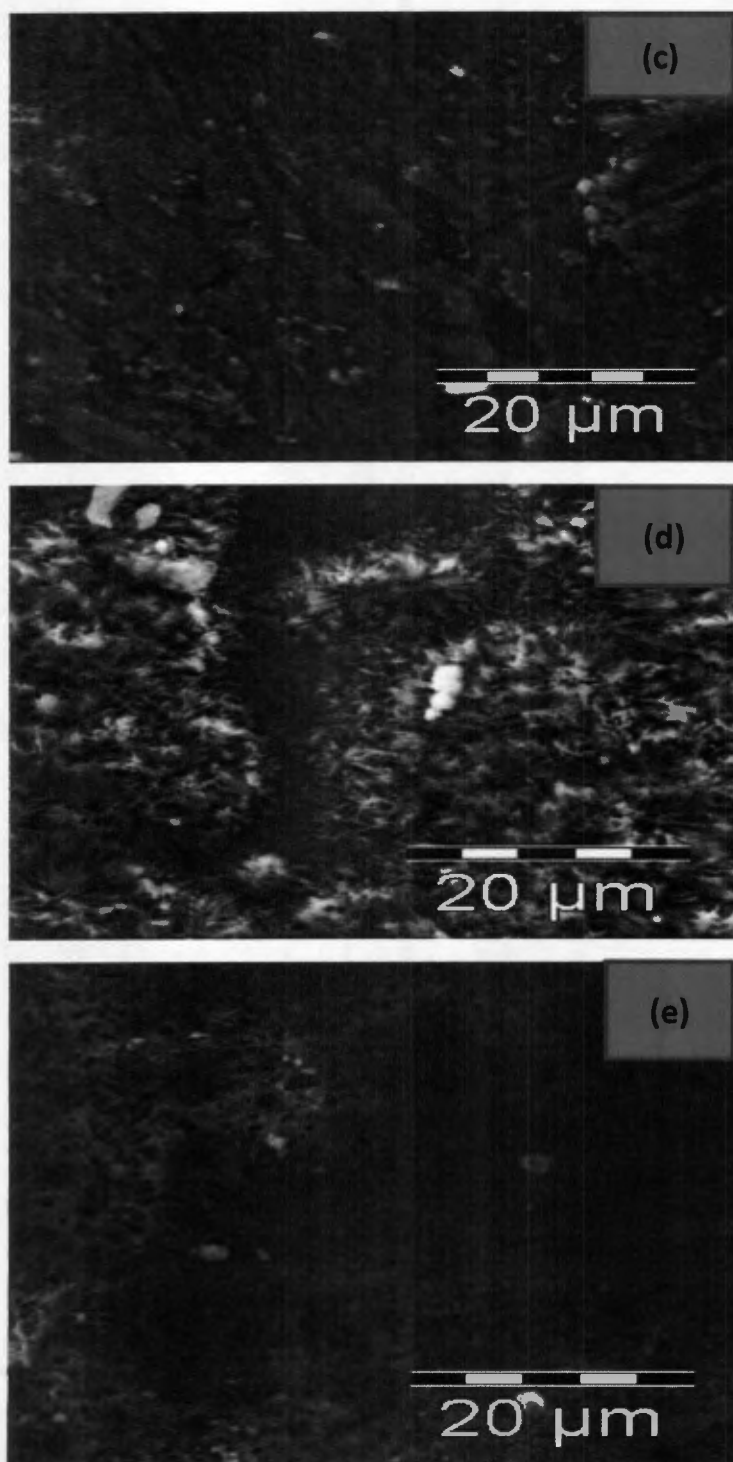


Figure AI-4. SEM images of mild steel surfaces immersed in 1 M HCl with 100 ppm of the studied inhibitors (c) THCZ (d) HCZ (e) EHCZDCA.

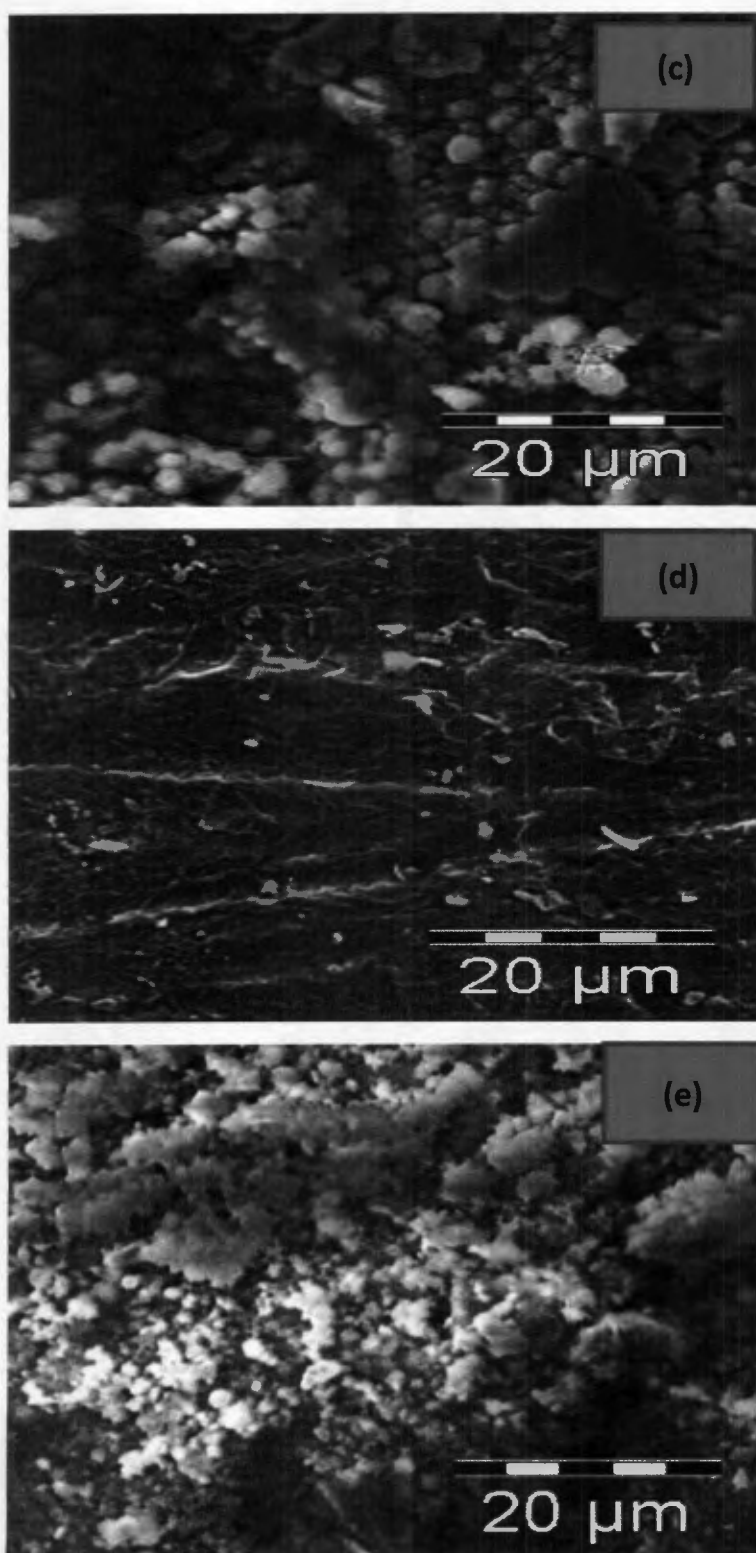


Figure AI-5. SEM images of mild steel surfaces immersed in SRB culture with 100 ppm of the studied inhibitors (c) THCZ (d) HCZ (e) EHCZDCA.

