

Inhibition of aluminium corrosion using phthalocyanines- Experimental and computational studies

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By

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DEDICATION

This work is dedicated to all **MEN** of **GOODWILL** and particularly to my parents Cornelius Amaefula Nnochiri Nnaji (father) and Mary Nwanneamaka Nnaji (mother).

My beautiful and lovely wife Chinyere and daughters Nwaihe and Chidimma.

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Glory be to **ALMIGHTY GOD**, the father of all creation, for HIS grace, provision and protection. To HIM I say thank YOU FATHER.

Abstract

Metal deterioration over time is a process known as corrosion, an electrochemical process, which can occur by surface chemical actions on metals by its environment. Metal corrosion have great economic, security, and environmental consequences, and its control is a major research area in corrosion science. Amongst the different corrosion protecting approaches, the use of corrosion inhibitors and protective coatings have attracted enormous research interest in this area of scholasticism. This has necessitated the computational and electrochemical investigations of aluminium corrosion inhibitive potentials of some compounds in 1M HCl.

Metal free (**5**_{H₂}), ClGa(III) (**5**_{Ga}) and Co(II) (**5**_{Co}) tetrakis(4-acetamidophenoxy)phthalocyanines as well as Co(II) 2,9,16-tris(4-(tert-butyl)phenoxy)-23-(pyridin-4-yloxy)phthalocyanine (**6**) and Co(II) 2,9,16,24-tetrakis(4-(tert-butyl)phenoxy)phthalocyanine (**7**) were synthesized for the first time and studied for corrosion inhibition. The reported ClGa(III) tetrakis(benzo[d]thiazol-2-yl-thio)phthalocyanine (**1**), ClGa(III) tetrakis(benzo[d]thiazol-2-ylphenoxy)phthalocyanine (**2**), ClGa(III) tetrakis-4-(hexadecane-1,2-dioxy)-bis(phthalocyanine) (**3**) and ClGa(III) tetrakis-4,4'-((4-(benzo[d]thiazol-2-yl)-1,2-bis(phenoxy)-bis(phthalocyanine) (**4**) were also employed for corrosion inhibition of Al in HCl.

Corrosion inhibition measurements using electrochemical techniques showed that increased π conjugation caused (**1**) to (**2**) to outperform (**1a**) and (**2a**) respectively as aluminium corrosion inhibitors in 1.0 M hydrochloric acid. For

similar reason, (4) outperformed 2. (1) and (2) were successfully electrodeposited onto aluminium for corrosion retardation in 1.0 M hydrochloric acid solution. Measurements obtained from electrochemical impedance spectroscopy gave corrosion inhibition efficiency values of 82% for 1 and 86% for 2 in 1.0 M hydrochloric acid solution and showed that electrodeposited phthalocyanines have enhanced aluminium corrosion retardation than when in solution. The use of reduced graphene oxide nanosheets (rGONS) alone as aluminium corrosion inhibitor is discouraged because of poor aluminium corrosion inhibition in 1M HCl. However, synergistic effects were observed when rGONS was mixed each with (4) and (3). (5_H₂), (5_Ga) and (5_Co) decreased aluminium corrosion in 1M HCl and observation was that the heavier the atom the more decreased the protection and the free base performed best of the three. Studied tertbutylphenoxy-derived CoPcs (6 and 7) exhibited good aluminium corrosion inhibition properties in studied acidic solution and the unsymmetric CoPc (6) which has more heteroatoms, gave better performance. Quantum chemical calculations involved the use of density functional theoretical (DFT) approaches and gave results which corroborated with experimental findings.

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Abbreviations

AcPhPn	–	4-acetamidophenoxyphthalonitrile
Co(OAc) ₂	–	cobalt acetate
DBU	–	1,8-diazabicyclo [5.4.0] undec-7-ene
DCM	–	dichloromethane
DFT	–	density functional theory
DMSO	–	dimethylsulphoxide
DMF	–	dimethylformamide
EDX	–	energy-dispersive X-ray spectrometer
EtOH	–	ethanol
FTIR	–	Fourier-transform infrared
GO	–	graphene oxide
HOMO	–	highest occupied molecular orbital
LUMO	–	lowest unoccupied molecular orbital
MALDI-TOF	–	matrix-assisted laser desorption/ionization-time of flight
MPcs	–	metalated phthalocyanines
MeOH	–	methanol
Pcs	–	phthalocyanines
¹ H-NMR	–	proton nuclear magnetic resonance
rGONS	–	reduced graphene oxide nanosheets
SEM	–	scanning electron microscopy
TBABF ₄	–	tetrabutylammonium tetrafluoroborate

TLC	–	thin layer chromatography
THF	–	tetrahydrofuran
UV-vis	–	ultraviolet visible
XRD	–	X-ray diffraction

List of symbols

T	–	absolute temperature
C	–	concentration
j_{corr}^0	–	corrosion current density without coating
j_{corr}	–	corrosion current density with coating
K_{EI}	–	El-Awady equilibrium constant
Y_{EI}	–	El-Awady adsorption parameter
ΔE	–	energy gap
E_{HOMO}	–	energy of the highest occupied molecular orbital
E_{LUMO}	–	energy of the lowest unoccupied molecular orbital
K_{ads}	–	equilibrium adsorption constant
ΔN	–	fraction of electron transferred from inhibitor to metal
K_{F}	–	Fruendlich equilibrium constant
n	–	Fruendlich adsorption parameter
R	–	gas constant
ΔG_{ads}^0	–	Gibbs free energy of adsorption
η	–	global hardness
δ	–	global softness
χ	–	global electronegativity
A_0	–	infrared absorbance peak for corroded aluminum without inhibitor
A_x	–	infrared absorbance peak for corroded aluminum with inhibitor
IE	–	inhibition efficiency
H_{wi}	–	peak height of corroded metal in the presence of inhibitor

- H_w – peak height of corroded metal in the presence of inhibitor
- IR – relative corrosion rate
- IR_{wi} – relative corrosion rates of the metal with inhibitor
- IR_w – relative corrosion rates of the metal without inhibitor

CHAPTER ONE

INTRODUCTION

Chapter One

Introduction

1. Introduction

The introduction discusses the problem of aluminium corrosion, mechanisms of corrosion and corrosion inhibition. The adsorption properties of corrosion inhibitors, electrochemistry of phthalocyanines and computational techniques applied in describing properties of corrosion inhibitors are discussed herein. The chapter highlights the rationale for use of phthalocyanines and a few precursors as corrosion inhibitors separately, when combined with nanomaterial (reduced graphene oxide nano sheets) and when electrodeposited on the Al metal.

1.1 Corrosion inhibiton

1.1.1 Background on corrosion

Man's recent civilization advancements depend on aluminium and its alloys, for example in aerospace, automotive, construction, electronics, house hold appliances and defense/military applications [1]. The usefulness of aluminium and its alloys is derived from their very good physical and mechanical properties such as their high strength-to-weight ratio, recyclability, good machining properties, as well as their out-standing resistance to corrosion. The corrosion resistance of aluminium and its alloys is attributable to the formation of a stable protective thin film of aluminium oxide when exposed to the atmosphere. Nevertheless, when exposed to an aggressive environment (acidic), aluminium is prone to corrosion and degradation. The protective oxide film is of amphoteric

character and easily dissolves in strong acidic media [2] leading to a sequence of electrochemical reactions. Corrosion control of aluminium can be enhanced by the addition of some inorganic substances to the corrodent. These substances include phosphates, chromates, dichromates, silicates, arsenates, tungstates, molybdates, chlorides and so on [3, 4]. These inorganic inhibitors exhibit toxic effects and are therefore not environmentally friendly. As a result, there has been a search for corrosion inhibitors which are not harmful to the environment.

Fortuitously, certain organic substances containing polar functionalities with nitrogen, sulphur and/or oxygen atoms in the conjugated system have been reported to exhibit good corrosion inhibiting properties of aluminium in acidic environments [5, 6]. The results of all these studies suggest that the inhibitory behaviour of the organic compounds is by forming a protective layer between the metal surface and the corrodent. The adsorbate layer formed, isolates the metal surface from the corrodent thereby reducing the corrosion rate of the metal surface. These studies have also yielded some insights into the adsorption mechanisms responsible for the inhibitive properties of organic inhibitors. It has been recognized organic inhibitors are viable and highly beneficial for metal corrosion protection in acidic environment. A major setback is that most of the organic corrosion inhibitors reportedly are effective at high concentrations and are of environmental concern due to their toxicity.

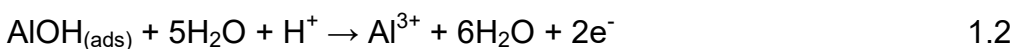
Despite the vast number of corrosion inhibition investigations, much has not been achieved as it concerns designing organic corrosion inhibitors which can effectively protect metals from rapid corrosion in acidic environments at low

concentrations. The need for an eco-friendly corrosion inhibitor has therefore attracted the investigation of aluminium corrosion inhibition properties of selected phthalocyanines and their precursors.

1.1.2 Mechanism of corrosion

Different mechanisms have been proposed to represent aluminium corrosion steps in different environments and in the presence of chloride ions [7].

Mechanism of aluminium corrosion in acid is shown by equations 1.1 to 1.4 [6]:



where X = halide

In alkaline medium, the dissolution mechanism proposed is shown by equations 1.5 and 1.6 [8]:

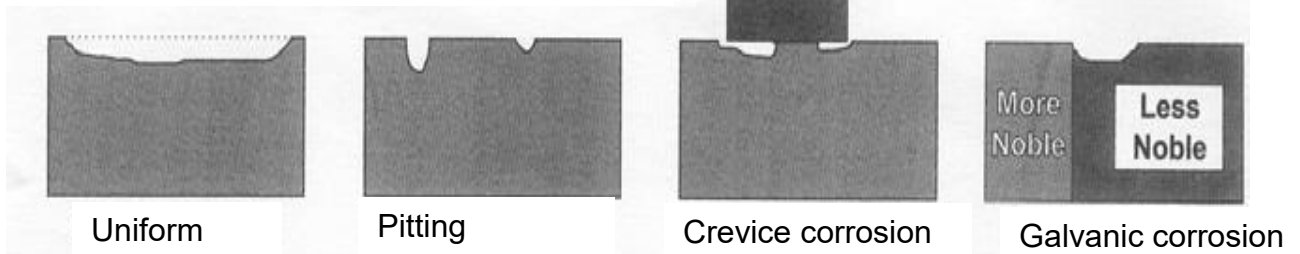


These metal surface interactions lead to their deterioration based on their modes/mechanisms of actions and cause types of corrosion as described in Table 1.1 and shown in Figure 1.1 from a lecture series [9].

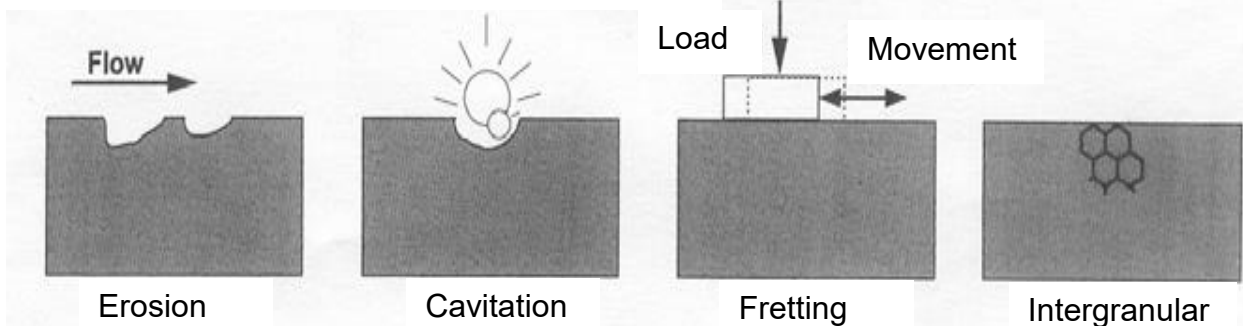
Table 1.1: Types of corrosion [9]

Types	Description
Uniform	whole metal surface deteriorates and surface becomes thin
Pitting	formation of pits on metal surface due to random corrosion attacks
Crevice	concentration cell corrosion caused by the trapping of corrosive liquid between the gaps of the metal
Galvanic	different metals in contact deteriorate in the presence of an electrolyte
Erosion	also flow-assisted corrosion, caused by the movement of corrosive liquids on metal surface.
Cavitation	occurs when bubbles/droplets are formed during flow-assisted corrosion
Fretting	type of erosion-corrosion due to the combined effect of corrosion and metal fretting
Intergranular	corrosion preferably at grain boundaries
Exfoliation	type of intergranular corrosion found at elongated grain boundaries
De-alloying	a type found in some alloys whereby more reactive metal is lost and more corrosion-resistant metal retained in a porous state
Stress-corrosion cracking	corrosion type from external deformation (strain) of the metal due cracking
Corrosion fatigue	combination of cyclic stress and corrosion

Group I: identifiable by visual inspection



Group II: identifiable with special inspection tools



Group II: identifiable by microscopic examination

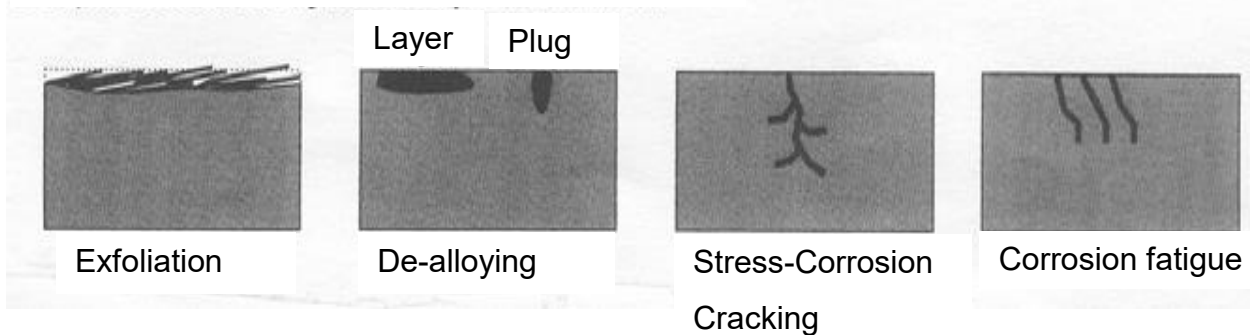


Figure 1.1: Types of corrosion [9]

1.1.3 Corrosion Inhibition

Corrosion inhibitors are substances which when added to corrosive environment decrease the rate of attack on a metal or alloy. Therefore, they are mainly used to control the corrosion rate and are classified according to their effect on the electrochemical reactions, which make up the overall corrosion process. They are classified into three main types: anodic, cathodic and mixed inhibitors.

1.1.3.1 Classification of corrosion inhibitors

Anodic Inhibitors: These inhibitors affect the anodic reaction and its polarization curve, such that a large potential change results from a small current flow. Usually the potential shifts to more positive direction (anodic direction), Fig. 1.2. As an illustration, the anodic reaction of aluminium whereby a metal dissolves while releasing electron are represented by equations 1.1, 1.2 and 1.5. Calcium nitrate, calcium nitrite and potassium nitrate are examples of anodic corrosion inhibitors [10].

Cathodic Inhibitors:- These types of inhibitors mainly influence the cathodic reaction and the cathodic polarization curve, in a way that values of potential shift towards more negative values (cathodic direction) as shown in Figure 1.2. An examples of a cathodic inhibitor is *Jasminum nudiflorum* leaf extract [11].

Mixed Inhibitors:- Mixed inhibitors work to inhibit both anode and cathode reactions. Examples are 1,3,4-thiadiazole-2,5-dithiol and 5-(3-aminophenyl) tetrazole [12, 13]. Mixed inhibitors work to inhibit both anode and cathode reactions.

Corrosion inhibition can be accomplished by one or more of the following mechanisms [14]:

- some inhibitors retard corrosion by adsorbing as a thin and invisible film on the material surface;
- other inhibitors form visible bulky precipitates, which coat the metal and protect it from attack;

- in some other cases, the mechanism consists of causing the metal to corrode in such a way that a combination of adsorption and corrosion products form a passive layer.

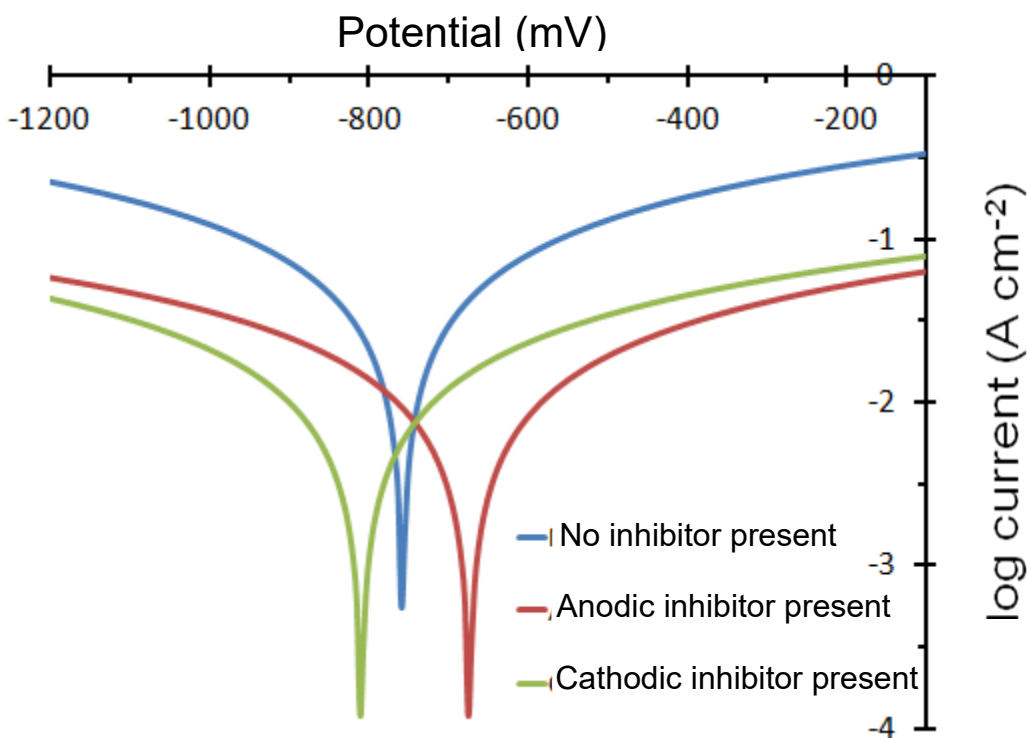
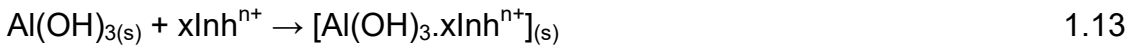


Figure 1.2: Schematic diagram showing effect of inhibitors on polarization curve

1.1.3.2 General corrosion inhibition mechanism

The aluminium surface possesses a positive charge in aqueous acidic solutions [15], this attracts the negatively charged chloride ions which adsorb onto the metal surface and subsequently attracts the inhibitor molecules in their protonated forms leading to the formation of the protective thin film. A proposed

corrosion inhibition mechanism for aluminium corrosion is shown by equations 1.7 to 1.13 [16]:



where n = number of protonated sites on the inhibitor (inh) molecule, x = stoichiometric number of inhibitor molecules, aq = aqueous and s = solution.

Eqs. 1.7 and 1.8 respectively show acid ionization and water hydrolysis reactions involved in the corrosion process. Others are Eq. 1.9 (metal oxidation or corrosion), Eqs. 1.10 and 1.11 (formation of corrosion products) and Eqs. 1.12 and 1.13 (protective film formation). In the case of aluminium metal in the absence of acid or alkaline environment, water hydrolyses and attacks the metal to give little corrosion. This quickly forms the hydroxide or oxide (bayerite or alumina) which passivates the surface and prevents further corrosion. In the presence of acid or alkaline medium however, corrosion inhibitor should prevent further corrosion as equations 1.12 and 1.13 suggest. Similar to eqs. 1.12 and 1.13, metal-inhibitor complex formation was proposed earlier by researchers [16].

1.1.4 Isotherms

Adsorption isotherms help in understanding the nature of adsorption and also to determine various kinetic parameters of the adsorbate and adsorbent. There are many adsorption isotherms, but few will be discussed briefly here: Langmuir, Freundlich, Temkin and El-Awady.