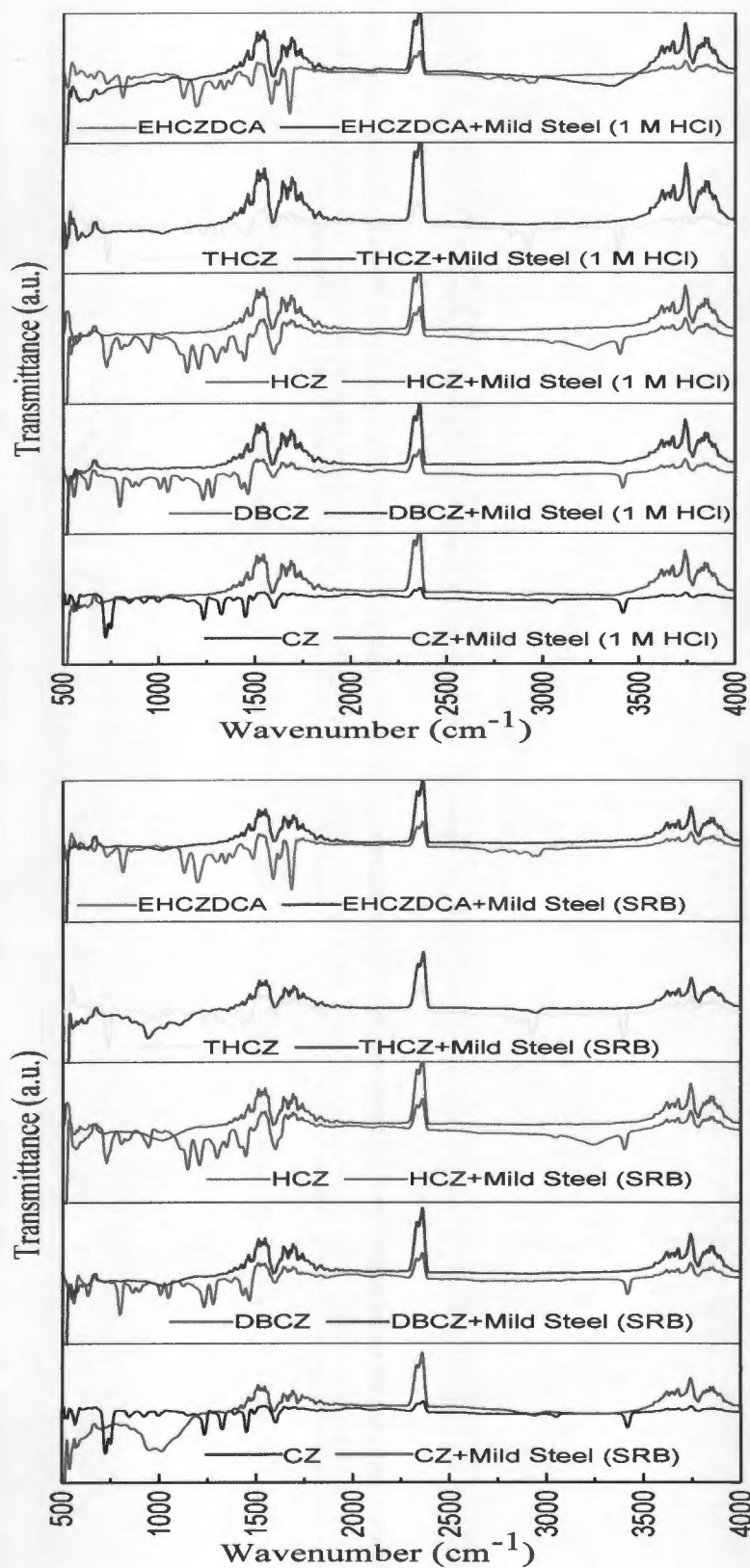
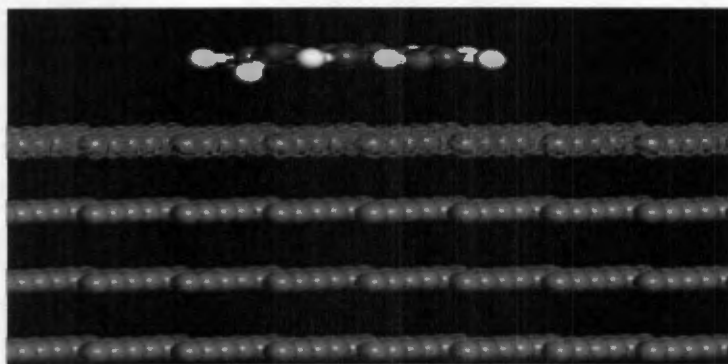


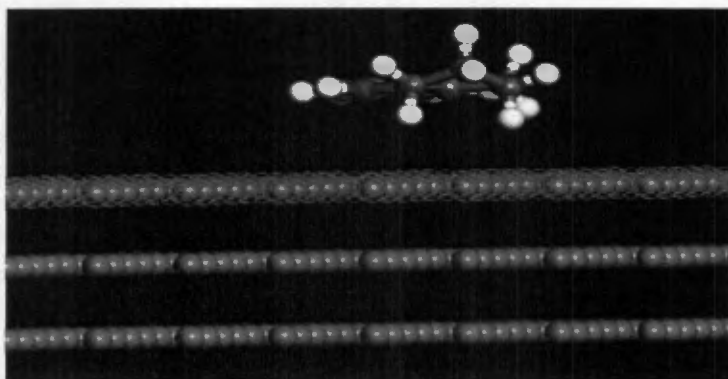
Figure AI-6. FTIR spectra of the inhibitor molecules and their resulting surface powder after mild steel immersion in acidic medium (top) and SRB culture (bottom).

Table AI-1. The set of quantum chemical descriptors and derived QSAR empirical models.

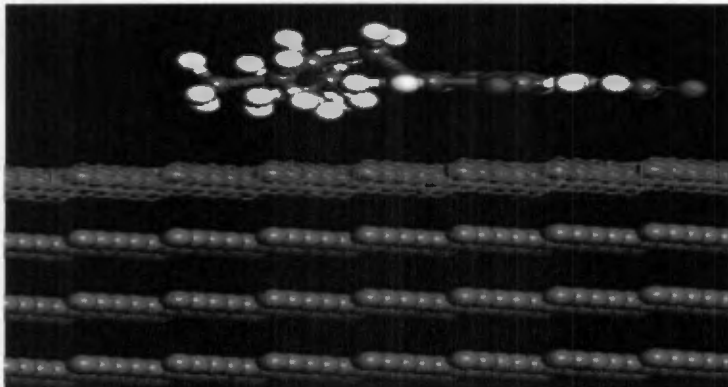
Descriptors	Model	R ²	MSE	RMSE
E _{LUMO} , Dipole, MV	$\%IE_{pred} = 75.576 + 14.221 \cdot E_{LUMO} + 6.278 \cdot \text{Dipole} - 8.617 \times 10^{-2} \cdot MV$	0.709	46.891	6.848
E _{HOMO} , Dipole, MV	$\%IE_{pred} = 213.151 + 27.283 \cdot E_{HOMO} + 5.755 \cdot \text{Dipole} - 5.965 \times 10^{-2} \cdot MV$	0.719	45.235	6.726
E _{HOMO} , E _{LUMO} , Dipole	$\%IE_{pred} = -1476.098 + 180.666 \cdot \Delta E + 3.522 \cdot \text{Dipole} + 1582.664 \cdot \sigma$	0.745	41.080	6.409
ΔE , Dipole, σ	$\%IE_{pred} = -1476.098 + 180.666 \cdot \Delta E + 3.522 \cdot \text{Dipole} + 1582.664 \cdot \sigma$	0.793	33.372	5.777
E _{HOMO} , E _{LUMO} , σ	$\%IE_{pred} = -7326.397 - 998.129 \cdot E_{HOMO} + 802.063 \cdot E_{LUMO} + 5827.399 \cdot \sigma$	0.898	16.385	4.048
$MSE = \sqrt{\sum_{i=1}^N (IE_{pred} - IE_{exp})^2} ; RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^N (IE_{pred} - IE_{exp})^2} ; IE_{pred} = \text{predicted inhibition efficiency; } IE_{exp}$ = experimental efficiency, n is the number of observations (n=5).				



Fe(110)/HCZ



Fe(110)/THCZ



Fe(110)/EHCZDCA

Figure AI-7. Equilibrium configurations of Fe(110)/inhibitor systems for the studied molecules.

APPENDIX II: SUPPLEMENTARY FIGURES GROUP II

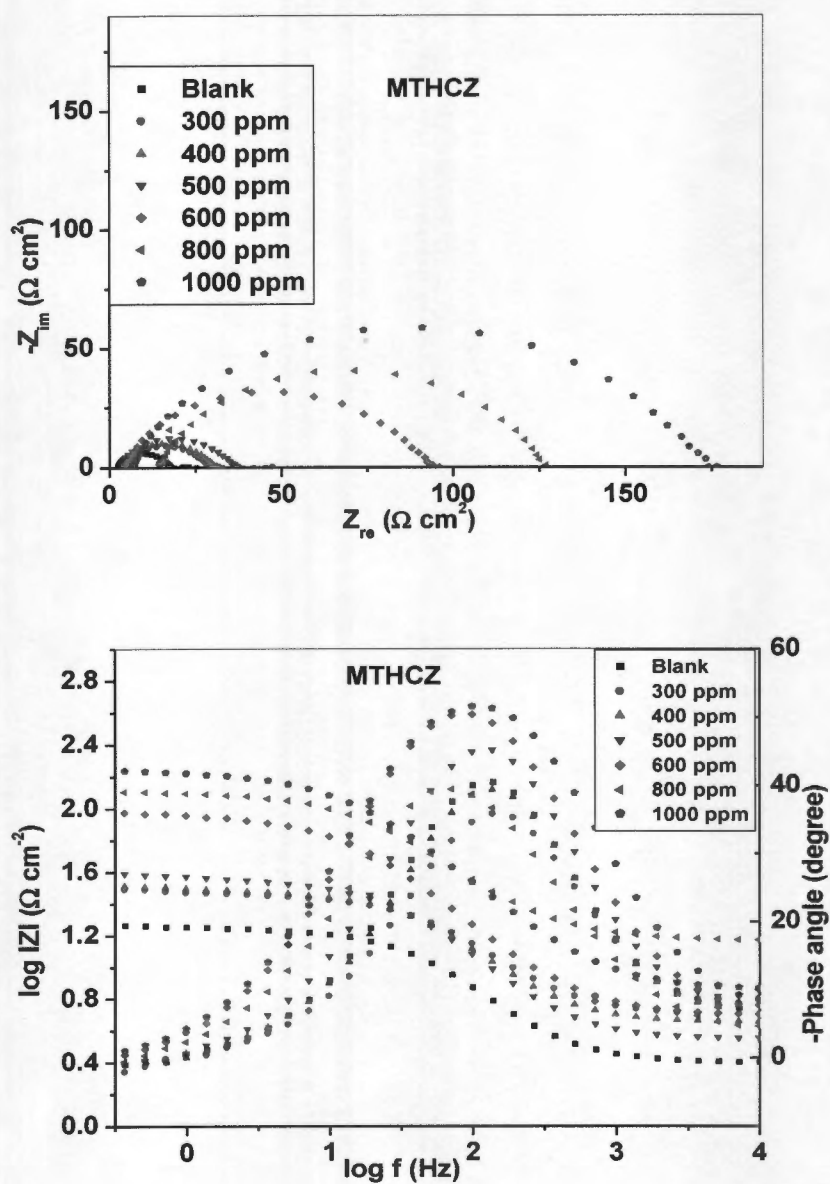


Figure AII-1. Nyquist and Bode plots for MS in 1 M HCl without and with different concentrations of MTHCZ.

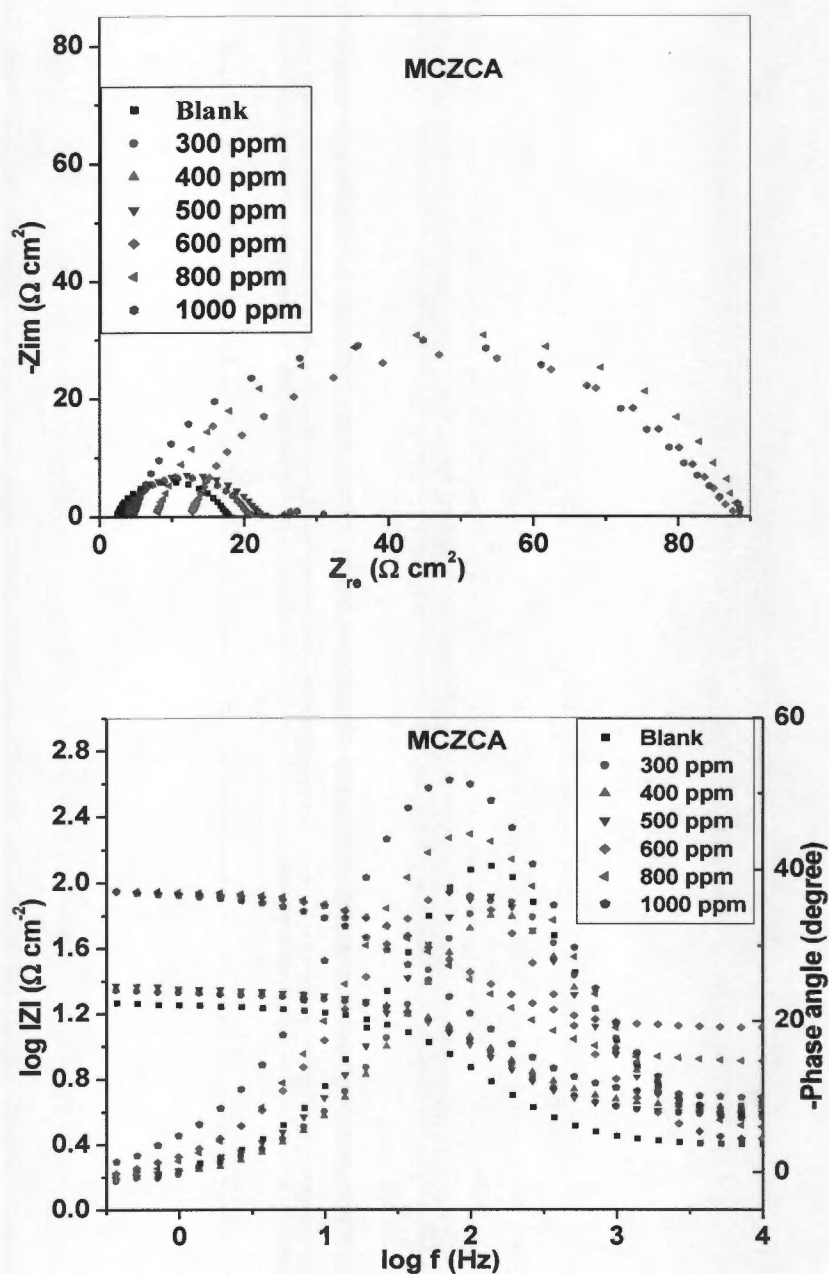


Figure AII-2. Nyquist and Bode plots for MS in 1 M HCl without and with different concentrations of MCZCA.

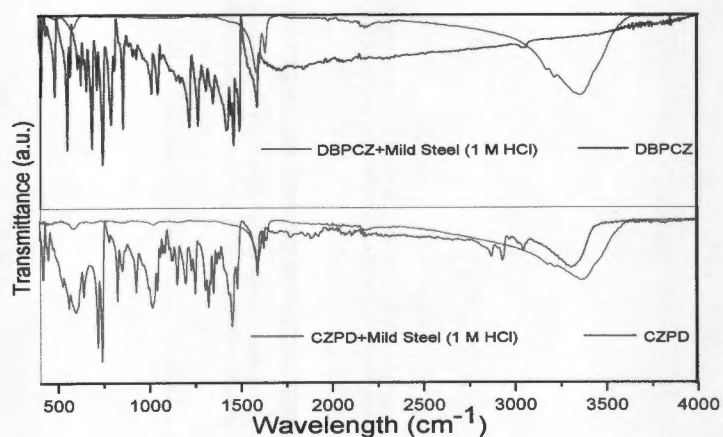
Table AII-1. Selected quantum chemical parameters for the studied carbazoles.