1.1.4.1 Langmuir Adsorption Isotherm

Adsorbate molecule (A) interacts with adsorbent site (S) to form (AS) [17],



Equation 1.15 is the derived Langmuir isotherm and also known as the saturation growth rate model, a non linear function which has one of its linear forms as:

$$C/\theta = 1/K_L + C \quad 1.15$$

The inhibitor concentration is represented by C, θ represents surface coverage and K_L is the Langmuir isotherm parameter which characterizes the equilibrium constant of the adsorption process.

From equation 1.15, a plot of C/θ versus C should give a slope of unity and intercept from which K_L is determined. A situation whereby the slope of unity is obtained, Langmuir type of adsorption is obeyed.

Langmuir types of adsorptions are characterized as follows:

1. adsorption of adsorbate can only cover monolayer of adsorbent;
2. adsorption sites on adsorbent are similar and accommodate an adsorbate molecules; and
3. adsorbed adsorbate molecules do not interact with themselves.

1.1.4.2 Freundlich Adsorption Isotherm

Freundlich isotherm describes a reversible and non-ideal adsorption process whereby adsorption heat (ΔH_{ads}) does not need to be uniformly distributed on the heterogeneous surface [18]. Freundlich isotherm is described by equation 1.16 [19]:

$$\ln \theta = \ln K_F + (1/n) \cdot (\ln C) \quad 1.16$$

K_F is the Freundlich isotherm parameter which characterizes the equilibrium constant of the adsorption process, n is an Freundlich isotherm parameter which characterizes the number of inhibitor adsorbed layers. C and θ are described above.

1.1.4.3 Temkin Adsorption Isotherm

This isotherm models adsorption at moderate/intermediate concentration range, assumes that adsorption heat is a function of temperature and decreases linearly as surface coverage of molecules increase [20]. Temkin adsorption isotherm is represented by eq. 1.17:

$$\theta = (1/f) \cdot (\ln K_T + \ln C) \quad 1.17$$

K_T is the Temkin isotherm parameter that characterizes equilibrium constant of the adsorption process. C and θ are as described above. The parameter ' f ' describes molecular interactions in the adsorbed layer and if it has positive values, it indicates attraction forces between the adsorbed molecules while negative values indicate repulsive forces between the adsorbed molecules [21].

1.1.4.4 EI-Awady Adsorption Isotherms

The linear adsorption isotherm (equation 1.18) derived by EI-Awady and co-workers [22] was based on kinetic-thermodynamic assumptions.

$$\ln \left[\frac{\theta}{(1-\theta)} \right] = \ln K_{EI} + Y_{EI} \ln C \quad 1.18$$

K_{EI} is the EI-Awady isotherm parameter which characterizes equilibrium constant of the adsorption process, C and θ are as described above. The parameter ' Y_{EI} ' describes molecular interactions in the adsorbed layer.

1.1.5 Organic corrosion inhibitors from plants with deforestation concern

Metal corrosion is known to be inhibited by extracts from plant materials. Earlier, the inhibitive action of *Sansevieria trifasciata* leaf extracts on aluminium corrosion in 2 M HCl and 2 M KOH solutions appeared in literature [4]. Another example was earlier reported for stem bark extracts of *Moringa oleifera*, *Terminalia arjuna* and *Mangifera indica* on the corrosion protection of aluminium alloy in 1 M NaOH [23]. Corrosion inhibition properties are reported for extracts of *Xanthium strumarium* leaves, *Valeriana wallichii* root, Fenugreek leaves, olive roots, stems, and leaves, and alcoholic extracts of *Lycium shawii*, *Teucrium oliverianum*, *Ochradenus baccatus*, *Anvillea garcinii*, *Cassia italica*, *Artemisia sieberi*, *Carthamus tinctorius*, and *Tripleurospermum auriculatum* [24–28]. Phytochemicals are responsible for the exhibited metal corrosion retardation properties of plant extracts. Examples are as reported in the work of Al-Otaibi and co-workers [28] which are: neo-clerodane diterpenoids and their derivatives: *Ochradenus baccatus* flavanoids and their glycosides, *Anvillea garcinii*

germacranolides, *Cassia italica* coumarins, carotenoids, flavonoids, sterols, anthraquinones and triterpenes, *Artemisia sieberi* flavanoids, terpenoids and their glycosides, *Carthamus tinctorius* unsaturated fatty acids, flavanoids and their glycosides, adenosine, adenine, uridine, thymine, uracil, roseoside, acetylenic and aromatic glycosides, *Tripleurospermum auriculatum* unsaturated fatty acids and sterols.

Aforementioned reports affirmed good metal retardation properties of studied plant extracts, however, deforestation concerns arise. Some of the challenges of deforestation are soil erosion, excessive leaching of soil nutrients, global warming and challenges associated with it. The use of plant extracts as replacements to inorganic corrosion inhibitors therefore is not encouraged, this has necessitated the use of organic corrosion inhibitors as alternatives.

1.1.6 Synthesized organic corrosion inhibitors

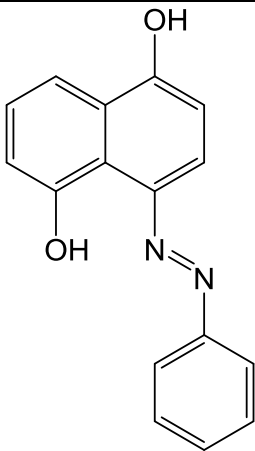
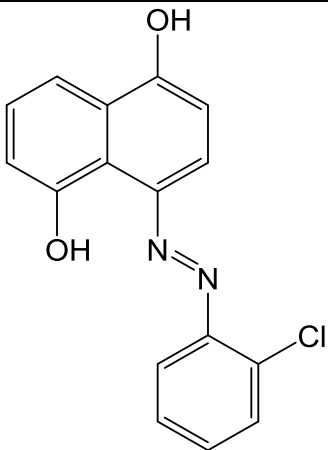
Some organic aluminium corrosion inhibitors include: benzotriazole, sodium benzoate, 8-hydroxyquinoline, 2-mercaptobenzotriazole and 3-amino-1,2,4-triazole-5-thiol [29]. Earlier study reported aluminium corrosion inhibition properties of three mono azo dyes [30].

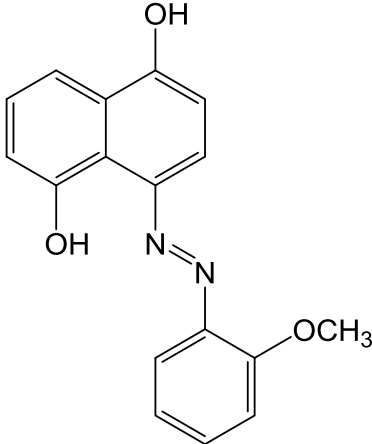
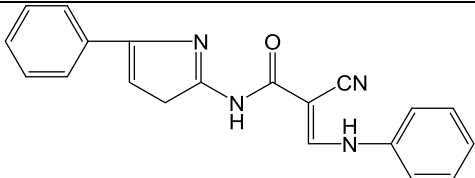
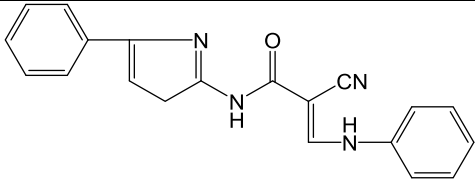
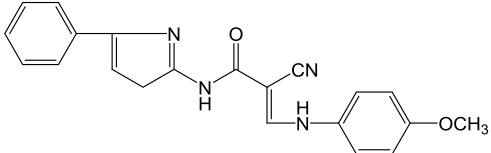
Some of the organic molecules shown in Table 1.2 have been reported for aluminium corrosion inhibition [30, 31].

These aforementioned organic inhibitors did not perform too well, therefore the need arose to look at other classes of compounds that possess more conjugated

π -electrons which translates to more planarity and more hetero-atoms. The lot fell on phthalocyanines.

Table 1.2: Organic corrosion inhibitors for Al in 0.01 M NaOH

Compound	Inhibition efficiency	Reference
	45.6%	[31]
	55.8%	[31]

	73.6%	[31]
	31.7 %	[30]
	44.1 %	[30]
	55.2 %	[30]

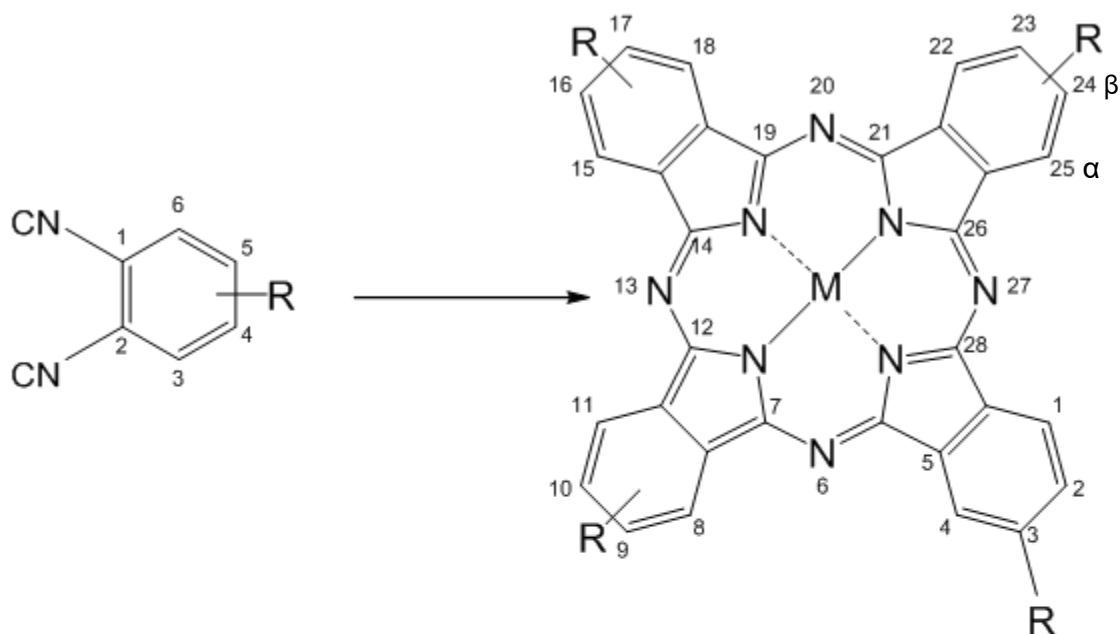
1.2 Phthalocyanines

1.2.1 Phthalocyanines- history, syntheses and general applications

Phthalocyanines (Pcs) are synthetic macrocycles which are structurally similar to porphyrins that exist in nature, such as hemoglobin, chlorophyll, and vitamin B12. A phthalocyanine was accidentally discovered during the preparation of 2-cyanobenzamide [32] and much later, Diesbach and co-worker [33] obtained a

Pc from 1,2-dibromobenzene in 1927. In an attempt to elucidate its structure, Linstead and his co-workers made metalated phthalocyanines (MPcs) via many synthetic routes [34, 35] and Robertson performed the X-ray diffraction analyses of them [36, 37].

Schemes 1.1 and 1.2 present the syntheses of symmetric and asymmetric phthalocyanines, respectively. The syntheses of α and β substituted tetrasubstituted Pcs require respectively the use of 3-nitrophthalonitrile for nonperipheral (α) and 4-nitrophthalonitrile for peripheral (β) as the starting materials. Modification of these phthalonitriles afford different types of substituted phthalocyanines. Symmetric Pcs are synthesized using similar phthalonitriles and four isomers obtained which are difficult to separate. Asymmetric types are synthesized using two dissimilar phthalonitriles forming six isomers and the desired asymmetric type AAAB is separated through extensive chromatography, Scheme 1.2. These were done in this work.



Conditions of reactions

-appropriate solvents (1-pentanol, nitrobenzene, quinoline and others) **R** = H for unsubstituted Pc or substituent choice

-reflux in an inert atmosphere (N_2 or Ar)

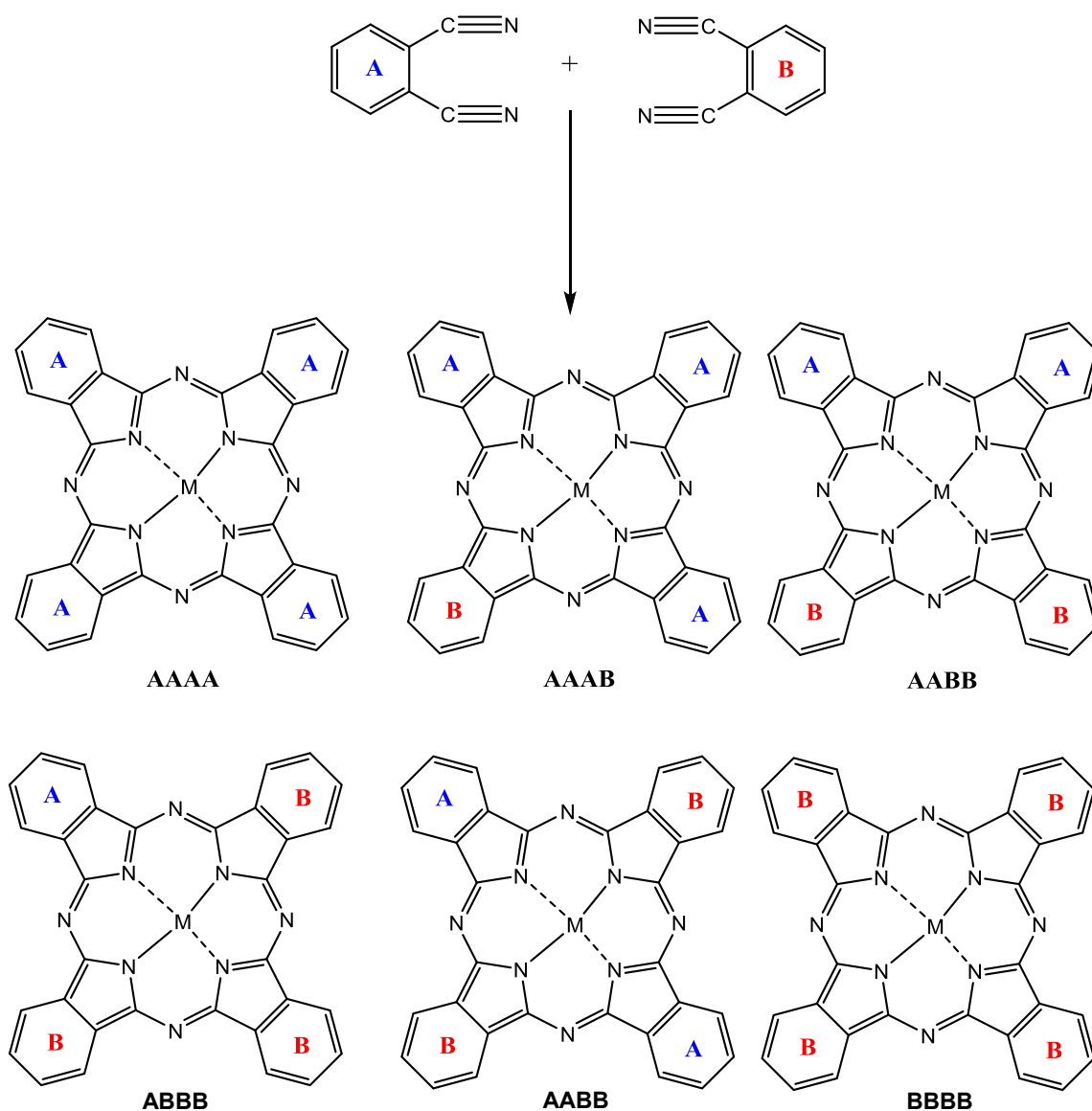
M = H_2 for metal free Pc or metal ion for MPc

-absence or presence of metal salts

R on position 4 gives peripheral tetrasubstituted Pc and on position 3 gives non-peripheral tetrasubstituted Pc

-catalyst (1, 8- diazobicyclo-[5,4,0]-undec-7-ene also known as (DBU), urea)

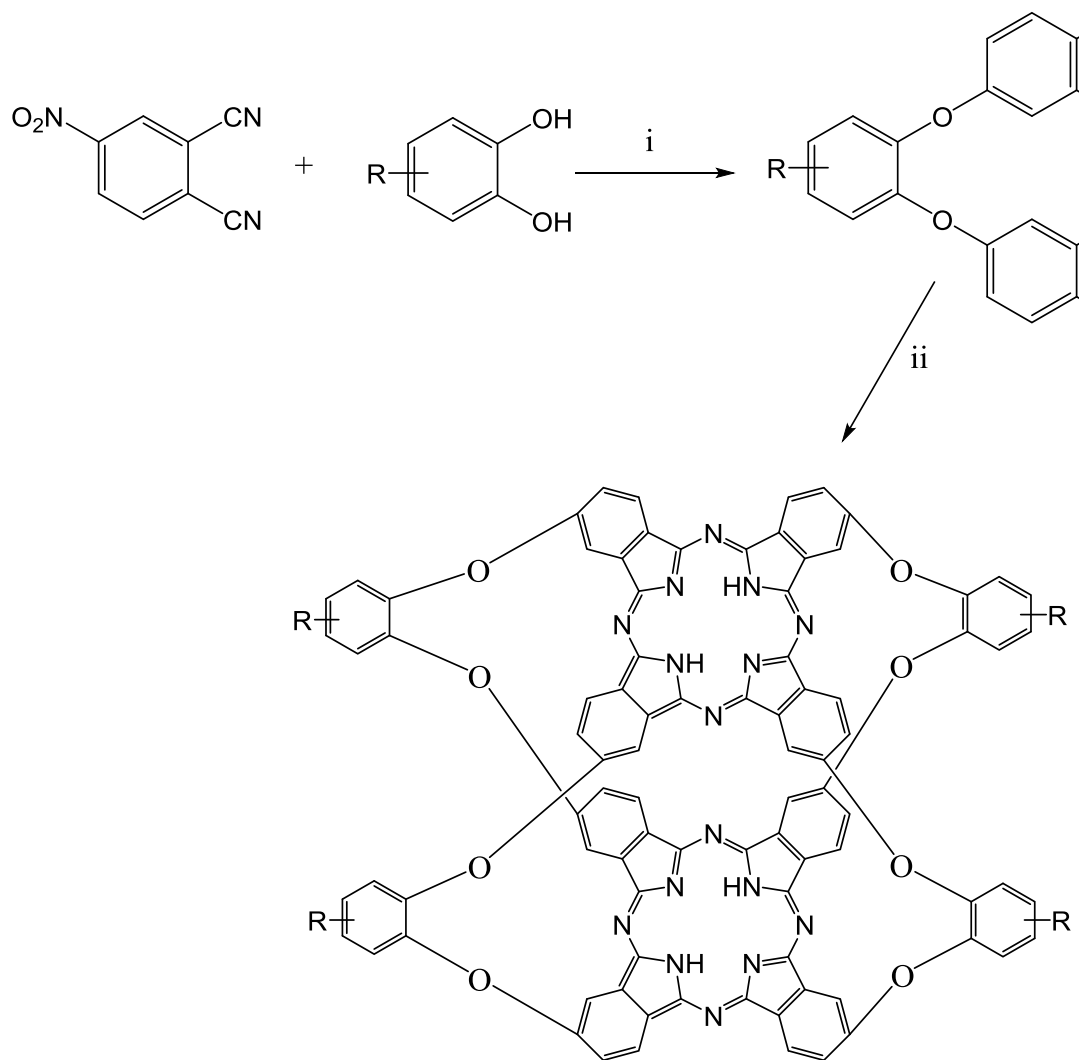
Scheme 1.1: A synthetic route for symmetrical phthalocyanines



Scheme 1.2: Synthetic route for asymmetrical phthalocyanines

Scheme 1.3 presents the synthetic route for ball-type Pcs which are two Pc monomers arranged cofacially with four bridging substituents on the peripheral positions of the benzene rings [38]. There seem to be a dearth of knowledge on the use of ball-type phthalocyanines as corrosion inhibitors therefore, binuclear ball-type phthalocyanines are studied in this work for metal corrosion inhibition

for the first time. The phthalonitrile precursors as corrosion inhibitors are also reported for the first time in this work.



Conditions of reaction

i: -appropriate solvent (dimethylformamide, dimethylsulphoxide)

- Na_2CO_3

-sometimes with heating at 50-100°C

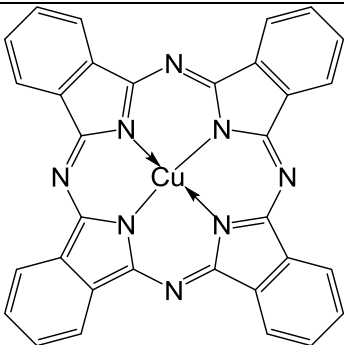
ii: -appropriate solvent (1-pentanol, hexanol)

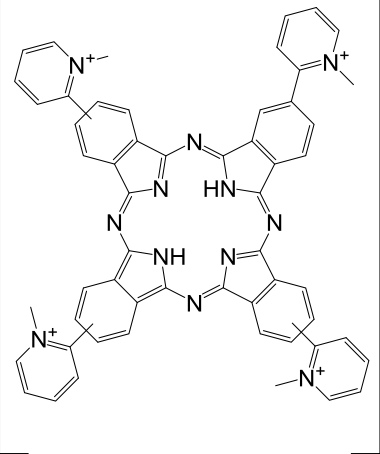
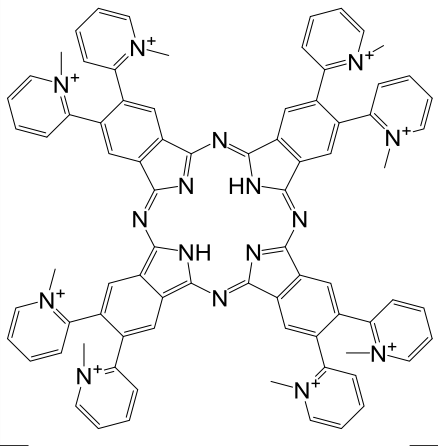
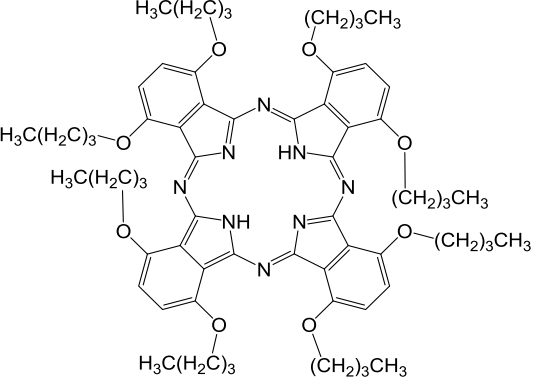
Scheme 1.3: Synthetic route for ball-type phthalocyanines [38]

Phthalocyanines have found usage in colour filters for liquid crystal displays, organic semiconductors, electrophotography, ink jet printing, solar screen, flash fusion of toners, laser thermal transfer, optical data storage, security, singlet oxygen production (washing powders and photodynamic therapy, non-linear effects (reverse saturable absorbers) [39] and corrosion inhibition.

Table 1.3 shows works reported elsewhere [40–42] on phthalocyanines as corrosion inhibitors. The reports do not seem to address the following: the effect of increased π -electron system on aluminium corrosion protection; the synergistic effect of the Pc/nanomaterials on protecting aluminium corrosion; the effect of central metal on aluminium corrosion inhibition efficiency; and the effect of symmetry. In the light of these, this study therefore seeks to fill these gaps in this area of study.

Table 1.3: Structures of phthalocyanine used as corrosion inhibitors

Compound	Metal	Solution	Inhibition efficiency	Reference
	Steel	16% HCl	94%	[40]

 2SO₄²⁻	Al	0.1 M HCl	83%	[41]
 4SO₄²⁻	Al	0.1 M HCl	63%	[41]
	Al	1 M HCl	90.3%	[42]

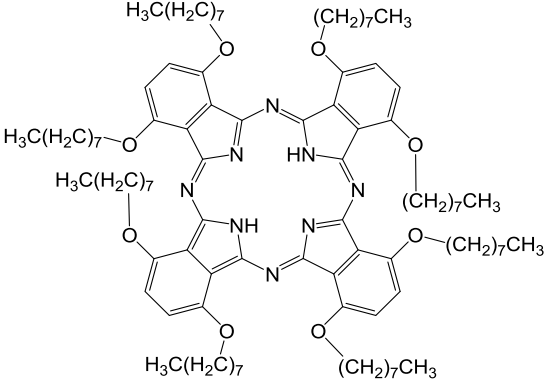
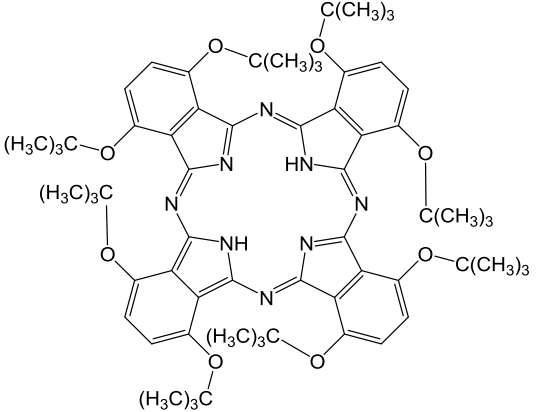
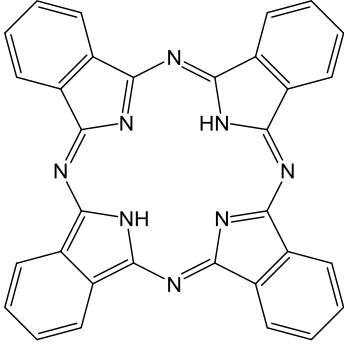
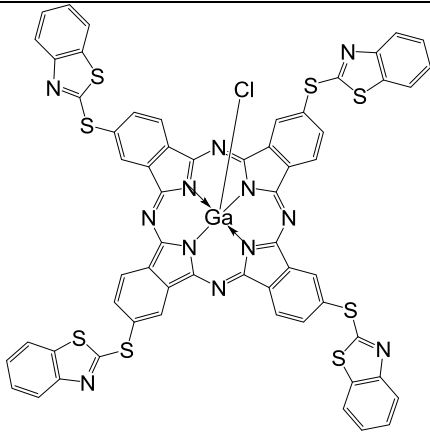
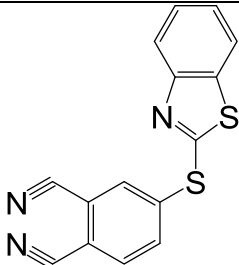
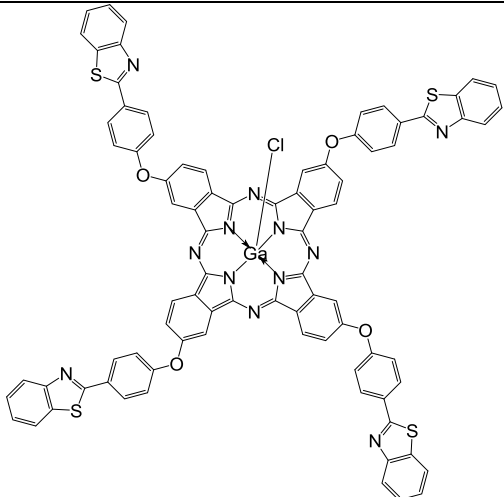
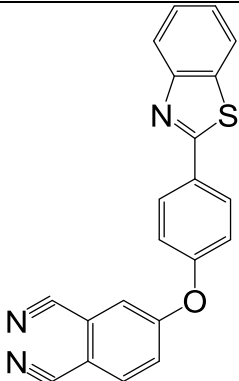
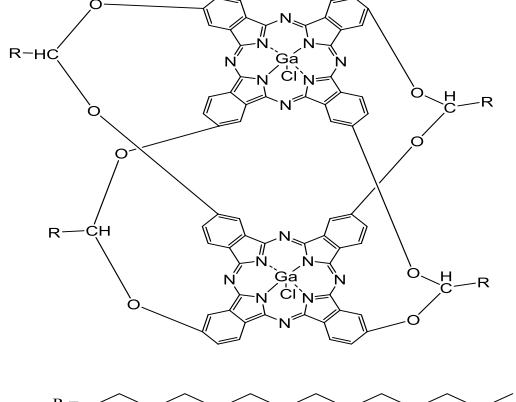
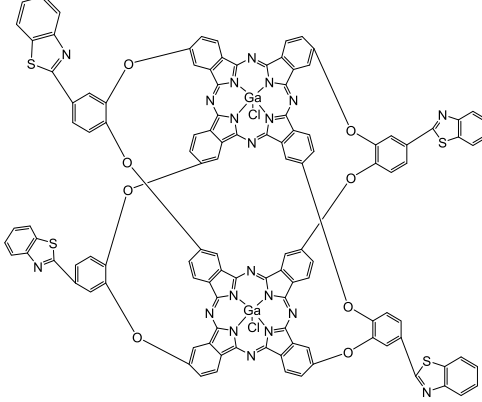
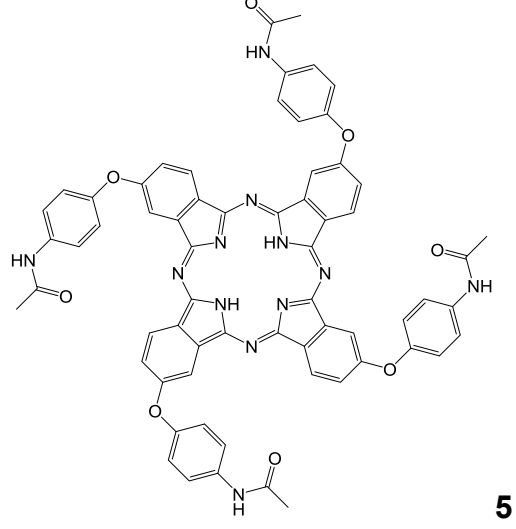
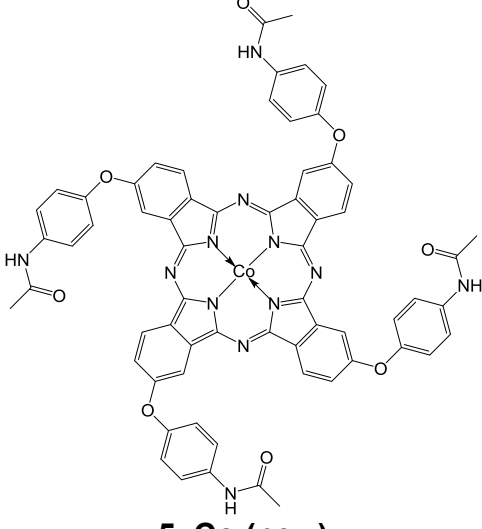
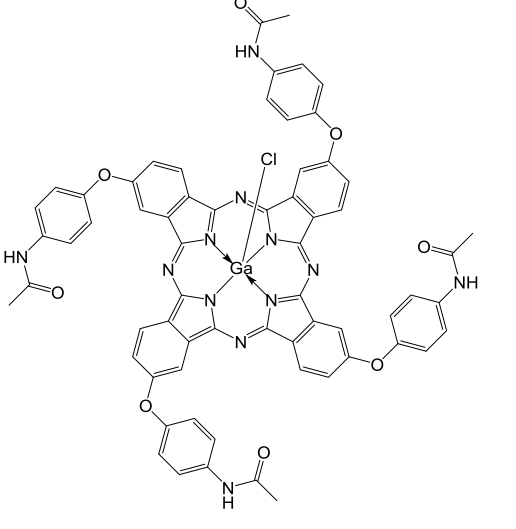
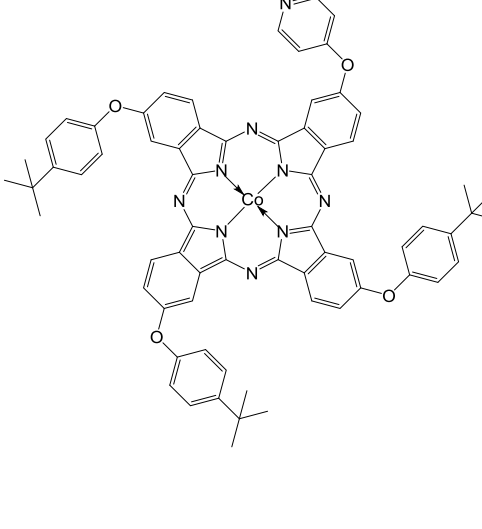
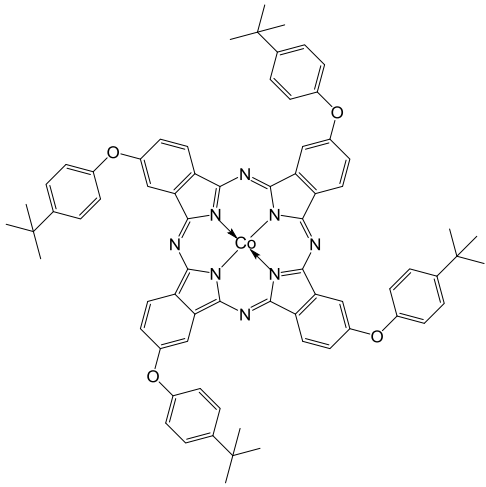
	Al	1 M HCl	77.4%	[42]
	Al	1 M HCl	86.9%	[42]
	Al	1 M HCl	91.5%	[42]

Table 1.4 presents phthalocyanines used in this work. Complexes **1**, **2** and **3** are known [43–46], the rest are new.

Table 1.4: Structures of phthalocyanines and precursors investigated in this study

Compound		Reference
 1 (not new)	 1a (not new)	[43]
 2 (not new)	 2a (not new)	[42, 44]

 3 (not new)	 4 (not new)	[45, 46]
 5 _H₂ (new)	 5_Co (new)	New
		New

5_Ga (new)	6 (new)	
 7 (new)	New	

1.2.2 Summary of aims

Broadly stated, the aim of this study was to further investigate the corrosion inhibition potentials of selected phthalocyanines on aluminium in dilute HCl solution. The aims of this work are summarized as follows:

1. syntheses of phthalocyanines and precursors
2. corrosion inhibition by phthalocyanines
3. the corrosion inhibition of phthalocyanine/reduced graphene oxide nanomaterials (rGONS) synergy
4. the effect of increased π -electron system of **1a** compared with **1** and **2a** compared with **2** on aluminium corrosion protection;
5. the effect of ball type Pc (**4**) over mono-Pc (**2**)

6. whether the nature of substituents of complexes **3** and **4**, **5_Co** and **6** have significant effect on aluminium corrosion inhibition;
7. if the effect of central metal is a significant factor of aluminium inhibition efficiency considering complexes **5_H2**, **5_Co** and **5_Ga**; and
8. the effect of symmetry by comparing complexes **6** and **7** inhibition efficiencies on aluminium corrosion.

1.2.3 Phthalocyanine electrochemistry (as regards electrodeposition)

The electron rich properties of MPcs has resulted in their uses in electrocatalytic processes as electron mediators on conducting substrates such as glassy carbon, indium tin oxide (ITO), or gold and give excellent electrochemical activities.

Neutral phthalocyanine exists as a dianion (Pc^{2-}) and oxidation or reduction may occur in successive steps. Oxidation involves electron removal from the highest occupied molecular orbitals (HOMO), a_{1u} , reduction is addition of electron to the HOMO (a_{1u}), to form the reduced complexes Pc^{3-} , Pc^{4-} , Pc^{5-} and Pc^{6-} [47], Fig. 1.3.

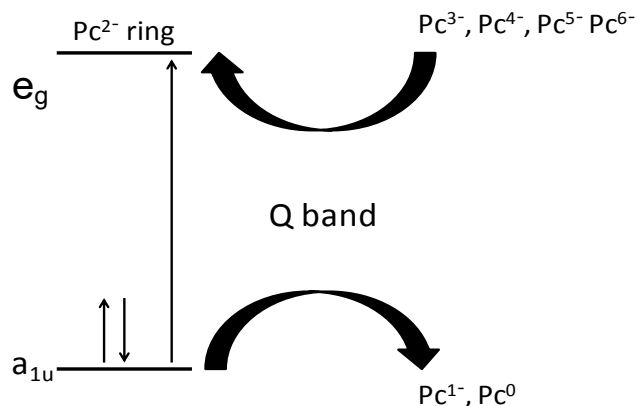


Figure 1.3: Phthalocyanine ring reduction and oxidation

In this work, Pcs were electrodeposited onto the electrode for use in corrosion inhibition. They are electrodeposited on the electrode by cyclic voltammetry. The amount of phthalocyanine deposited on the electrode is affected by the number of cyclic voltammetry scans [48].

1.3 Reduced graphene oxide nanoparticles (rGONS)

Corrosion inhibitors (such as polyaniline, dodecylamine, p-aminophenol) have been employed together with graphene oxide for improved corrosion inhibition [49–52]. Electrochemical deposition of polyaniline–reduced graphene oxide composite gave strong passivation of the Al alloy. The authors theorized that reduced graphene oxide possess active sites for the electro-polymerization of aniline which made the coating more complete and denser [49]. The presence of sp^2 hybridization in rGONS allows for interactions with other π containing molecules such as MPcs and this is employed in this work. GONS are reduced since this improves their performance [53]. Little or nothing is known about

rGONS/MPcs composites, for the first time, this study reports the corrosion inhibition properties of rGONS alone and in combinations with MPcs.

1.4 Quantum Chemical Calculations- role of modelling

Quantum chemical methods and molecular modeling techniques helps to define a large number of molecular quantities characterizing the reactivity, conformation, and molecular binding properties of a whole molecule, its fragments or substituents. The use of theoretical parameters presents two main advantages: firstly, the compounds and their various fragments or substituents can be directly characterized on the basis of their molecular structure only; and secondly, the proposed mechanism of action can be directly accounted for in terms of the chemical reactivity of the compounds under study [54].

Quantum mechanical methods (ab initio, density functional theory (DFT) and semi-empirical) are all based on solving the time independent Schrödinger equation for the electrons of a molecular system as a function of the positions of the nuclei.

The term ab initio indicates that the calculation is from first principles and that no empirical data is used. The simplest type of ab initio electronic structure calculation is the Hartree–Fock (HF), in which the instantaneous Coulombic electron–electron repulsion is not specifically taken into account and only its average effect is included in the calculation. This is a variational procedure, and, therefore, the obtained approximate energies, expressed in terms of the system wave function, are always equal to or greater than the exact energy, and

approach a limiting value called the Hartree–Fock limit as the size of the basis is increased [55]. Many types of calculations (Moller-Plesset perturbation theory and coupled cluster theory) begin with a Hartree–Fock calculation and subsequently correct for electron–electron repulsion, referred to also as electronic correlation. Earlier report [56] investigated the corrosion inhibition efficiency of dibenzo-diaza-15-crown-5 (N) and its heterocyclic analogs by ab initio MP2 calculations in aqueous phase.

Density functional theory (DFT) is used to investigate the electronic structure, principally the ground state of many-body systems, in particular atoms, molecules and the condensed phases. For example, it was used to study the corrosion inhibition performance of 1,3-thiazole and its amino derivatives by Guo and co-workers [57].

Semi-empirical approaches neglect many smaller integrals to speed up the calculations. In order to compensate for the errors from these approximations, empirical parameters are introduced into the remaining integrals and calibrated against reliable experimental or theoretical reference data [58]. Over the years, a large number of methods with different acronyms have been developed, including modified neglect of differential overlap (MNDO) [59], Austin model 1 (AM 1) [60], parameterized model number 3 (PM 3) [61]. Semi-empirical methods differ in the details of the approximations (e.g. the core–core repulsion functions) and in particular in the values of the parameters. The semi-empirical methods can be optimized for different purposes. The MNDO, AM 1 and PM 3 methods were designed to reproduce heats of formation and structures of a large

number of organic molecules. Other semi-empirical methods are specifically optimized for spectroscopic properties (e.g. INDO/S or CNDO/S). Semiempirical techniques (AM1, PM3, MNDO, MINDO/3, and INDO) were used to study the efficiency of 1,3-benzodioxole derivatives as corrosion inhibitors [62].

Herein, density functional theory (DFT) and semiempirical (PM3) techniques were used in the optimizations and calculations of molecular parameters of the studied corrosion inhibitors.