Inhibitor	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE	Dipole moment (Debye)	η	σ	ω
In gas phase							
THCZCA	-6.069	-1.897	4.172	2.296	2.086	0.479	3.803
MTHCZ	-5.323	-0.322	5.001	2.192	2.501	0.400	1.593
MCZCA	-5.957	-1.368	4.589	4.524	2.295	0.436	2.923
In aqueous phase							
THCZCA	-6.082	-1.964	4.118	3.276	2.059	0.486	3.93
MTHCZ	-5.462	-0.506	4.956	3.113	2.478	0.404	1.797
MCZCA	-5.969	-1.563	4.406	6.363	2.203	0.454	3.219

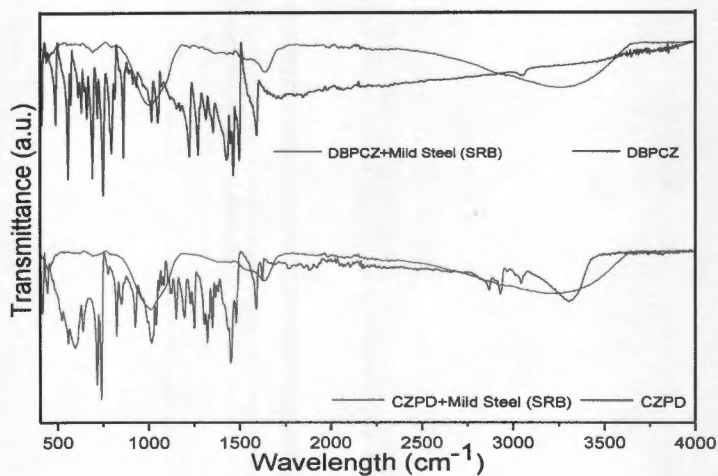
APPENDIX III: SUPPLEMENTARY FIGURES GROUP III

Table AIII-1. EDX elemental constituents (in weight %) of mild steel surface retrieved from the acidic and SRB corrosive media without and with 100 ppm of the inhibitors.

Inhibitors	C	Al	P	Cl	S	Ca	Mn	Fe	O
Acidic media									
1 M HCl Blank	6.86	-	-	34.6	-	-	-	34.55	23.99
DBPCZ	5.89	0.07	-	3.97	-	-	-	57.76	32.31
CZPD	6.18	-	-	10.51	-	-	-	51.95	31.36
<i>D. vulgaris</i> Culture media									
<i>D. vulgaris</i> Blank	12.83	0.1	0.77	-	0.21	0.47	0.15	76.57	8.9
DBPCZ	11.98	0.1	1.88	-	-	-	-	40.12	45.92
CZPD	7.92	-	-	-	-	-	-	55.19	36.9



(a)



(b)

Figure AIII-1. FTIR spectra of the inhibitor molecules and their resulting surface powder after mild steel immersion in acidic medium (top) and SRB culture (bottom).

Table AIII-2. Selected quantum chemical parameters for the studied DBPCZ and CZPD.

Inhibitor	E_{HOMO} eV	E_{LUMO} eV	ΔE	Dipole moment	logP	MV $\text{\AA}^3$	η	σ	μ	ω
DBPCZ	-5.898	-1.552	4.346	5.3622	5.93	306	2.173	0.460	-3.725	3.193
CZPD	-5.530	-0.968	4.562	4.2288	1.81	255	2.281	0.438	-3.249	2.314

APPENDIX IV: SUPPLEMENTARY FIGURES GROUP IV

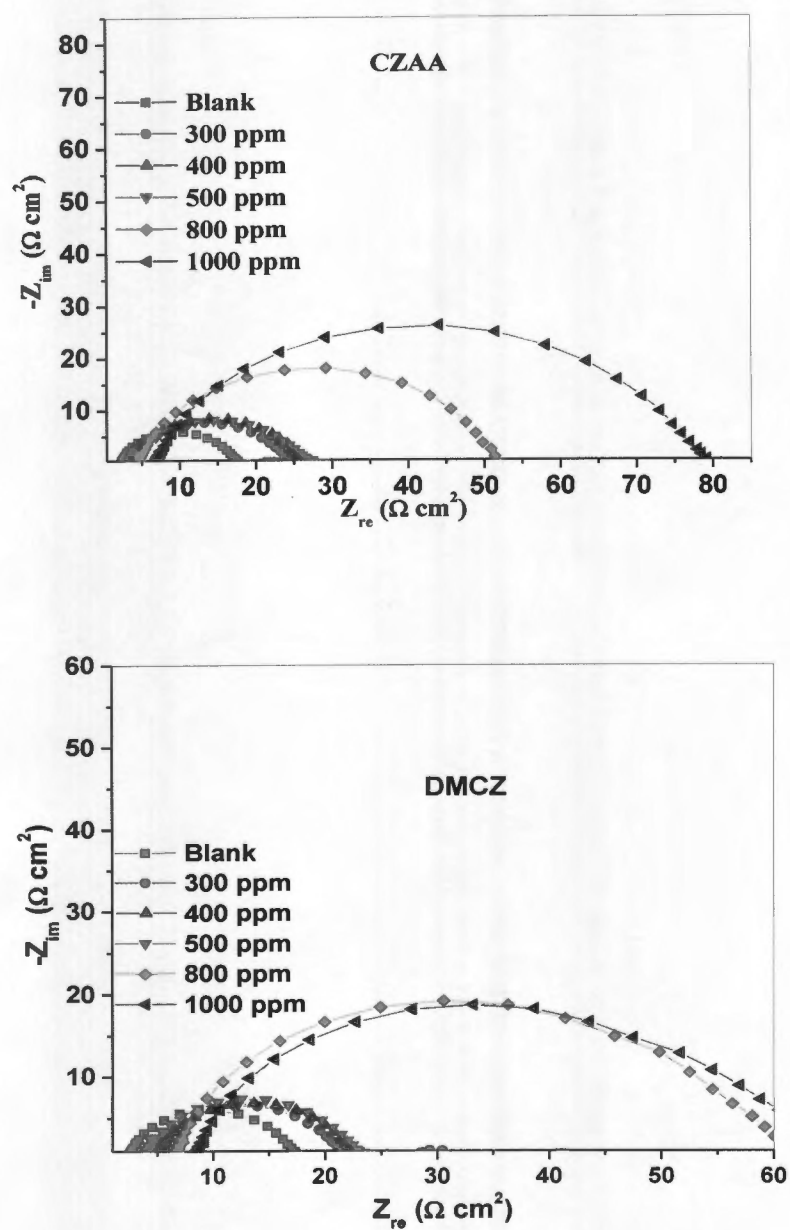


Figure AIV-2. Nyquist plots for MS in 1 M HCl without and with different concentrations of CZAA and DMCZ.

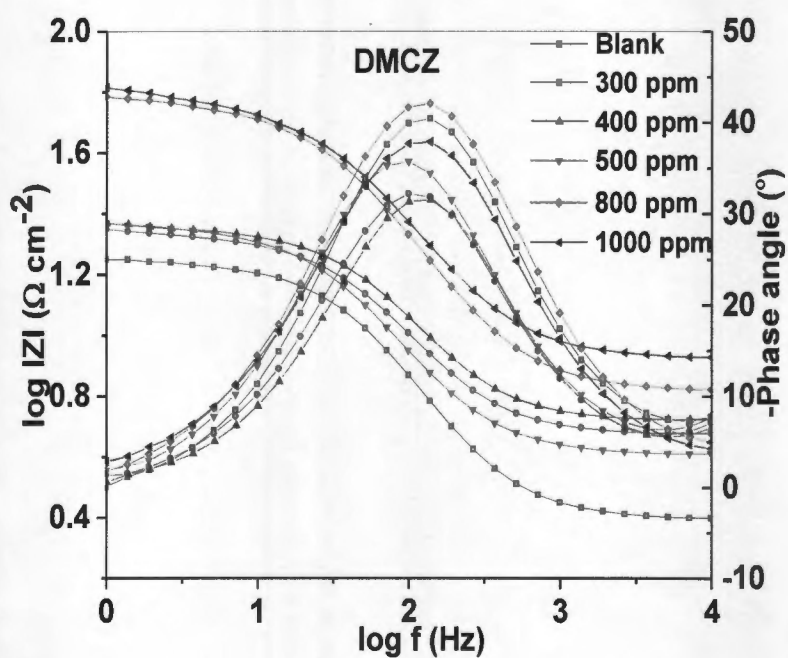
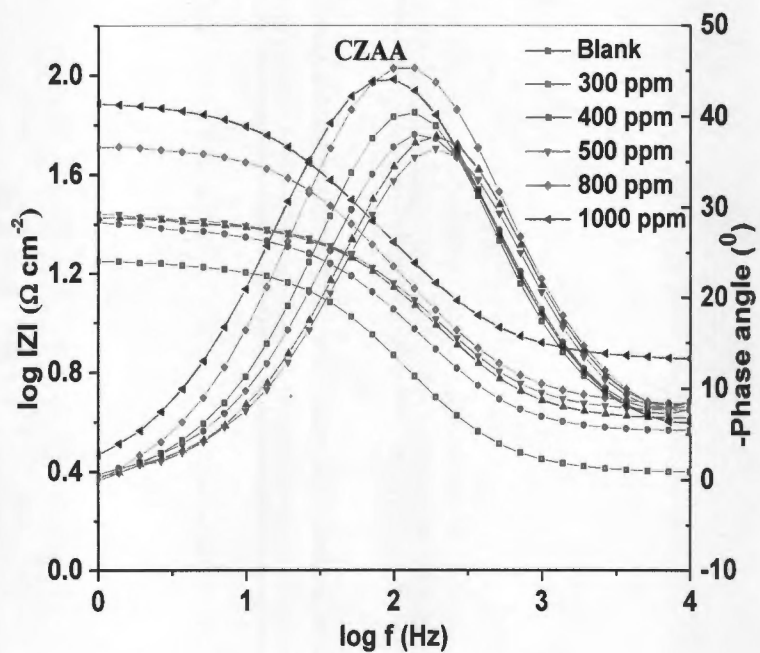