CHAPTER TWO

Materials and Experimental

2. Experimental

2.1 Materials

LiCl, n-pentanol, dimethylformamide (DMF), gallium (III) chloride, cobalt acetate ($\text{Co}(\text{OAc})_2$), chloroform, ethanol (EtOH), methanol (MeOH), acetone, graphene oxide (GO), tetrabutylammonium tetrafluoroborate (TBABF_4) and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) were obtained from Sigma-Aldrich. The progress of the reactions and chemical purity of the compounds were monitored using thin layer chromatography (TLC) and silica gel 60-HF254 as an adsorbent. Benzene and tetrahydrofuran (THF) were purchased from Sigma-Aldrich, dimethylsulphoxide (DMSO), toluene and dichloromethane (DCM) were purchased from Merck. All solvents were dried and purified as reported by Perrin and Armarego [63] before use. Aluminium coupons (>99%) were cut into $2 \times 2 \times 0.1$ cm sizes from metal sheets. The area of the working electrodes exposed to the electrolyte was 3.0 cm^2 . Hydrochloric acid (Merck) used was of the highest available purity (>37%). Type II (millipore) water was obtained from an Elga PURELAB Chorus 2 (RO/DI) system.

2.2 Equipment

- Shimadzu UV-2550 spectrophotometer was used for ground state electronic absorption spectra. Solutions for UV–visible spectra were in the $10^{-5} - 10^{-6}$ M concentration range.
- Scanning electron microscopy (SEM) images were obtained using a JSM 840 scanning electron microscope (JEOL, Tokyo, Japan). Energy-

dispersive X-ray spectrometer (EDX, INCA PENTA FET coupled with VAGA TESCAM operated at 20 kV) was used to qualitatively determine the elemental compositions.

- Perkin Elmer TGA 800 thermogravimetric analyser was used for thermogravimetric analyses (TGA) at a heating rate of 20 °C min⁻¹ in a high-purity nitrogen and air atmosphere, the resultant data was analysed with Pyris Version 13.1.1 software.
- X-ray diffraction (XRD) patterns were recorded using Bruker D8 Discover equipped with a Lynx Eye detector, using Cu-K α radiation (λ = 1.5405 Å, Nickel filter).
- Electrochemical studies were performed using an PGSTAT 30 Potentiostat (Autolab, KM Utrecht, The Netherlands) equipped with GPES software version 4.9.
- Potentiodynamic polarization and cyclic voltammetric experiments were carried out using a BAS 100B electrochemistry setup
- Electrochemical impedance spectroscopy (EIS) studies and open circuit potential measurements were performed using an PGSTAT 30 Potentiostat (Autolab, KM Utrecht, The Netherlands) equipped with GPES software version 4.9.
- ¹H NMR measurements in deuterated DMSO were performed using a Bruker® AVANCE 600 MHz NMR spectrometer.
- Elemental analyses were performed using a Vario-Elementar Microcube ELIII

- Bruker AutoFLEX III Smartbeam MALDI-TOF mass spectrometer was employed for the recording of mass spectra and α -cyano-4-hydroxycinnamic acid matrix was used.
- FTIR spectra of the films were obtained on an Alpha IR (100 FT-IR) spectrophotometer (Bruker, Billerica, MA, USA) with a universal attenuated total reflectance (ATR) sampling accessory.
- Theoretical calculations were done using Gaussian 09 program with Intel/Linux cluster [64]. The Gausview 4.1 or Avogadro program was used for all visualization.

2.3. Preparation of reduced Graphene oxide nanosheets (rGONS) and conjugates

2.3.1 Preparation of reduced Graphene oxide nanosheets (rGONS)

Reduced graphene oxide nanosheets (rGONS) were synthesized as reported in literature [65]. Ultrasonication aided the dispersion of 0.1 g graphene oxide nanosheets in 100 mL millipore water, followed by reduction using NaBH_4 (0.57 g, 15 mmol) and then heating at 70 °C for 3 h. The obtained black solid product was filtered over a fritted glass funnel, washed with water (5 × 50 mL) and dried in an oven at 70 °C. Treatment of the resulting sample with 98% H_2SO_4 was done to eliminate the aliphatic functionality and dehydrate the remaining hydroxyl functionalities to form alkenes that resemble graphitic sp^2 carbon network [65] to give rGONS.

2.3.2. Preparation of Pc-rGONS conjugates, Scheme 3.1

Non-covalent conjugation of rGONS to Pcs was performed as follows: rGONS (3 mg) were mixed with Pc **3** (6.8 mg) or Pc **4** (6.6 mg) in 30 mL of DMSO. The mixtures were then sonicated in a bath sonicator for 4 h followed by overnight stirring for 24 h. Thereafter, the mixtures were centrifuged at 3000 rpm for 10 min in ethanol to precipitate rGONS-**3**($\pi\pi$) and rGONS-**4**($\pi\pi$) nanohybrids out of the solution and to remove unreacted Pc or rGONS. The resulting nanoconjugates were left to dry in a fume hood for 96 h. Experiments where rGONS and complexes **3** and **4** were either mixed without allowing time for $\pi\pi$ stacking, represented as rGONS_**3** and rGONS_**4** respectively, were also undertaken.

2.4. Syntheses of phthalocyanines

The synthesis of 4-acetamidophenoxyphthalonitrile (AcPhPn) has been reported [66]. 4-(4-pyridyloxy) phthalonitrile and 4-tert-butylphenoxy phthalonitrile were synthesized according to literature methods [67, 68].

2.4.1 Tetrakis (4-acetamidophenoxy) phthalocyanine (**5**_{H₂}), Scheme 3.2

The free-base phthalocyanine (**5**_{H₂}) was synthesized as follows: 4-acetamidophenoxyphthalonitrile (AcPhPn) (0.3 g, 1.08 mmol) was dissolved in n-pentanol in the presence of LiCl (0.450 g, 10.08 mmol) and catalytic amount of DBU and degassed with nitrogen. The mixture was heated and stirred at 140 °C for 18 h under a N₂ atmosphere. The mixture of acetic acid/water was added, followed by cooling to room temperature and stirring for 2h. The formed

precipitate was collected by centrifugation. The product was washed several times with water and ethanol and further purification was carried out by dissolving in DMF and precipitating in ethanol (3 times). The desired pure **5**_{H₂} was obtained as a green solid.

Yield: 50% (0,15 g). FT-IR (UATR-TWOTM) ν max/cm⁻¹: 3285 (N-H stretching), 3051 (C-H asymmetric stretching), 1606 (C=C stretching), 1540 (C-H bending), 1212 (C-N bending and C=C stretching), 1096 (C-H in plane deformation), 1010 (N-H bending), 931, 830 and 739 (C-H out of plane deformation). UV-Vis (DMSO) λ max (nm) (log ϵ): 338 (4.43), 673 (4.41), 702 (4.38). ¹H-NMR (DMSO) δ (ppm): 10.09 (bs, 2H, NH-core), 8.14 (s, 4H, NH-amide), 7.95 (s, 4H, CH-Ar ring-core), 7.18 (d, 4H, CH-Ar ring-core), 7.09 (d, 8H, CH-Ar ring-amide), 7.01 (d, 4H, CH-Ar ring-core), 6.86 (d, 8H, CH-Ar ring-amide), 2.09 (s, 12H, CH₃). MALDI-TOF MS m/z: Calculated: 1110.36; found: m/z = 1067.32 [M-C₂H₃O]⁺, 1024.32 [M-2(C₂H₃O)]⁺ and 981.32 M-C₂H₃O]⁺, [M⁺] = 1110.32. Elemental analysis: Anal. Calc. For C₆₄H₄₆N₁₂O₈ (%): C, 69.18; H, 4.17; N, 15.13; found (%): C, 69.21; H, 4.14; N, 15.10.

2.4.2 Tetrakis (4-acetamidophenoxy) phthalocyaninato gallium(III) (5**_{Ga}),**

Scheme 3.2

The free-base phthalocyanine (**5**_{H₂}) (0.050 g, 0.045 mmol) was dissolved in DMF (5 mL) containing GaCl₃ (0.0079 g, 0.051 mmol) in the presence of DBU (0.013 ml, 0.09 mmol) and the mixture was refluxed for 5h. The completion of metalation reaction was monitored by UV-Vis spectroscopy. The resultant

product was obtained by adding MeOH to the final mixture to allow for precipitation. The formed precipitate was collected by centrifugation. The product was washed several times with water and ethanol and further purifications were performed by dissolving in DMF and precipitating in ethanol (3 times). The target GaPc (**5_Ga**) was obtained as a green solid.

Yield: 27% (0,015 g). FT-IR (UATR-TWOTM) ν max/cm⁻¹: 3233 (N-H stretching), 3050 (C-H asymmetric stretching), 1610 (C=C stretching), 1547 (C-H bending), 1214 (C-N bending and C=C stretching), 1092 (C-H in plane deformation), 1010 (N-H bending), 932, 874, 825 and 733 (C-H out of plane deformation). UV-Vis (DMSO) λ_{max} (nm) (log ϵ): 636 (4.64), 680 (4.65). ¹H-NMR (DMSO) δ (ppm): 8.25 (s, 4H, NH-amide), 7.97 (s, 4H, CH-Ar ring-core), 7.62 (d, 4H, CH-Ar ring-core), 7.33 (d, 8H, CH-Ar ring-amide), 7.04 (d, 4H, CH-Ar ring-core), 6.83 (d, 8H, CH-Ar ring-amide), 2.22 (s, 12H, CH₃). MALDI-TOF MS m/z: Calculated: 1214.31; found: m/z = 1223.61 [M-Cl+2Na]⁺, 1028.25 [M-3(CH₃NHCO)+Na]⁺. Elemental analysis: Anal. Calc. For C₆₄H₄₄ClGa₁₂N₈O₈(%): C, 63.30; H, 3.65; N, 13.84; found (%): C, 63.34; H, 3.62; N, 13.81.

2.4.3. Synthesis of tetrakis (4-acetamidophenoxy) phthalocyaninato cobalt (II) **5_Co, Scheme 3.2**

The 4-acetamidophenoxyphthalonitrile (**AcPhPn**) (0.3 g, 0.27 mmol) was mixed with anhydrous Co(OAc)₂ (0.095 g, 0.54 mmol) and catalytic amount of DBU in n-pentanol (4 mL). The mixture was degassed with nitrogen and stirred at reflux temperature for 18 h. After being brought to ambient temperature, the mixture

was allowed to precipitate with the addition of water/methanol (1/1) and subsequently collected by centrifugation. The collected compound was washed several times with ethanol, acetone and water to remove the soluble by-products and any un-reacted metal salt. A better quality of the Pc was supplied by dissolving in DMF and precipitating in hot ethanol (3 times). The pure CoPc (**5**_Co) was accomplished as a green solid.

Yield: 38% (0,120 g).

FT-IR (UATR-TWOTM) ν max/cm⁻¹: 3280 (N-H stretching), 3047 (C-H asymmetric stretching), 1600 (C=C stretching), 1540 (C-H bending), 1216 (C-N bending and C=C stretching), 1091 (C-H in plane deformation), 946, 828 and 740 (C-H out of plane deformation). UV-Vis (DMSO) λ_{max} (nm) (log ϵ): 337 (4.29), 677 (4.57). MALDI-TOF MS m/z : Calculated: 1167.27; found:[M]⁺ = 1167.56. Elemental analysis: Anal. Calc. For C₆₄H₄₄CoN₁₂O₈ (%): C, 65.81; H, 3.80; N, 14.39; found (%): C, 65.76; H, 3.81; N, 14.42.

2.4.4 Cobalt (II) 2,9,16-tris(4-(*tert*-butyl)phenoxy)-23-(pyridin-4-yloxy) phthalocyanine (6)- and cobalt (II) 2,9,16,24-tetrakis(4-(*tert*-butyl)phenoxy) phthalocyanine (7), Scheme 3.3

4-(4-Pyridyloxy)phthalonitrile (0.1 g, 0.45 mmol), 4-*tert*-butylphenoxy phthalonitrile (0.372 g, 1.35 mmol) and Co(OAc)₂ (0.08 g, 0.45 mmol) and a catalytic amount of DBU in dry *n*-pentanol (3 mL) was heated at 160 °C with stirring under nitrogen for 24 h. After cooling to room temperature, the reaction mixture was precipitated by adding methanol. The product was collected by

centrifuge and was washed several times with methanol and ethanol to remove any unreacted precursor and then dried in vacuo. The crude material was subjected to silica gel column chromatography and eluted with CHCl_3 and the two different phthalocyanine (**6** and **7**) were obtained.

(**6**)- Yield: 3% (15 mg). FT-IR (UATR-TWOTM) $\nu_{\text{max}}/\text{cm}^{-1}$: 3066 (Ar-CH), 2955-2868 (Aliph., CH), 1599, 1508 (C=C), 1463-1362 (C-C), 1235 (Asym C-O), 1045 (sym.C-O), 959, 823, 744 (C-H out of plane deformation). UV-Vis (DMSO) λ_{max} (nm): 607 (3.36), 668 (3.81), MALDI-TOF MS m/z : Calculated: 1109.17; found: $m/z = 1111.13$ $[\text{M}+2\text{H}]^+$. Elemental analysis: Anal. Calc. for $\text{C}_{67}\text{H}_{55}\text{CoN}_9\text{O}_4$ (%): C, 72.55; H, 5.00; N, 11.37; found (%): C, 72.61; H, 4.95; N, 11.42.

(**7**)- Yield: 7.6% (40 mg). FT-IR (UATR-TWOTM) $\nu_{\text{max}}/\text{cm}^{-1}$: 3042 (Ar., CH), 2955-2859 (Aliph., CH), 1608, 1505 (C=C), 1465-1339 (C-C), 1235 (Asym C-O), 1085 (sym.C-O), 951, 816, 752 (C-H out of plane deformation). UV-Vis (DMSO) λ_{max} (nm): 338 (4.49), 602 (4.08), 663 (4.63). MALDI-TOF MS m/z : Calculated: 1164.29; found: $m/z = 1165.33$ $[\text{M}+\text{H}]^+$. Elemental analysis: Anal. Calc. for $\text{C}_{72}\text{H}_{64}\text{CoN}_8\text{O}_4$ (%): C, 74.28; H, 5.54; N, 9.62; found (%): C, 74.33; H, 5.66; N, 9.49.

2.5 Electrochemical methods

The inhibitors studied are not water soluble, therefore their solutions were first prepared by weighing the required amount and dissolving in 10 mL

dimethylsulphoxide (DMSO) then making up to 100 mL using 1.0 M hydrochloric acid to give a 10 μ M solution. The rest of the concentrations (8 μ M, 6 μ M, 4 μ M and 2 μ M) were prepared by serial dilution from the 10 μ M solution. Before the Al coupons were employed for electrochemical studies, their surfaces were abraded with emery papers of 400 and 800 grit sizes, washed in acetone, Type II water and then dried. The Al corrosion inhibition performances of phthalocyanines were studied in 1.0 M hydrochloric acid solution after a 30 min immersion period and at room temperature $28\text{ }^{\circ}\text{C} \pm 0.05\text{ }^{\circ}\text{C}$. A three-electrode electrochemical cell containing aluminium coupons, a platinum wire, and an Ag/AgCl electrode (in 3.0 M KCl) as the working, counter and reference electrodes, respectively, was employed for corrosion inhibition studies. The open circuit potential (OCP) experiments were carried out after stabilization time of 30 min and the open circuit potentials (E_{OCP}) were determined for the metal/HCl systems with and without the corrosion inhibitors. EIS measurements were performed at the OCP between 0.1 Hz and 10 kHz, using a 5 mV root-mean-square (rms) sinusoidal modulation. A non-linear least squares (NLLS) method based on the EQUIVCRT program was used for automatic fitting of the obtained EIS data. The accuracy of the fitting (by Chi-square) is in the order of 10^{-6} for all the experimental data. The measurements were performed in duplicate and the results are presented in the relevant tables.

Electrodeposition of complexes **1** and **2** (each $\sim 10^{-4}$ M) were done using cyclic voltammetry in DCM containing 0.1 M TBABF₄ in the potential range of - 2.3 and + 1.0 V and scan rate (v) of 100 mVs⁻¹. The electrodes were rinsed

with DCM and water, finally they were dried in a desiccator before use. A glassy carbon electrode (GCE) was employed as working electrode for the characterization of the MPcs. The surface of GCE was polished on a Buehler-felt pad using alumina (0.05 μm) to remove impurities, thereafter it was sonicated in ethanol then, in Millipore water and dried before use. The Al corrosion inhibition of electrodeposited-1 and electrodeposited-2 were studied in 1.0 M hydrochloric acid solution after a 30 min immersion period and at room temperature $28\text{ }^{\circ}\text{C} \pm 0.05\text{ }^{\circ}\text{C}$.

2.6 Sample preparation for various equipment

For SEM analyses, the electrode surfaces were captured/accessed directly.

For FTIR analyses on Al metal alone before corrosion, aluminium coupons preserved in a desiccator were scratched, metal powder obtained from doing so was employed for FTIR. Adsorbed films on the metal surface after exposure to HCl solution (in the absence and presence of studied inhibitors) were carefully removed by scraping with a clean stainless steel blade, and care was taken to avoid contamination during the collection of the corrosion products. The obtained powders were employed for FTIR. For XRD, the films after exposure to HCl solution were removed by scraping with a clean stainless steel blade, and the underlying Al coupons were analysed. Powders of rGONS and conjugates were employed for TGA. For the electrodeposition experiments, the electrodeposited films before and after exposure to HCl solution were carefully removed by scraping with a clean stainless steel blade, and care was taken to avoid

contamination during the collection of the corrosion products. The obtained powders were employed for TGA.

2.7 Computational Studies

The optimized structures of the studied corrosion inhibitors were obtained using the Density functional theory (DFT) technique. For complex **3** and **4**, optimized structures were calculated for two sets of methyl-substituted model structures for the corrosion inhibitors with similar bridging patterns but axial chloride atoms aligned in parallel or opposite directions, an **rGONS** model sheet and combined π - π stacked structures involving the corrosion inhibitors and the **rGONS** model sheets by using the Density functional theory (DFT) technique. B3LYP is a hybrid functional comprising the Becke's three parameter exchange functional [69] and Lee-Yang-Parr correlation functional [70, 71], used in conjunction with SDD basis sets contained in the Gaussian 09 software package [64]. The calculated parameters include the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the HOMO-LUMO energy gap (ΔE), the global softness (σ), the global hardness (η), the fraction of electrons transferred (ΔN) and the electronegativity (χ).

A deeper insight into the molecular properties of graphene-based materials can be achieved by using the density functional theory [72]. Herein, the geometry optimizations of the inhibitor/rGONS systems were carried out by first using preliminary semi-empirical calculations (Parametric Method 3) followed by DFT

calculations carried out by using the B3LYP functional with 3-21G basis sets. The interaction energies (E_{int}) of the analyzed systems were calculated as the difference between the total energy of the inhibitor/rGONS system complex and the energies of the isolated inhibitors using equation 2.1 [73].

$$E_{\text{interaction}} = E_{\text{complex}} - (E_{\text{rGONS}} + E_{\text{inhibitor}}) \quad 2.1$$

where $E_{\text{interaction}}$ is the interaction energy of the inhibitor/**rGONS** complex, E_{complex} represents the energy of the (final) inhibitor/**rGONS** complex, E_{rGONS} is the energy of the optimized rGONS and $E_{\text{inhibitor}}$ is the energy of the optimized inhibitor.

Publications

The following are papers published or submitted from which the work presented in this thesis emanate:

1. **Nnaemeka Nnaji**, Pinar Sen, Tebello nyokong, Symmetry effect of cobalt phthalocyanines on the aluminium corrosion inhibition in hydrochloric acid, Mats. Letts. Submitted.
2. **Nnaemeka Nnaji**, P Sen, T Nyokong (2021). Aluminum corrosion retardation properties of acetamidophenoxy phthalocyanines: effect of central metal. J. Mol. Struct. 1242 ID 130806 – 14 pages.
3. **Nnaemeka Nnaji**, Njemuwa Nwaji, John Mack, Tebello Nyokong (2021). Ball-type phthalocyanines and reduced graphene oxide nanoparticles as separate and combined corrosion inhibitors of aluminium in HCl. J. Mol. Struct. 1236 ID 130279 – 13 pages.
4. **Nnaemeka Nnaji**, Njemuwa Nwaji, Tebello Nyokong (2020). Electrodeposited Benzothiazole Phthalocyanines for Corrosion Inhibition of Aluminium in Acidic Medium. Int. J. Electrochem. 2020 ID 8892559 – 11 pages.
5. **Nnaemeka Nnaji**, Njemuwa Nwaji, John Mack, Tebello Nyokong (2019). Corrosion resistance of aluminium against acid activation: impact of benzothiazole-substituted gallium phthalocyanine. Molecules 24 (1): 207.
6. **Nnaemeka Nnaji**, Njemuwa Nwaji, Gertrude Fomo, John Mack, Tebello Nyokong (2019). Inhibition of aluminium corrosion using benzothiazole and its phthalocyanine derivative. Electrocatalysis 10 (4): 445-458.