Figure AIV-3. Bode plots for MS in 1 M HCl without and with different concentrations of CZAA and DMCZ.

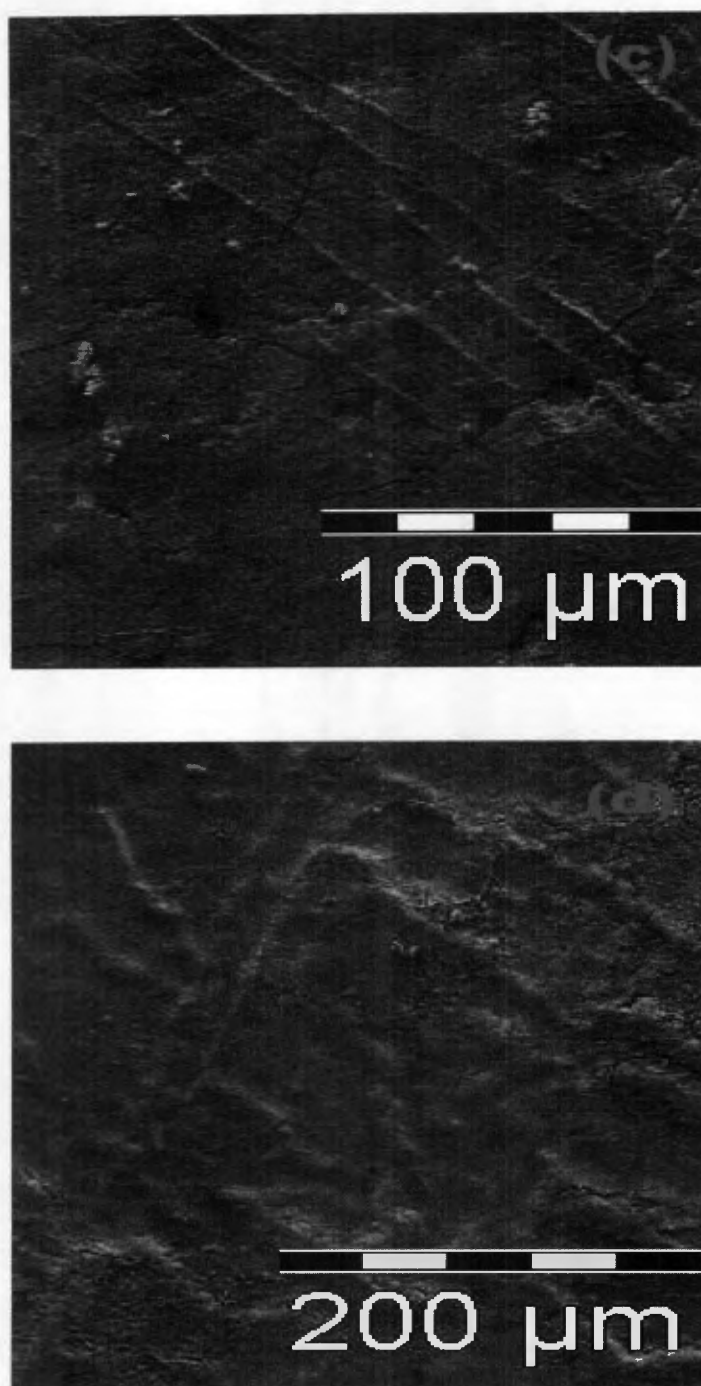


Figure AIV-4. SEM images of mild steel surfaces immersed in 1 M HCl with 100 ppm of the studied inhibitors (c) DMCZ (d) HTHCZ.

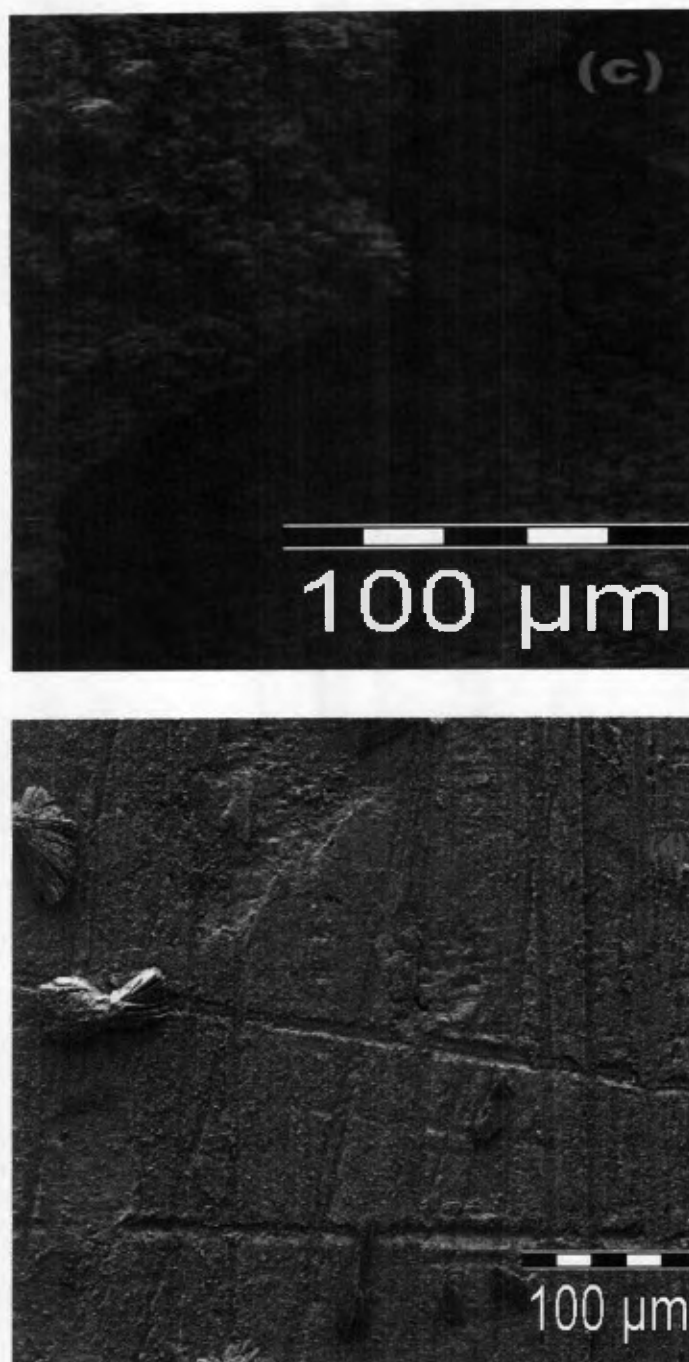


Figure AIV-5. SEM images of mild steel surfaces immersed in *D. vulgaris* culture with 100 ppm of the studied inhibitors (c) DMCZ (d) HTHCZ.