CHAPTER THREE

Characterization

Characterization of the phthalocyanines and nanomaterial (rGONS) used in this work are dealt with in this chapter. Complexes **1** to **4** are known [43–46] therefore only their spectra will be discussed. Complexes **5** to **7** are new hence their syntheses and full characterization are provided.

3.1 Characterizations of complexes **1** and **2**

Figure 3.1a shows that UV-visible spectra of complexes **1** and **2** in THF are characteristic of monomeric metalated Pcs which possess single Q bands. The Q band absorptions of complexes **1** and **2** respectively in THF (Table 3.1) are at 693 nm and 689 nm. Aggregation is known to limit the application of MPcs in corrosion inhibition [42]. Concentration studies, Figs. 3.1b and 3.1c, show that aggregation was not observed within $1.0 \times 10^{-6} - 1.0 \times 10^{-5}$ M range because Beer-Lambert law was obeyed. In agreement with the foregoing, the presence of Ga(III) as a central metal allowed the attachment of axial ligands and expectedly reduced aggregation of complexes **1** and **2** [42].

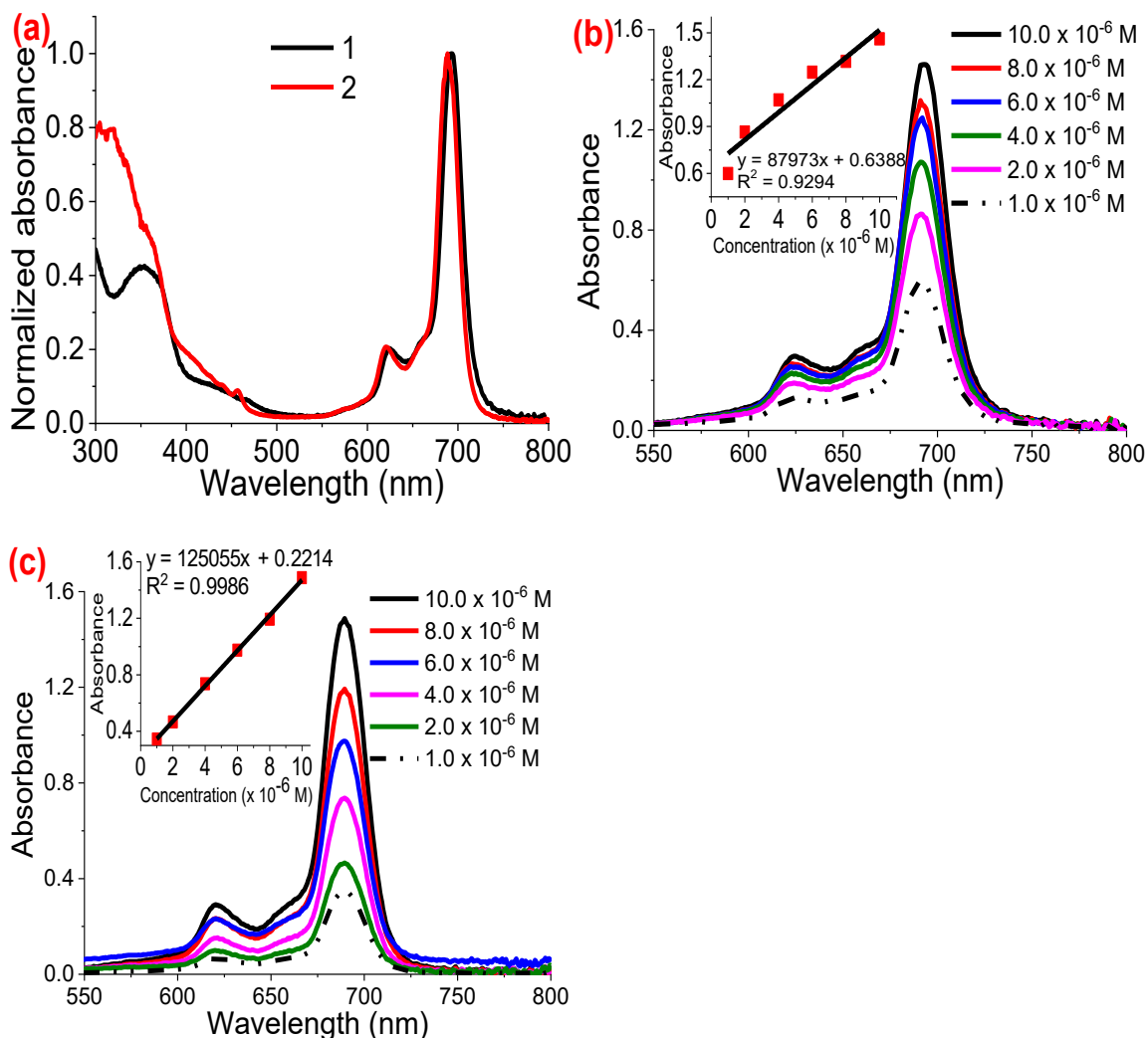


Figure 3.1: Absorption spectra of (a) complexes **1** and **2** (conc. = 1.0×10^{-5} M), (b) complex **1**, (c) complex **2** in THF at 1.0×10^{-6} - 1.0×10^{-5} M range.

3.2 Characterization of complexes **3**, **4**, rGONS and conjugates

The structures of complexes **3** and **4** (Scheme 3.1) were earlier reported [45, 46]. Complexes **3** and **4** were linked to rGONS by π - π stacking as shown in Scheme 3.1. The nanoconjugates were characterised by uv-visible spectra (Figure 3.2), Raman spectra and thermogravimetric analysis (TGA), Figure 3.3.

3.2.1 UV-visible spectra

The peak for rGONS appeared at 279 nm which is close to 270 nm reported earlier [74], Fig. 3.2. The conjugates, rGONS-**3**($\pi\pi$) and rGONS-**4**($\pi\pi$), show absorption intensities enhancement at 279 nm and indicate that the MPcs successfully $\pi\pi$ stacked onto rGONS.

The Q-band absorptions are at 697 nm and 693 nm for **3** and **4** respectively, in THF (Table 3.1). Aggregation is a property that limits the application of phthalocyanines, therefore concentration studies performed show that aggregation was not observed for complex **4** at concentrations $\leq 1.0 \times 10^{-5}$ M (not shown). Aggregation in phthalocyanines depends on solvents. Complex **3** and conjugates showed aggregation with a broad peak near 630 nm.

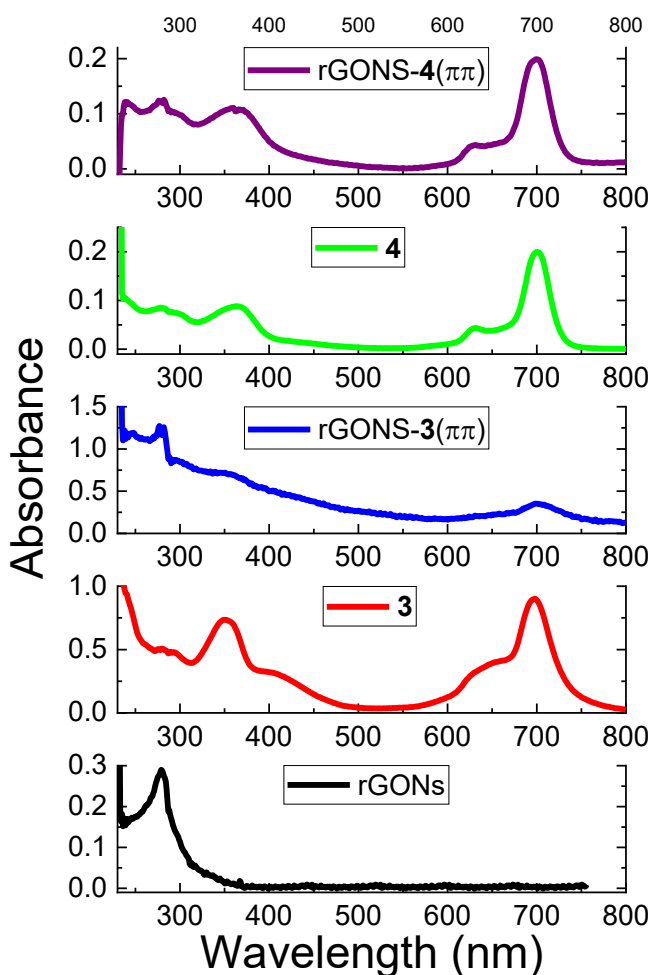


Figure 3.2: Electronic absorption spectra of rGONS, complexes **3** and **4**, and conjugates (rGONS-**3**($\pi\pi$) and rGONS-**4**($\pi\pi$)). Solvent = THF.

3.2.2 Thermogravimetric analyses (TGA)

Figure 3.3b presents the thermal degradation information of rGONS, **3**, **4** and the conjugates. These TGA curves show that the decomposition profile is of the order rGONS < **4** < **3** going by how steep the curves are below 600°C probably due to detachments of the substituents. This is because observed weight losses below 600°C are about 12%, 25% and 42% respectively for rGONS, **4** and **3**. However when $\pi\pi$ stacked, the weight losses below 600°C are about 19.5% and

8% respectively rGONS-**4**($\pi\pi$) and rGONS-**3**($\pi\pi$). These materials become more robust when $\pi\pi$ stacked onto rGONS. The improvement on thermal stability is known to enhance corrosion inhibition properties [75].

Mass loading ratios were calculated from TGA, using rGONS decomposition as a point of reference following previously reported method [76]. Equal masses (mg) for Pc and respective conjugate were weighed separately in the TGA pan and then heated in nitrogen to 850 °C. This was followed by comparing the masses of the Pc in a conjugate with that of the Pc before the conjugation. The mass loading of 0.64 mg **3**/mg rGONS-**3**($\pi\pi$), and 0.76 mg **4**/mg rGONS-**4**($\pi\pi$).

3.2.3 Raman spectra

The disordered (D) defective and graphitic (G) peaks indicated by sp^3 and sp^2 (respectively) from in plane vibrations investigated by laser Raman spectral technique, Fig. 3.3a. The G band is observed at 1603 cm^{-1} for rGONS alone and shifts to a lower value for rGONS-**4**($\pi\pi$) and higher value for rGONS-**3**($\pi\pi$). The D is observed as 1328 cm^{-1} for GONS alone and shifts to higher values for both conjugates. Raman shifts of G and D bands have been reported to indicate size [77], structural alterations [77] and strain effect on nanomaterial [78, 79]. The extent of interaction between rGONS and Pc is determined from $I_D: I_G$ ($sp^3:sp^2$) ratio. The intensity of the G band is not affected by defects, whereas the defects enhance the D-band and increase the $I_D: I_G$ ratio. The as-synthesized rGONS and respective conjugates gave I_D/I_G values 0.995, 0.975 and 0.972 respectively for rGONS, rGONS-**3**($\pi\pi$) and rGONS-**4**($\pi\pi$). These values decreased when

those of the conjugates are compared to rGONS and suggest that $\pi\pi$ stacking caused slight increase is the sp^2 structure of rGONS [80].

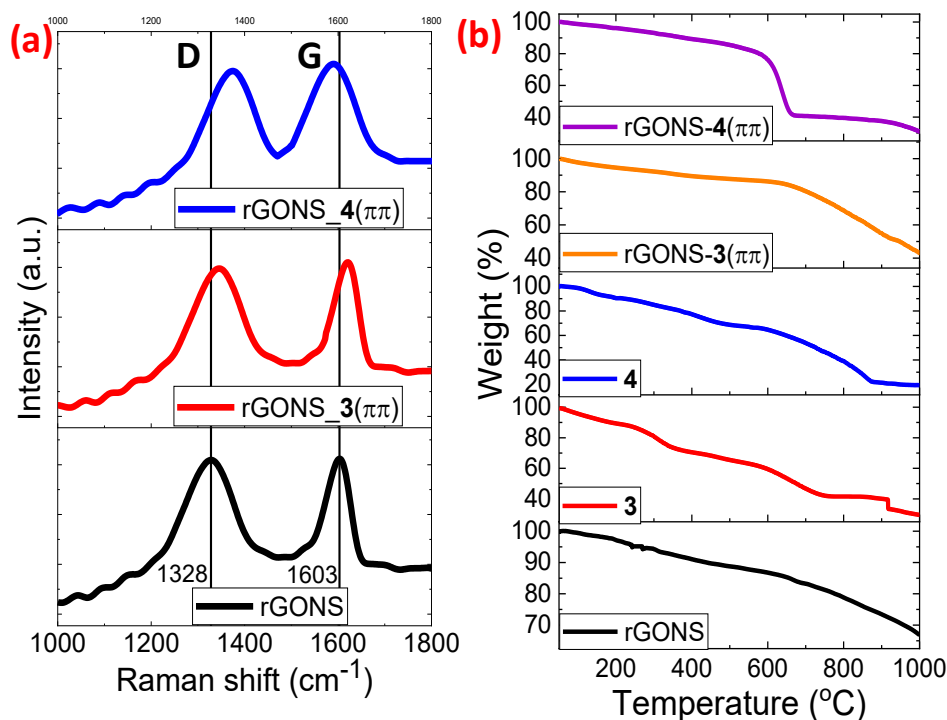
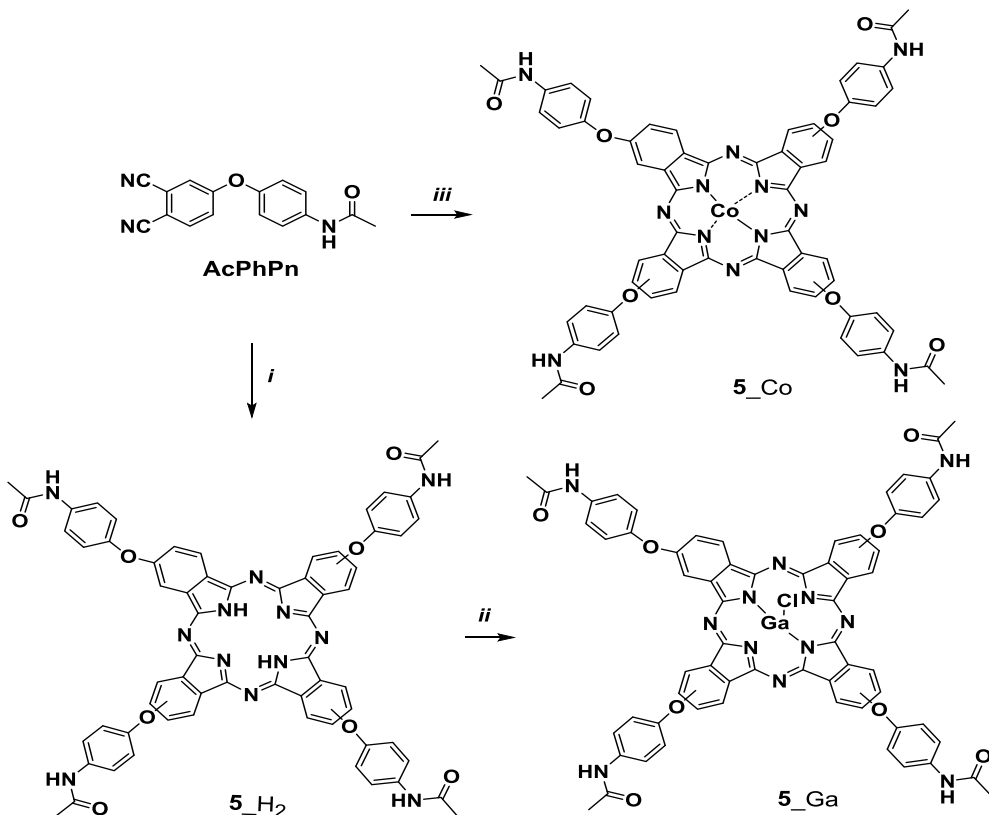


Figure 3.3: (a) Raman spectra of rGONS, complexes **3** and **4**, and conjugates and (b) Thermogravimetric curves of phthalocyanine derivatives **3** (a) and **4** (b) before and after electrodeposition, heated at 20°C min⁻¹ from 50 to 800°C in nitrogen.

3.3 Syntheses and chracterization of **5_H₂**, **5_Co** and **5_Ga**

The metal-free Pc (**5_H₂**) was synthesized by using the phthalonitrile derivative (**AcPhPn**) in presence of LiCl in pentanol reflux temperature. Acetic acid was then used to remove the Li metal from inner core to give the metal free derivative **5_H₂**. Pc (**5_Ga**) was obtained by metallization reaction of free Pc (**5_H₂**) in the presence of gallium(III) chloride in dry DMF. The CoPc (**5_Co**) was

synthesized by using the cobalt salt with the tetramerization reaction of **AcPhPn**. All reaction pathways are outlined in Scheme 3.2. The expected chemical structures were confirmed with the spectroscopic methods such as ^1H -NMR, UV/Vis, FT-IR, and mass spectra (MS) and elemental analysis. The obtained spectral data confirmed the structures of the synthesized compounds.



Scheme 3.2: Synthesis route: (i) n-pentanol, LiCl, DBU, (ii) DMF, GaCl₃, DBU (iii) n-pentanol, DBU, Co(OAc)₂. Acetamidophenoxyphthalonitrile is represented by **AcPhPn**.

3.3.1 UV-visible spectra

Figure 3.4 shows that complex **5**_{H₂} has two Q bands typical of metal free Pc similar to earlier report [81]. The absorption spectra are shown in Fig. 3.4 with Q-band absorption maxima at 673 nm and 702 nm for **5**_{H₂}, 667 nm for **5**_{Co} in DMSO, Table 3.1. Complex **5**_{Ga} showed extensive aggregation as judged by a split Q band in DMSO but was less aggregated in dimethyl acetamide (DMAc) with maximum absorption at 715 nm. The Q band of complex **5**_{Ga} is red shifted, accounting for the non-planar effect of larger central atoms [82]. Concentration studies for **5**_{H₂} and **5**_{Co} in DMSO were performed (not shown) and results confirms that insignificant aggregation exist at $1.0 \times 10^{-6} - 1.0 \times 10^{-5}$ M range.

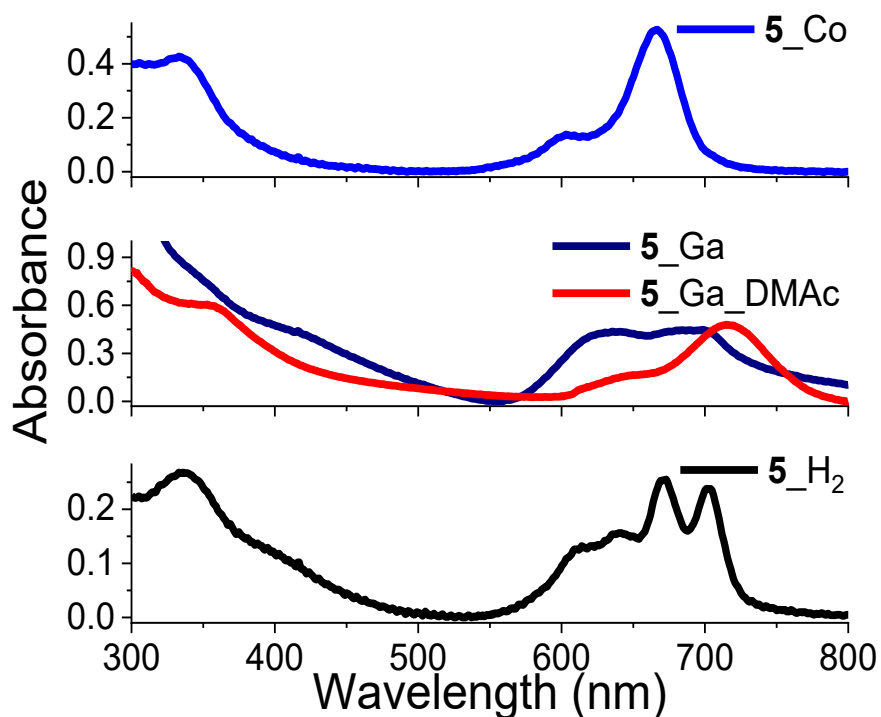


Figure 3.4: Electronic spectra of **5**_{H₂} and **5**_{Co} in DMSO and complex **5**_{Ga} in DMSO and DMAc. Conc. = 1×10^{-5} M.