Figure AIV-6. SEM images of mild steel surfaces immersed in *D. multivorans* culture without and with 100 ppm of the studied inhibitors (c) DMCZ (d) HTHCZ.

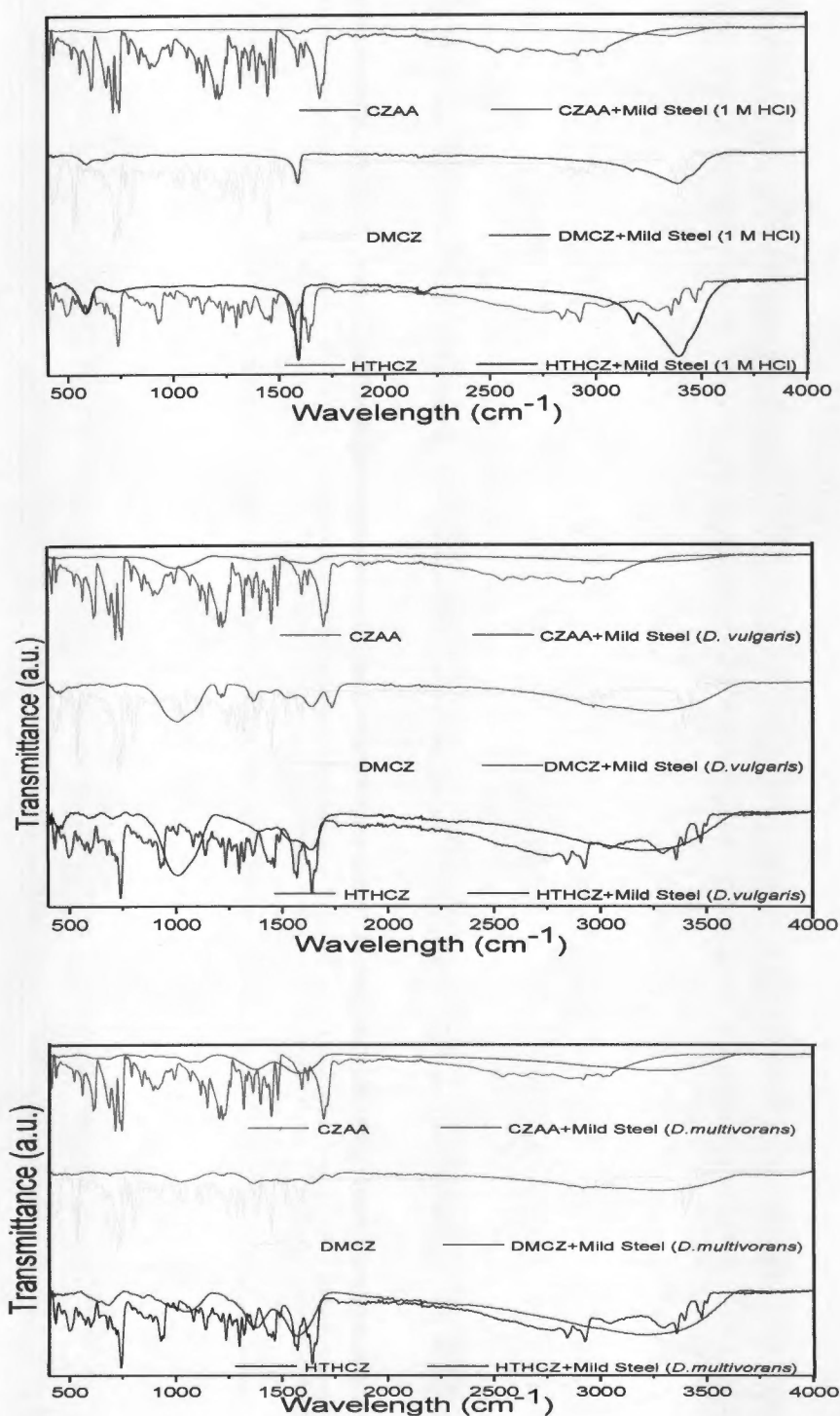


Figure AIV-7. FTIR spectra of the inhibitor molecules and their resulting surface powder after mild steel immersion in acidic medium (top), *D. vulgaris* (middle) and *D. multivorans* (bottom).

APPENDIX V: SUPPLEMENTARY FIGURES GROUP V

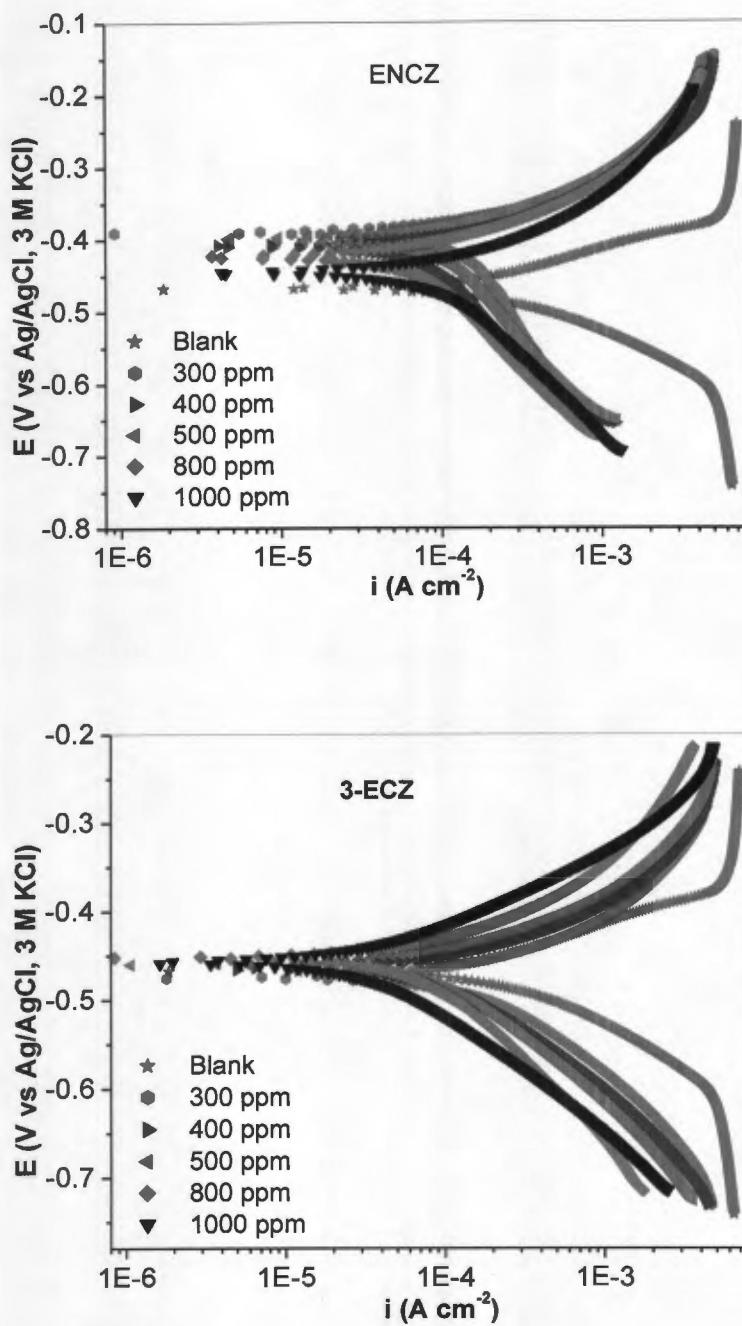


Figure AV-1. Polarization curves for mild steel in absence and presence of different concentrations of ENCZ and 3-ECZ.