3.3.2 Infrared spectra

The FT-IR spectra of **5**_{H₂} and **5**_{Co} showed disappearance of the C≡N peak observed at 2223 cm⁻¹ confirming the formation of the target complexes, Fig. 3.5. The FT-IR spectra of metallated Pc (**5**_{Co}) were similar to **5**_{H₂} except for the absorption signal of -NH originating from inner core of metal-free Pc (**5**_{H₂}) at 3285 cm⁻¹.

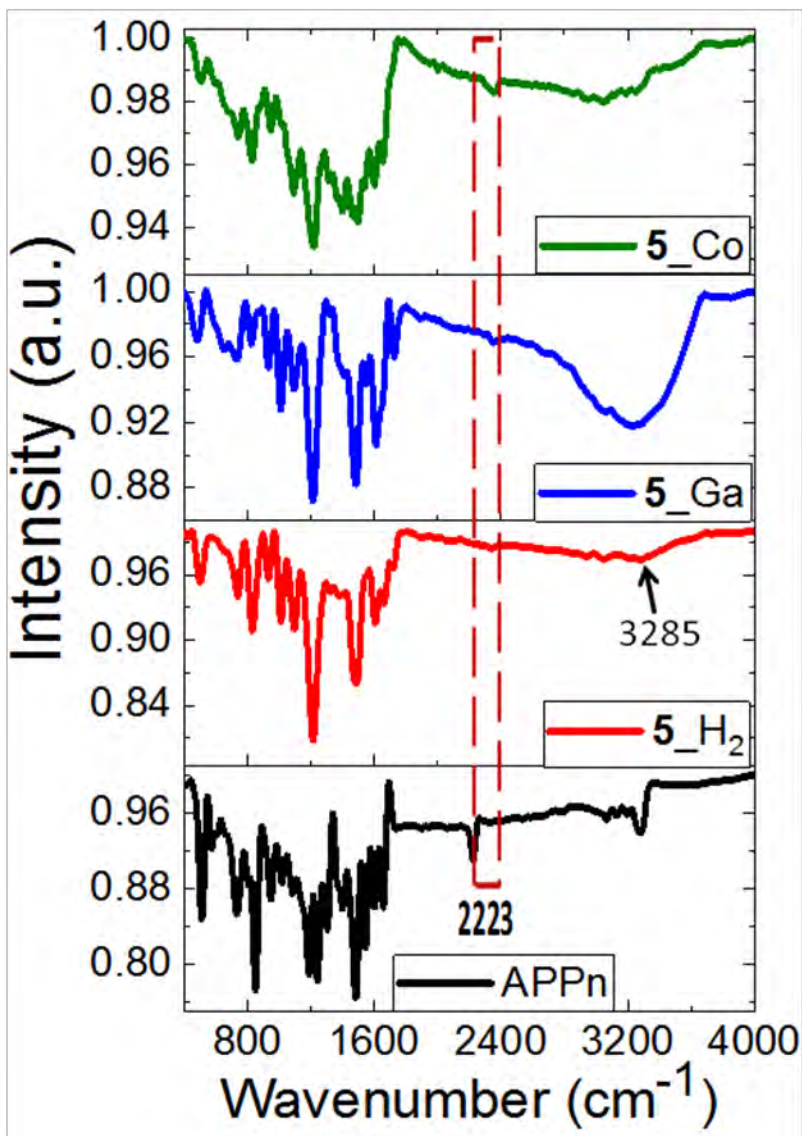
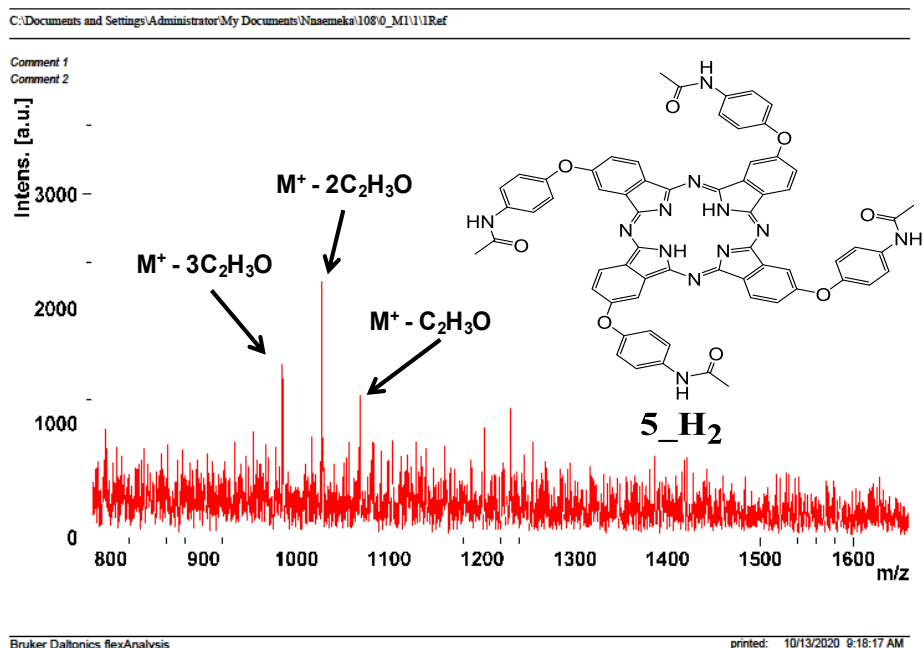


Figure 3.5: Infrared spectra of **5**_{H₂}, **5**_{Co} and **5**_{Ga}, **AcPhPn** represents acetamidophenoxyphthalonitrile.

3.3.3 Mass spectra

The MALDI-TOF Mass spectra of **5_H₂**, **5_Co** and **5_Ga** were obtained to confirm the proposed structures. The CHNS elemental analyses of the complexes agrees with the proposed structure. Molecular ion peaks of all Pcs were observed at $m/z = 1067.32$ $[M-C_2H_3O]^+$, 1024.32 $[M-2(C_2H_3O)]^+$ and 981.32 $[M-3C_2H_3O]^+$ 1110.32 $[M]^+$ for **5_H₂**, $m/z = 1223.25$ $[M-Cl + 2Na]^+$ and 1029.20 $[M-3(CH_3NHCO) + Na]^+$ 1167.56 $[M]^+$ for **5_Ga**, 1169.33 $[M]^+$ for **5_Co**, Fig. 3.6.



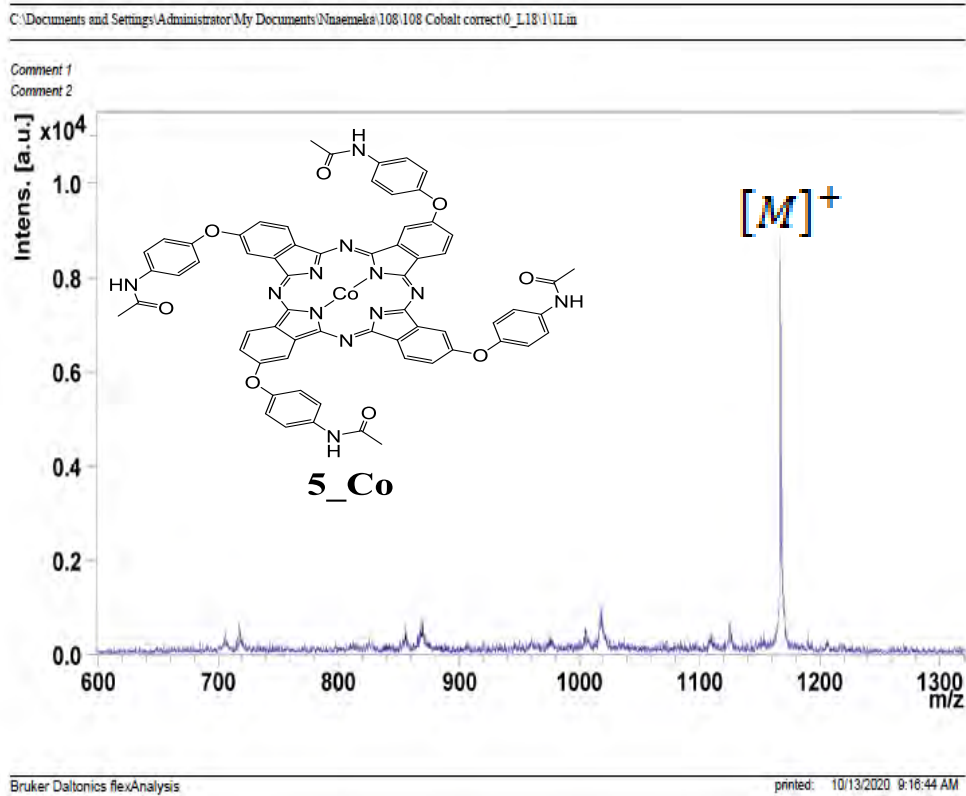
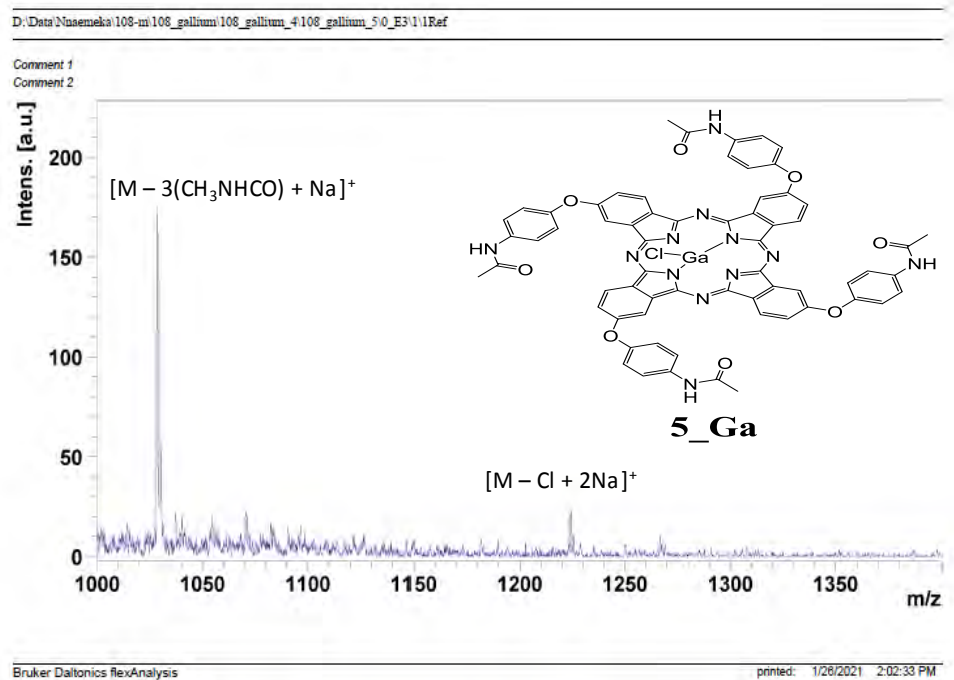
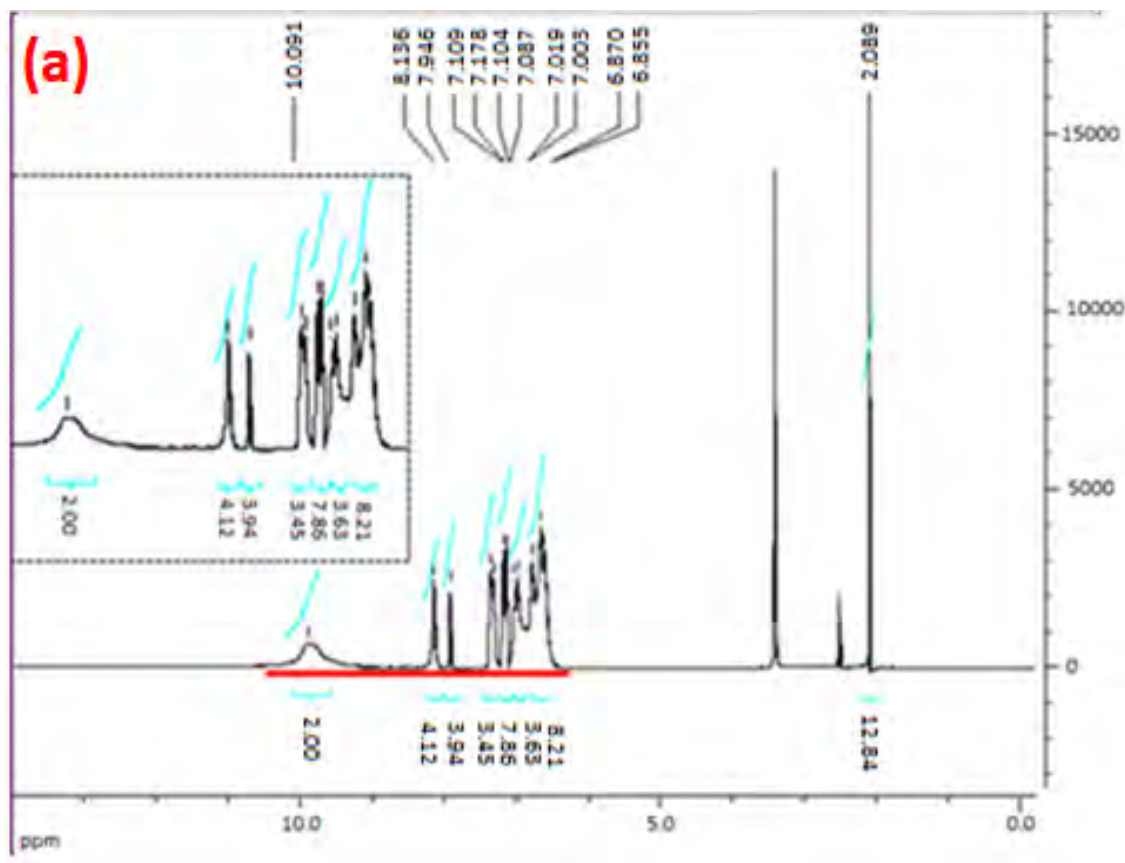
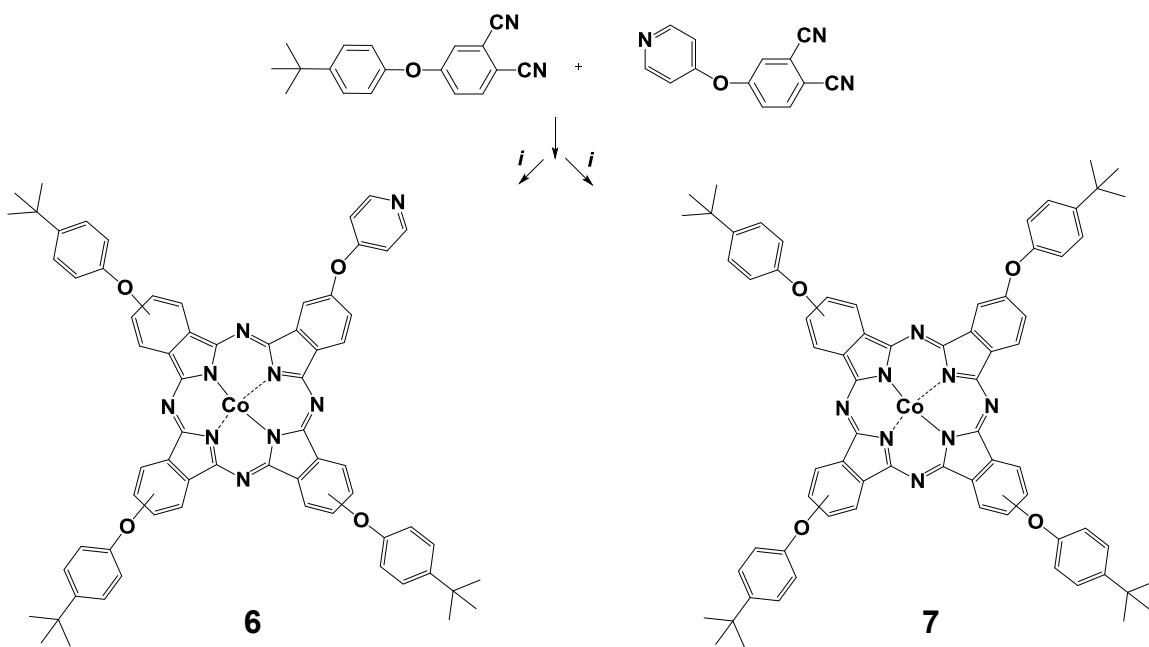


Figure 3.6: Mass spectra of complexes **5_H₂**, **5_Co** and **5_Ga**.

3.3.4 NMR spectra

The ^1H NMR spectra (Fig. 3.7), for **5**_{H₂} and **5**_{Ga}, showed aromatic ring and ring-amide protons between 7.95–6.83 ppm and they were all integrated to give the anticipated number of protons. The ^1H -NMR data presented consistent results for studied structures. The ^1H -NMR spectra of compound **5**_{H₂} and **5**_{Ga} differ by the disappearances of the NH peaks (at 10.09 ppm) coming from the inner core of the metal-free Pcs (**5**_{H₂}), Fig. 3.7. Methyl protons on the substituents of **5**_{H₂} and **5**_{Ga} were observed at 2.09 ppm and 2.22 ppm, respectively. The ^1H -NMR spectrum of compound **5**_{Co} could not be obtained due to paramagnetic nature of the sample.





Scheme 3.3: Synthesis route: (i) n-pentanol, DBU, Co(OAc)₂

The monomeric nature of complexes **6** and **7** are showed by the absorption spectra shown in Figure 3.8 with single Q-band absorption maxima between 665 nm and 663 nm for **6** and **7** in DMSO, Table 3.1. Concentration studies for **6** and **7** in DMSO have been performed, and results confirm that insignificant aggregation exist at $1.0 \times 10^{-6} - 1.0 \times 10^{-5}$ M range (not shown).

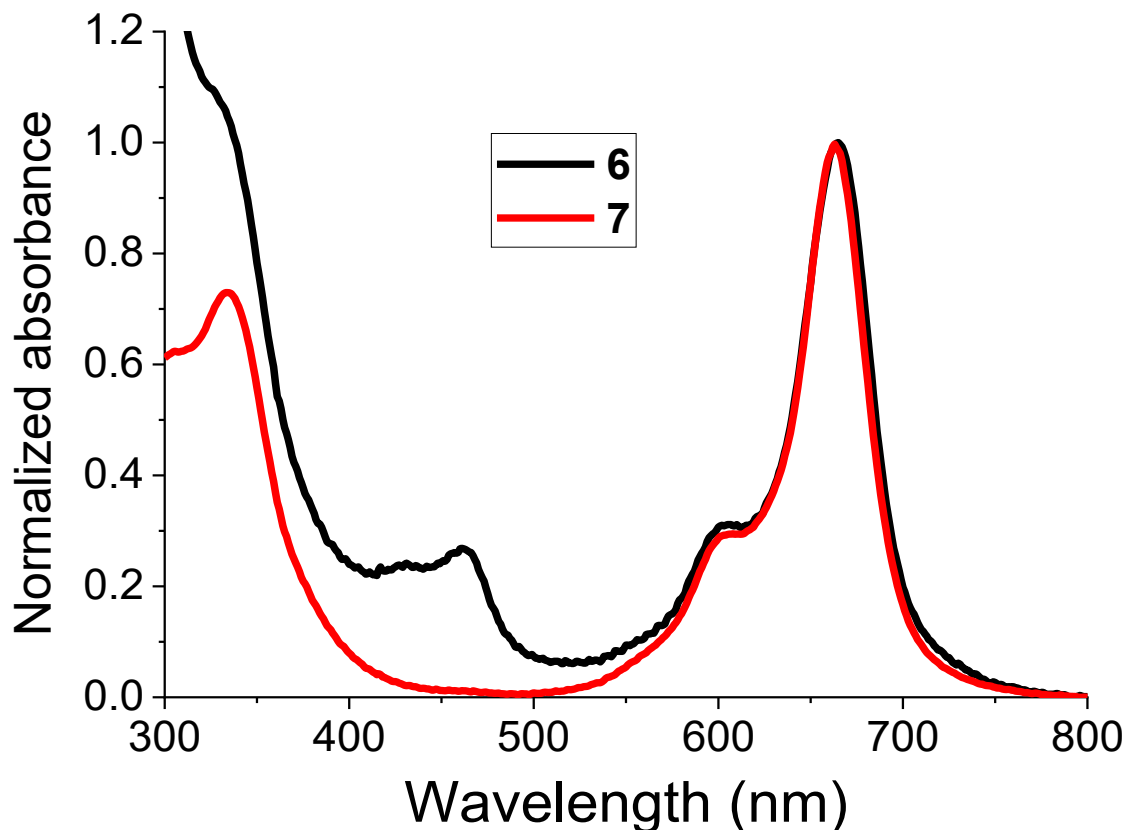


Figure 3.8: Absorption spectra of complexes **6** (a) and **7** (b) in DMSO at 1.0×10^{-6} .

The FT-IR spectra of **6** and **7** (Fig. 3.9) showed disappearance of the $\text{C}\equiv\text{N}$ peak observed at 2225 cm^{-1} for the phthalonitrile confirming the formation of the target complexes. The aliphatic C-H stretching were observed at $2955\text{--}2868\text{ cm}^{-1}$ for **6**, $2955\text{--}2859\text{ cm}^{-1}$ for **7**. The Ar-O bands were observed at 1235 cm^{-1} , 1045 cm^{-1} for **6** and 1235 cm^{-1} , 1085 cm^{-1} for **7** (Fig. 3.9).

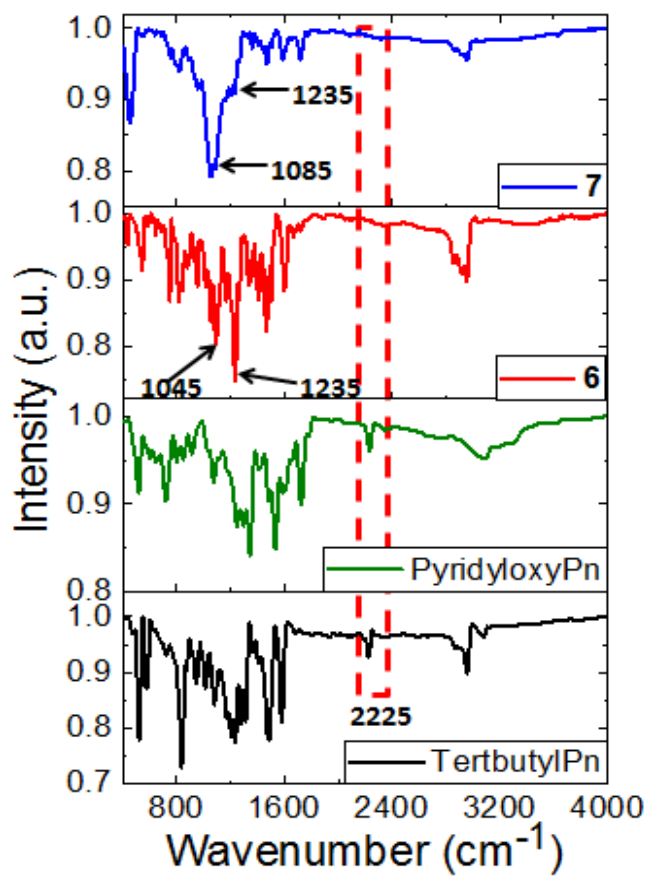


Figure 3.9: Infrared spectra of tertbutylPn (4-tert-butylphenoxy phthalonitrile), pyridyloxyPn (4-(4-pyridyloxy) phthalonitrile), **6** and **7**.

The MALDI-TOF MS data for **6** and **7** were consistent with the expected structures by showing the molecular ion peaks at 1110.04 $[M + H]^+$ for **6** (Fig. 3.10) and 1165.33 $[M+H]^+$ for **7** (not shown). The CHNS elemental analyses of the complexes agrees with the proposed structure.

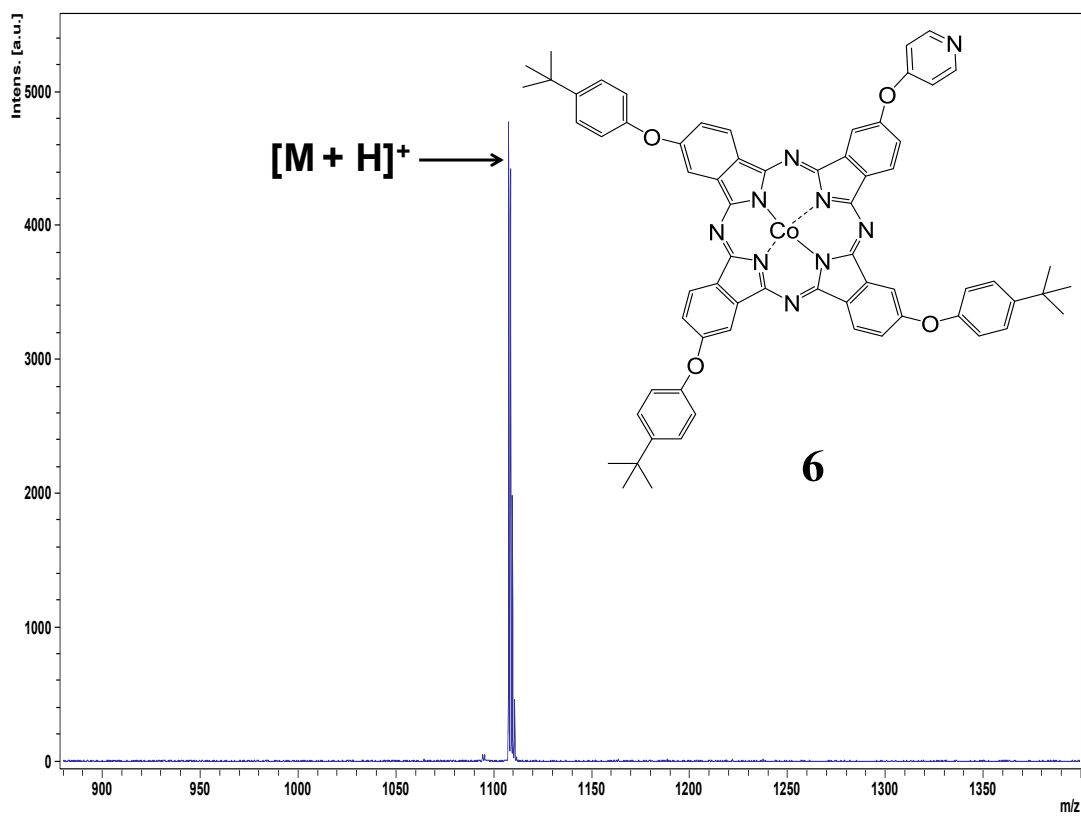


Figure 3.10: Mass spectrum of complex **6**

Table 3.1: Absorption wavelengths of studied phthalocyanines

Complexes	Solvent	Q-band maximum absorption wavelength (nm)
1	THF	693
2	THF	689
3	THF	697
4	THF	693
rGONS-3($\pi\pi$)	THF	701
rGONS-4($\pi\pi$)	THF	700
5 _H ₂	DMSO	673 and 702
5 _Co	DMSO	667
5 _Ga	DMAc	715
6	DMSO	665
7	DMSO	663

3.5 Conclusion for the chapter

The different phthalocyanine and metallophthalocyanines synthesized in this work were characterized using various spectroscopic techniques. Satisfactory results were obtained from the various spectroscopic techniques used in the identifications of synthesized compounds.

Chapter Four

Electrochemical and Adsorption Studies

In this chapter, the researcher presents the results of analyses of corrosion inhibition data collected in this study as well as the discussions. The chapter is concluded with answers to research questions and summary of findings.

4.1 Cyclic voltammetry

Cyclic voltammograms of corroded aluminium in HCl in the absence and presence of **2a** and **2** as examples are shown in Fig. 4.1. Fig. 4.1a is the curve recorded in the absence of inhibitor and shows prominent peak around -0.82 V which may be attributed to oxidation of Al^{3+} ions of corroded metal in the presence of chloride ions [83]. In the presence of **2a** and **2**, Figs. 4.1b and 4.1c, this peak is not observed. A plateau between -0.98 V and -1.12 V suggests passivation of the metal surface by **2a** and **2** [84]. This suggests effective inhibition by **2a** and **2**.

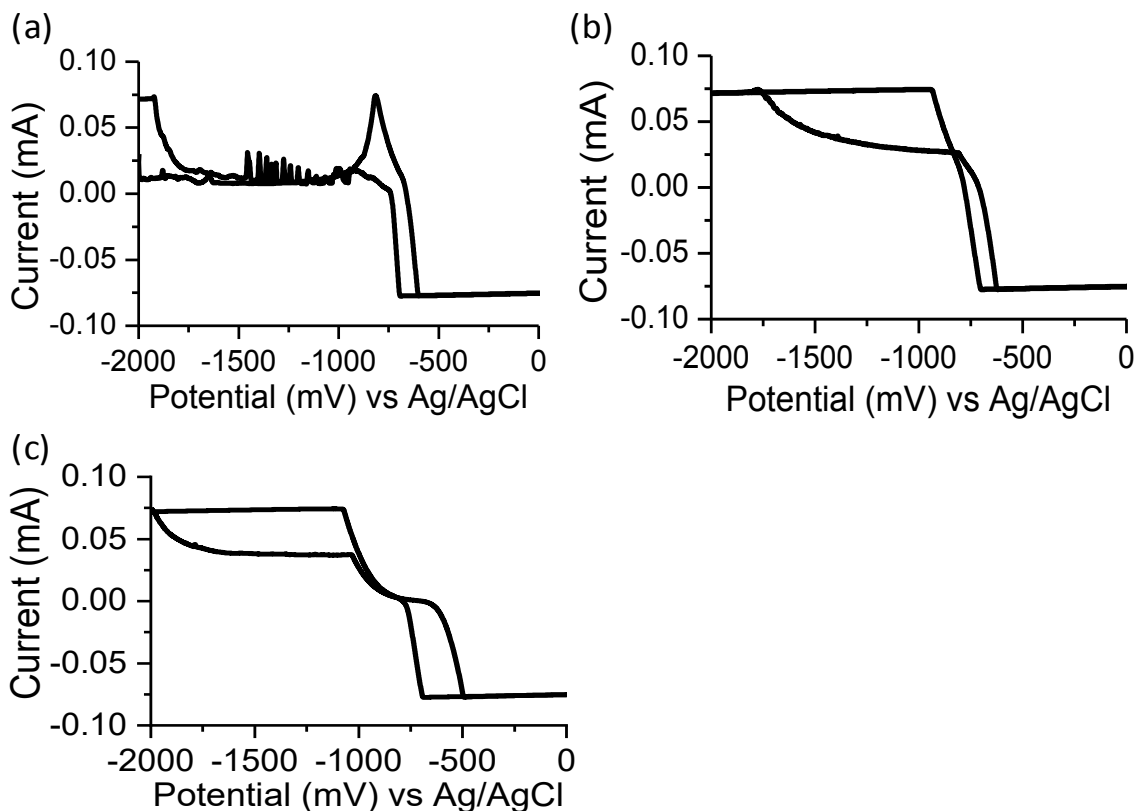


Figure 4.1: Cyclic voltammograms for aluminium in (a) 1.0 M hydrochloric acid alone and in the presence of (b) **2a** (10 μM) and (c) **2** (10 μM) (c) at $28 \pm 0.05^\circ\text{C}$.

4.2 Electrodeposition

Complexes **1** and **2** were studied for corrosion inhibition when electrodeposited and in solution, Fig. 4.2a shows the cyclic voltammogram for electrodeposition peaks of complex **1** on GCE as an example. All peaks in Fig. 4.2a are due to ring based processes since the central metals are inactive. Complexes **1** and **2** were electrodeposited onto the Al by scanning from 1.0 to - 2.3 V vs Ag/AgCl in dichloromethane (DCM) containing TBABF₄, Fig. 4.2b. On Al electrode, steady

state behaviour is observed on the anodic side. It is the shape of the electrode, that determines whether it will reach a steady state or not [85]. The peak near -1.6 V increased with continuous cycling indicating that a film was formed on the electrode as a consequence of electrodeposition. Electrodeposition is judged by increase in current without shift in potential or formation of new peaks as observed in Fig. 4.2b [48]. The steady state peaks only shift to more negative potentials with cycling, Fig. 4.2b. The colour of the phthalocyanine solution became less intense confirming electrodeposition of the Pc from the solution to the electrode.

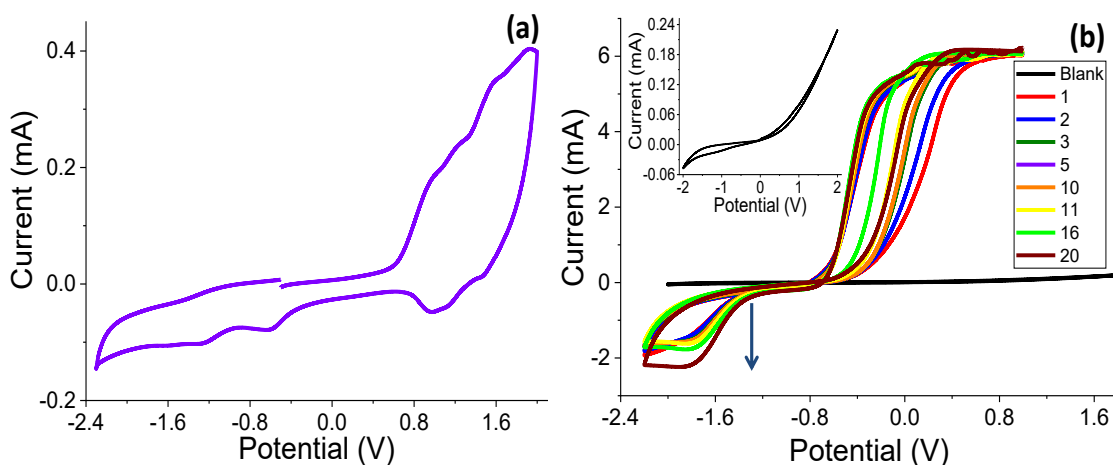


Figure 4.2: (a) Cyclic voltammogram of complex **1** in DCM containing 0.1 mol.dm⁻³ TBABF₄ at scan rate = 100 mV/s, concentration ~1 x 10⁻⁴ mol.dm⁻³, electrode = glassy carbon. (b) Evolution of the cyclic voltammograms of complex **2** in DCM containing 0.1 mol.dm⁻³ TBABF₄ during repeated successive scans (only 8 scans are shown), scan rate = 100 mV/s, concentration ~1 x 10⁻⁴ mol.dm⁻³, electrode = Al coupon. Inserted is the cyclic voltammogram of blank Al (without complex **2**).

Fig. 4.3 presents the thermal degradation information of complexes of **1** and **2** before and after electrodeposition. These TGA curves show that the studied Pcs are thermally stable (before electrodeposition) below 300 °C. Detachments of the substituents probably occur at temperature ranges of 250–360 °C and 230–370 °C for **1** and **2**, respectively. The Pcs seem to degrade rapidly from ~ 400 °C for **1** and ~ 370 °C for **2**. Electrodeposition is not expected to change the nature of complexes **1** and **2**. The decreased stability following electrodeposition could be a result of change in conformation during the electrodeposition process [86]. Thermograms obtained after HCl exposure are similar with those recorded for electrodeposited **1** and **2** before corrosion.

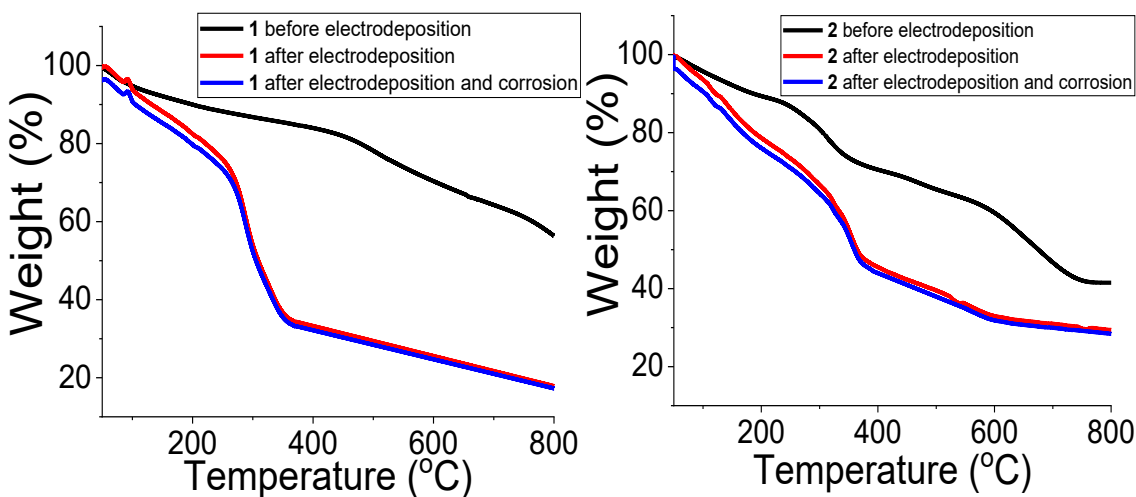


Figure 4.3: Thermogravimetric curves of phthalocyanine derivatives **1** and **2** before and after electrodeposition. Heated at 20 °C min⁻¹ from 50 to 800 °C in nitrogen.

4.3 Open Circuit Potential (OCP) Time Evolution

Figure 4.4 presents the effect of the absence and presence of the studied inhibitors on the OCP of aluminum in 1.0 M hydrochloric acid solution. The OCP of aluminum was monitored in the presence of different inhibitor concentrations.

Shifts towards positive values of the OCP for metal dissolution processes in the presence of the inhibitors compared to OCP values in their absence are generally explained to be due to the influence on the anodic metal corrosion process [87]. In literature, the influence of the cathodic metal corrosion process is generally ascribed to electrochemical OCP measurements recorded which shift towards negative values in the presence of inhibitors [88, 89].

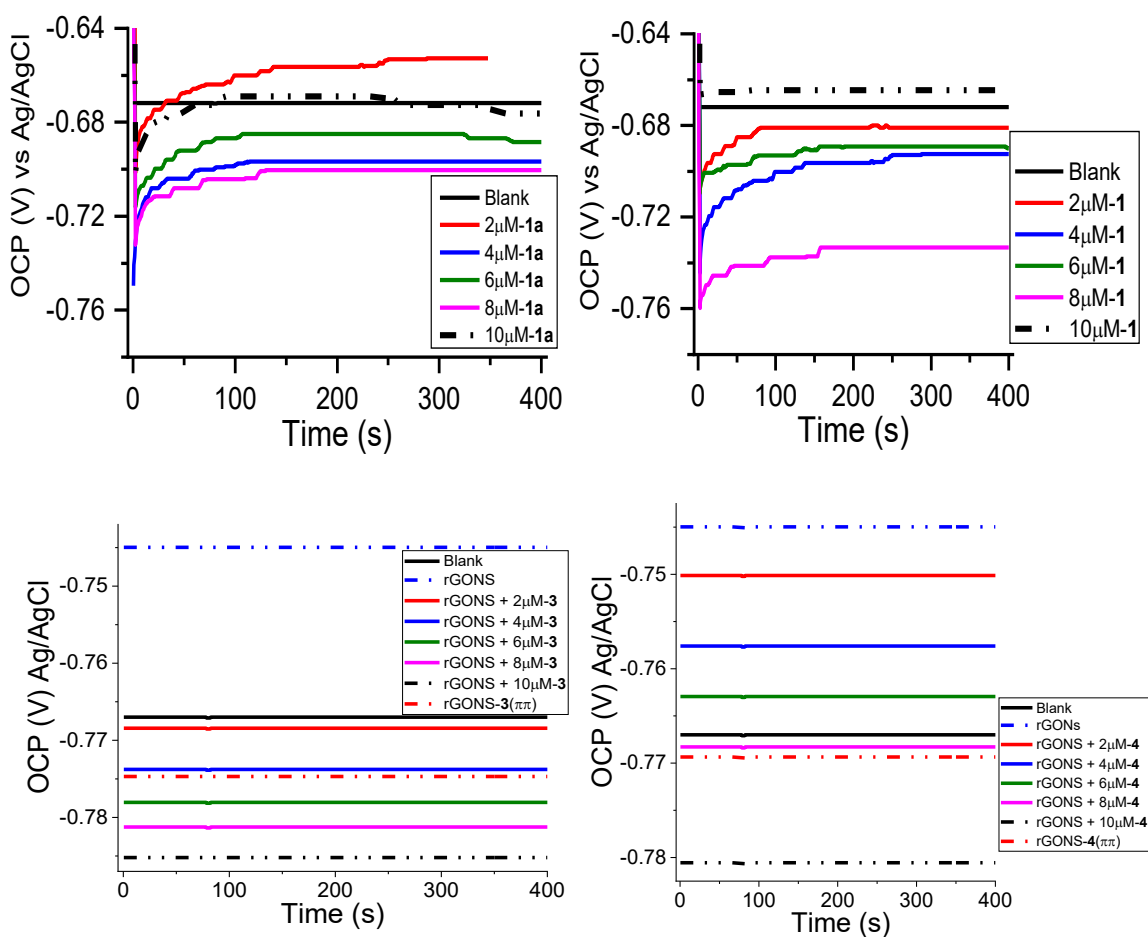
Figure 4.2a,b suggest that the presence of **1a** and **1** in solution predominantly affect the cathodic aluminum corrosion in 1.0 M hydrochloric acid. This assertion was made due to the results presented in Figures 4.4 a,b which show that OCP values of aluminum corrosion in the presence of the inhibitors (in most cases) are more negative compared to the OCP value in their absence suggesting predominantly cathodic character. Complex **1** gave more negative OCP values than **1a** showing more cathodic behavior for the former and can be attributed to the fact that **1** possesses more electron rich properties due to its extended conjugation. At the start in Figure 4.4, an abrupt shift of OCP towards positive potentials was noticed. This initial increase had been related to the formation and thickening of the oxide film on the metallic surface, suggesting corrosion protection [84]. The same predominant cathodic behaviour was observed for **2a**, **2**, **3** and **4** (not shown). Figs. 4.4c,d show that rGONS are

predominantly anodic in nature, which earlier has been described [87, 88]. In the presence of rGONS, complex **3** characteristic is predominantly cathodic (Fig. 4.4c) but complex **4** has mixed inhibitor behaviour (Fig. 4.4d). For phthalocyanine, similar trend has appeared in literature before [49]. There is no trend on the shift with increase in concentration.