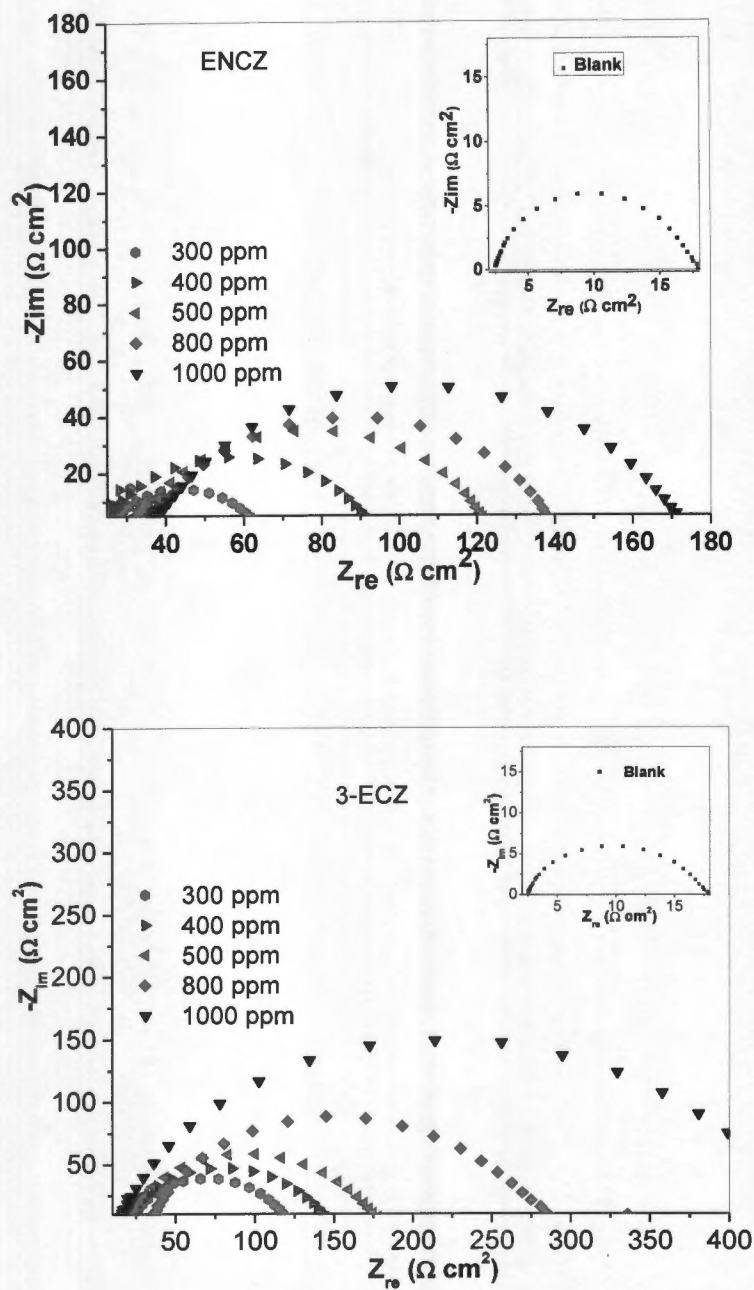


Figure AV-2. Nyquist plots for MS in 1 M HCl without and with different concentrations of ENCZ and 3-ECZ.

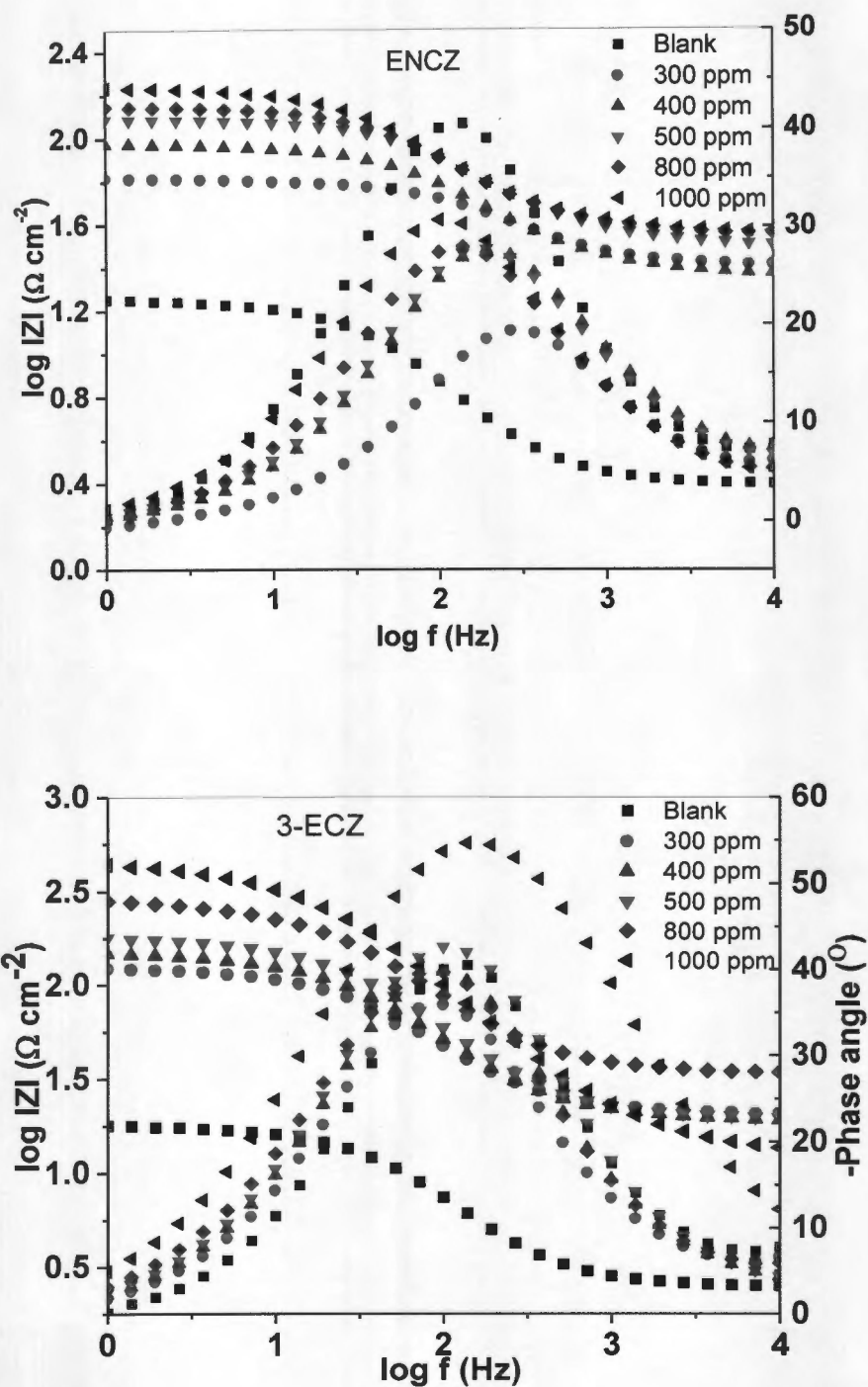


Figure AV-3. Bode plots for MS in 1 M HCl without and with different concentrations of ENCZ and 3-ECZ.

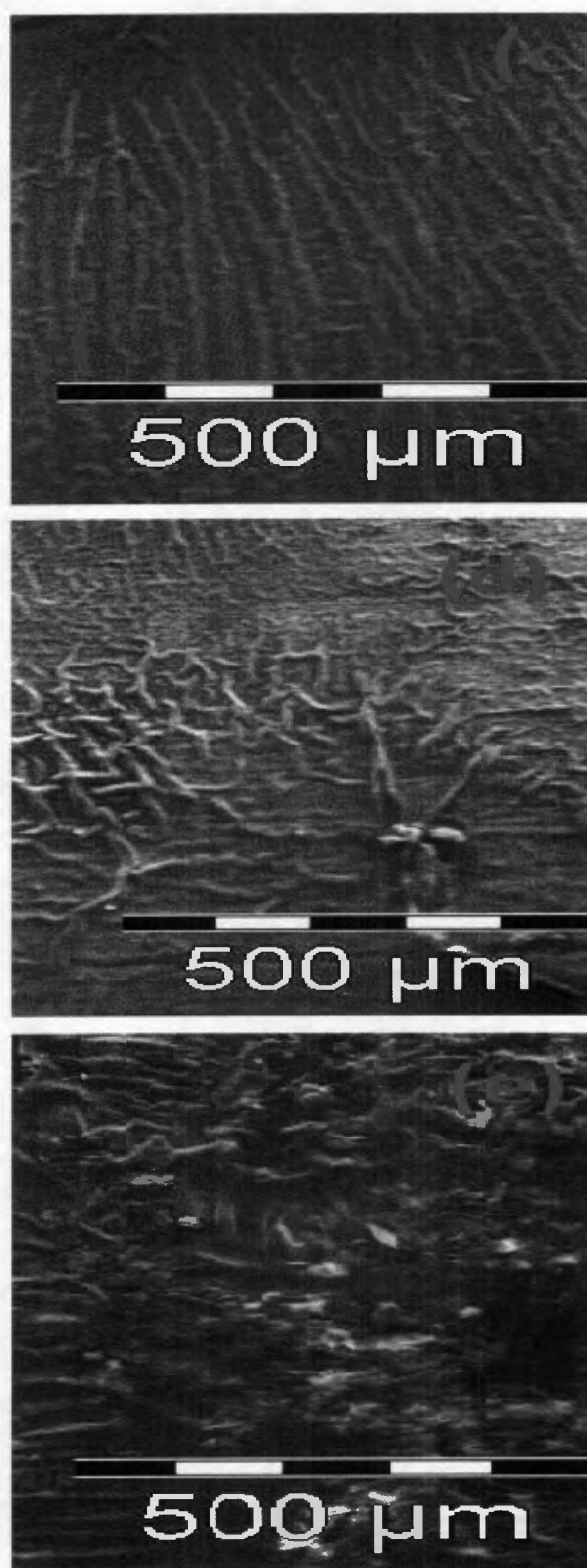


Figure AV-4. SEM images of mild steel surfaces immersed in 1 M HCl without and with 100 ppm of the studied inhibitors (c) ENCZ (d) CZE and (e) 3-ECZ.

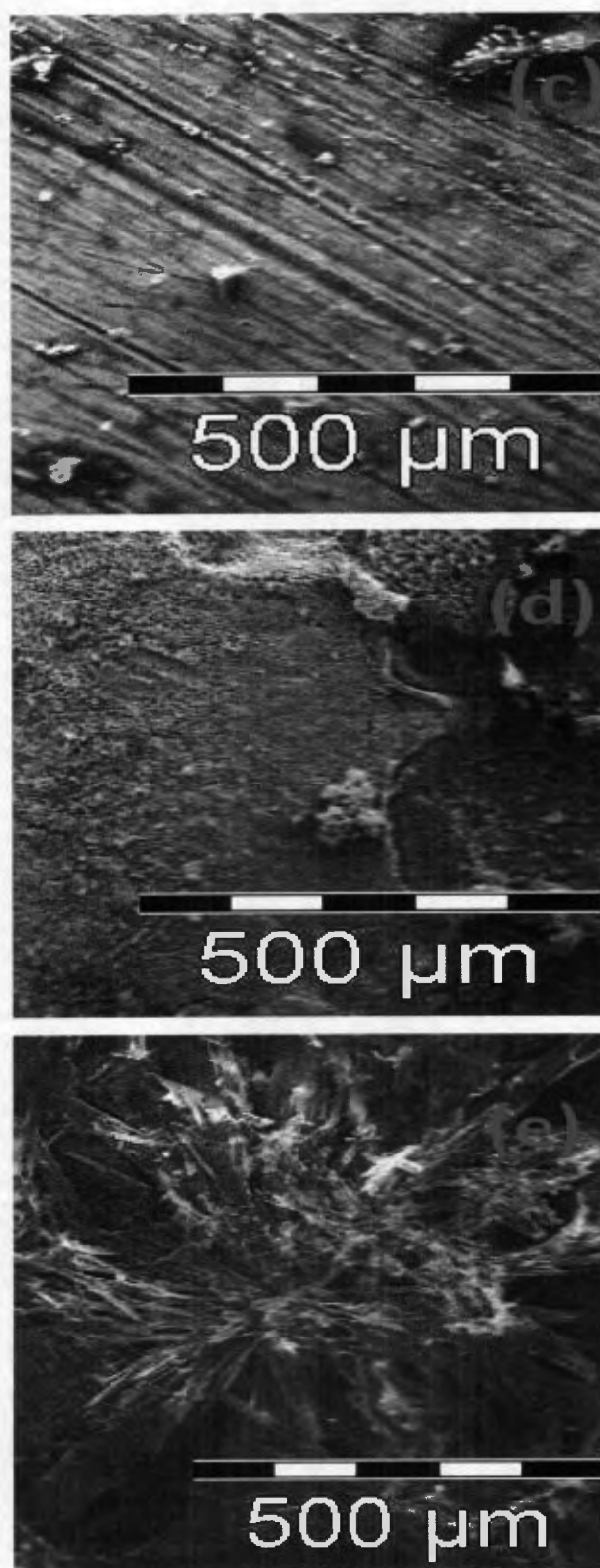
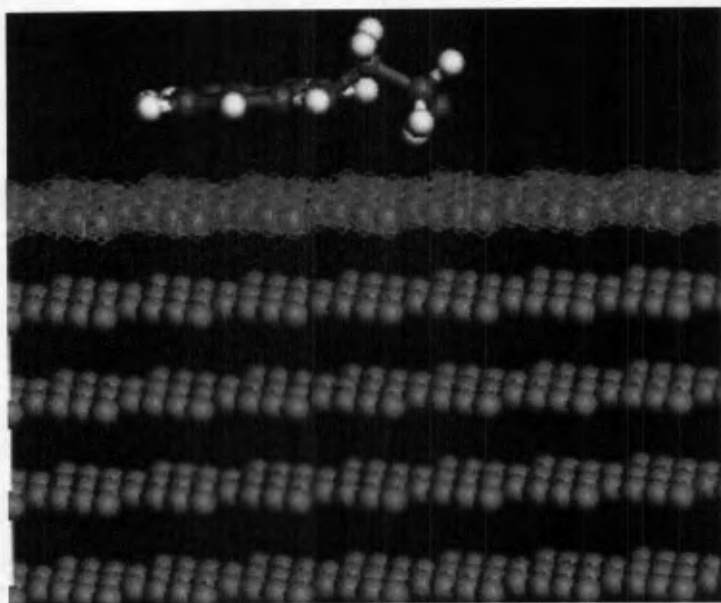
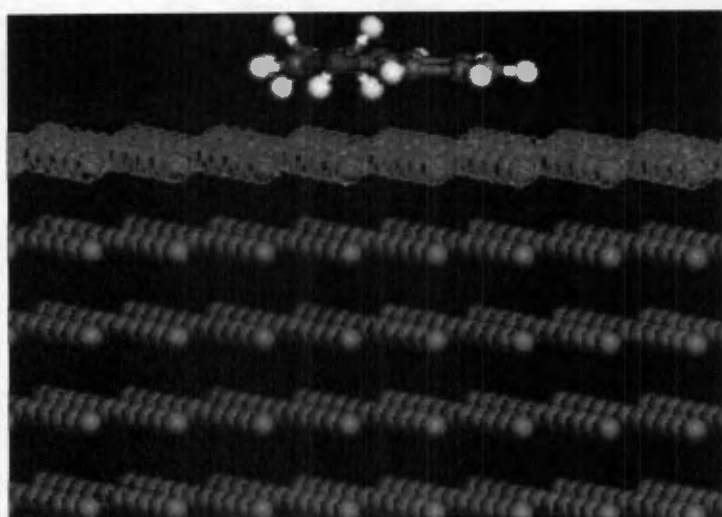


Figure AV-5. SEM images of mild steel surfaces immersed in *D.vulgaris* culture with 100 ppm of the studied inhibitors (c) ENCZ (d) CZE and (e) 3-ECZ.



Fe(110)/CZE



Fe(110)/3-ECZ

Figure AV-6. The most stable configurations for the adsorption of CZE and 3-ECZ on Fe(110)/inhibitor systems.

APPENDIX VI: PUBLISHED ARTICLES

1. **Henry U. Nwankwo**, Lukman O. Olasunkanmi, Eno E. Ebenso, Experimental, quantum chemical and molecular dynamic simulations studies on the corrosion inhibition of mild steel by some carbazole derivatives. *Scientific Reports*. 2017, 7, 1-18.

APPENDIX VII: CONFERENCES

1. SACI Young Chemists Symposium, October 2016, WITS School of Chemistry, South Africa.

Oral presentation: Biocidal and corrosion inhibition activities of some carbazoles: electrochemical, quantum chemical, surface morphological studies and weight loss analysis approaches.