The variation of OCP in the absence and presence of complexes **5**_H₂, **5**_Ga and **5**_Co in 1.0 M hydrochloric acid solution are presented in Figs. 4.4e–g. Figs. 4.4e–g reveal more positive OCP signals in the presence of **5**_H₂, **5**_Co and **5**_Ga than in their absence, except for complex **5**_Co gave a more negative OCP signal at 10 μ M. The more positive OCP signals suggests predominant anodic character for the inhibitors. The more negative OCP signal at 10 μ M for **5**_Co suggest predominantly cathodic character of the inhibitor. A shift to negative potential has also been associated with adsorption of inhibitors on the metal [88]. This would be possible in this work at high concentrations. The assertion of the anodic characters of the studied inhibitors follows the opinion that OCP shifts towards positive values when the inhibitors are present imply they influence anodic metal corrosion process more [89].

Generally, mono-Pcs with bulkier substituents possess predominant cathodic character but this behaviour is observed for ball-type phthalocyanine with less bulkier substituent. Apparently therefore, bulkier benzothiazole substituted Pcs (**1** and **2**) are predominantly cathodic and less bulkier substituted Pcs (**5**_H₂, **5**_Co, **5**_Ga, **6** and **7**) are predominantly anodic. Bulky substituted phthalocyanines are known to show reduced aggregation [90], improve solar cell performance [91],

anticancer and antibacterial properties [92], until now, literature [41, 93] shows no clear understanding of how these affect anodic and cathodic characters of phthalocyanine corrosion inhibitors. Aluminium is known to resist corrosion by forming oxide films [29] but in the presence of studied corrosion inhibitors, the oxide films thicken as observed by flattening of the curves shown in Fig. 4.4 which exhibit corrosion inhibition [84].



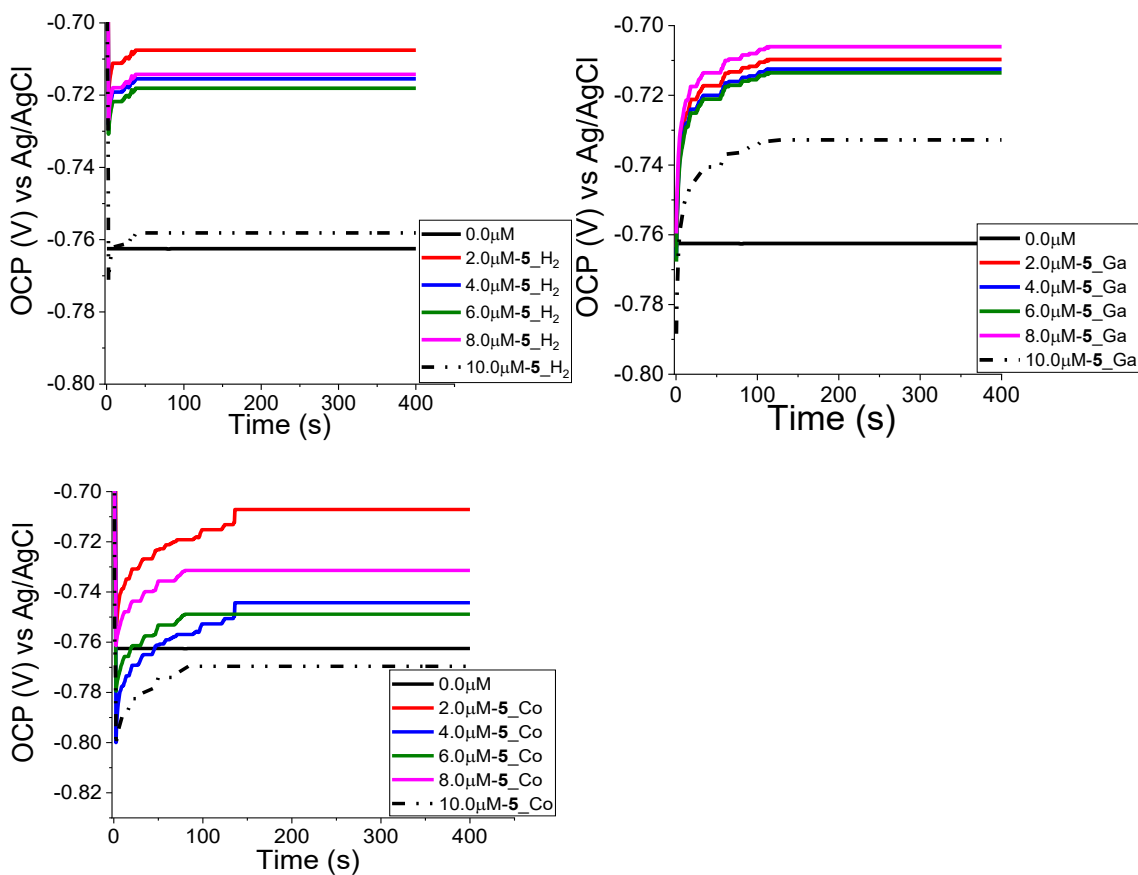


Figure 4.4: Plots of open circuit potential with time for aluminium (in 1.0 M HCl) in the absence (blank) and presence of inhibitors.

4.4 Potentiodynamic polarization measurements

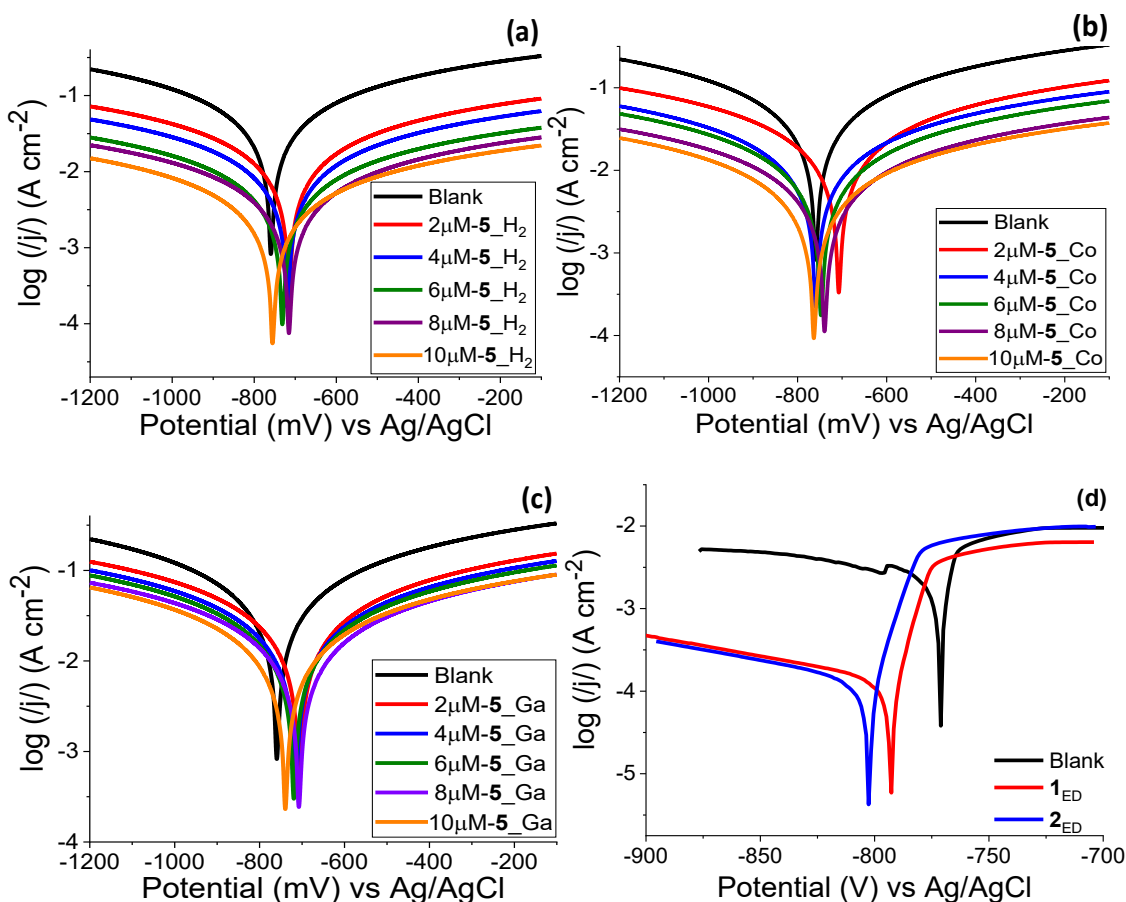
Fig. 4.5a–d present polarization plots. These studies were done in solution (complexes **5** as examples) and electrodeposited (complexes **1** and **2** as examples). In solution, the different concentrations of the inhibitors in 1.0 M hydrochloric acid solution show anodic or cathodic shifts compared to blank. Fig. 4.5d presents polarization curves for electrodeposited **1** and **2** 1.0 M hydrochloric acid solution. The electrochemical parameters determined from the plots include: corrosion current density (j_{corr}), corrosion potential (E_{corr}), anodic (β_a) and

cathodic (β_c) Tafel slopes and corrosion inhibition efficiency (IE%); and are shown in Table 4.1. Method of determination is shown in Fig. 4.5e.

4.4.1 Corrosion current density (j_{corr}):

A trend of decrease in corrosion current density (j_{corr}) was observed, as shown in Tables 4.1 to 4.4, for the metal corrosion processes in the presence of the studied inhibitors compared to the blank solution. This trend is also observed for electrodeposited complexes **1** and **2**. These observations indicate that the presence of the inhibitors retarded the Cl^- induced metal corrosion as supported by findings for the two pyridinecarboxaldehyde thiosemicarbazone compounds studied as corrosion inhibitors elsewhere [94]. Table 4.1 shows that the increase in inhibitor concentration caused a further decrease in corrosion current density. In all studied concentrations, in the presence of **1**, corrosion current densities are smaller than those obtained in the presence of **1a**. This is an indication that the Pc is a better corrosion inhibitor. For electrodeposited **1** though the j_{corr} values are higher than **1** in solution. Better corrosion protection of coated *Artemisia vulgaris* [95] was reported than when in solution [96]. The trend for the rest Pcs in Tables 4.1 to 4.4 shows that increase in concentration of the inhibitor caused a progressive decrease in the corrosion current density. Observed corrosion current density decrease when **3** or **4** are combined with rGONS reveal synergistic inhibition effect since the values are smaller than for individual components, except for $\pi\pi$ conjugates: rGONS-**3**($\pi\pi$) and rGONS-**4**($\pi\pi$) where the current is high, Table 4.2. The high current could be a result of the low

amounts of the Pcs $\pi\pi$ stacked on rGONS. The observed trend of j_{corr} values is of the order **5**_{H₂} < **5**_{Co} < **5**_{Ga}, Table 4.3. Thus, corrosion inhibition is largest for **5**_{H₂} and lowest for **5**_{Ga} comparatively, showing the larger the size of the central metal, the worse the performance as corrosion inhibitors. The j_{corr} values are lowest for complex **6** compared to **7** showing the better corrosion behavior, Table 4.4. The explanation for the observed improved corrosion inhibition of **6** than **7** is the presence of the heteroatom (N). In the presence of the studied inhibitors, a trend of decrease in corrosion current density (j_{corr}) indicates retardation of Cl^- induced metal corrosion. Similar explanation was opined for pyridinecarboxaldehyde thiosemicarbazone corrosion inhibitors [97].



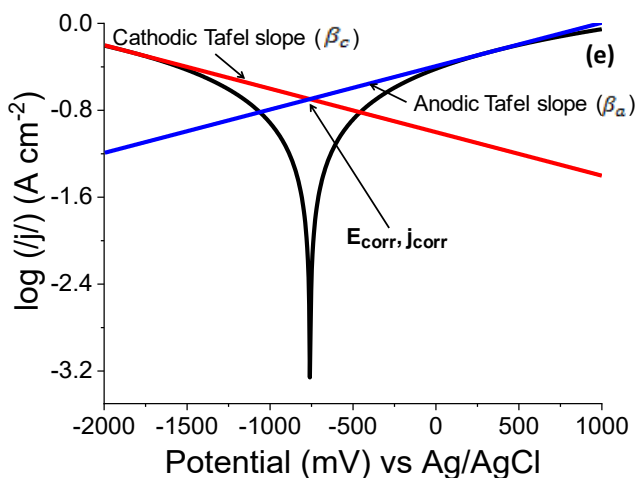


Figure 4.5: Potentiodynamic polarization curves for aluminium (in 1.0 M HCl) in the absence (blank) and presence of (a) **5**_H₂, (b) **5**_Ga, (c) **5**_Co, (d) electrodeposited **1** and **2**, (e) method for the calculation of E_{corr} , j_{corr} and Tafel slopes. Herein, the subscript ED represents electrodeposited.

4.4.2 Corrosion potential (E_{corr}):

Classification of an inhibitor as predominantly anodic or cathodic was reported by Yan and co-workers [94] to be when the difference in corrosion potential is more than 85 mV when compared to corrosion potential of the blank. There is less than 85 mV difference in corrosion potential for all compounds studied. The values in Table 4.1–4.4 therefore establish that the compounds studied behaved as mixed-type corrosion inhibitors. This also applies to electrodeposited **1** and **2**, Table 4.1.

4.4.3 Tafel slopes (β_a and β_c):

Further classification of the mode of inhibition as predominantly anodic or cathodic has been done earlier using the relative magnitudes of β_a and β_c [84, 98]. Values of cathodic Tafel slopes (β_c), presented (Tables 4.1–4.4), are all higher (more positive) in the presence of all inhibitors than in their absence

suggesting a predominant cathodic character for all. Anodic Tafel slopes (β_a) presented in Table 4.1–4.4 have lower values in the presence of the inhibitors than in the absence. This is a good indication the complexes also affected the anodic corrosion process, suggesting mixed type characters for the studied corrosion inhibitors.

4.4.4 Corrosion inhibition efficiency (IE%):

The following equation 4.1 are important for assessing the corrosion protection properties of the studied corrosion inhibitors coated on aluminium from polarization curves [99]:

$$IE\% = \frac{j_{corr}^0 - j_{corr}}{j_{corr}^0} \times 100 \quad 4.1$$

where IE% the inhibition efficiency, j_{corr}^0 and j_{corr} are the corrosion current densities without coating and with coating, respectively.

In the presence of corrosion inhibitors effective protection of the metal surface is achieved (as judged by the high IE% calculated as shown by equation 4.1). That is to say that the rate at which the metal dissolution proceeds decreased substantially during the corrosion process, leading to decreased metal corrosion as reflected in the calculated inhibition efficiency values presented in Table 4.1–4.4. Values of IE% presented in Table 4.1 increased with the concentration of **1a** and **1** (with the exception of **1** at 10 μ M concentration), indicating that the presence of the inhibitors retarded the metal corrosion process. It is generally believed that metal surfaces are protected by corrosion inhibitors via adsorption

of the inhibitor molecules onto metal surfaces [88, 94]. The corrosion inhibition efficiencies are higher for **1** compared to **1a**, showing superior inhibition (Table 4.1). The same applies to **2** and **2a** due to more conjugated π -electrons. When electrodeposited, IE% values are higher for **1** and **2** than in solution, Table 4.1, showing the importance of electrodeposition. Complex **4** gave better IE% values compared to **3** and the values increased with the concentration of the inhibitors. The better corrosion inhibition exhibited by **4** than **3** is because it has more hetero-atoms (S, N). The values increased in the presence of rGONS, Table 4.2. The values are low for $\pi\pi$ stacked conjugates: rGONS-**3**($\pi\pi$) and rGONS-**4**($\pi\pi$). The under performance of the $\pi\pi$ stacked conjugates, Table 4.2, could be a result of the low amounts of the Pc. The IE% value is slightly higher for rGONS-**4**($\pi\pi$) with higher Pc loading. The IE% values are larger for **5**_{H₂} compared to **5**_{Co} and **5**_{Ga}, showing the superior corrosion inhibition of metal free derivative. **5**_{Ga} performed worse than the **5**_{Co} at the same concentration, Table 4.3. The IE% values are larger for **6** compared to **7**, showing superior corrosion inhibition of asymmetric derivative which have more heteroatom (N), Table 4.4.

In recent past, a study reported four phthalocyanines: 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine, 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine, 2,9,16,23-tetratert-butyl-29H,31H-phthalocyanine and 29H,31H-phthalocyanine [42]. Comparatively, compounds **3**, **4**, **5**_{H₂} and **6** performed better than the earlier reported phthalocyanines as corrosion inhibitors because **5**_{H₂} and **6** have more heteroatoms and better inhibition

exhibited by compounds **3** and **4** is because of more heteroatoms necessitated by two phthalocyanine rings of ball types.

Table 4.1: Polarization polarization data for **1a**, **1**, **2a**, **2**, electrodeposited **1** and **2** in 1 M HCl.

Concentration (μM)	$-E_{\text{corr}}$ (mV)	j_{corr} (mA cm^{-2})	$-\beta_c$ (mV dec^{-1})	β_a (mV dec^{-1})	IE%
0	672.0 ± 4.0	8.68 ± 0.44	493.8 ± 3.1	91.8 ± 1.6	-
1a					
2	652.0 ± 8.0	4.64 ± 0.8	362.3 ± 4.8	231.1 ± 7.1	46.9 ± 6.5
4	686.0 ± 6.0	4.13 ± 0.24	369.8 ± 5.5	239.7 ± 1.3	52.5 ± 0.4
6	688.0 ± 16.0	3.48 ± 0.66	201.3 ± 4.3	129.1 ± 2.8	59.9 ± 1.8
8	700.0 ± 6.0	3.04 ± 0.11	279.4 ± 3.7	219.4 ± 6.3	64.9 ± 3.8
10	676.0 ± 14.0	2.54 ± 0.33	278.1 ± 2.1	236.8 ± 5.5	70.8 ± 1.3
1 (in solution)					
2	680.0 ± 4.0	3.50 ± 0.25	267.5 ± 3.8	131.6 ± 3.6	59.7 ± 0.8
4	692.0 ± 3.0	2.65 ± 0.23	139.5 ± 2.9	79.1 ± 2.8	69.5 ± 0.9
6	692.0 ± 4.0	2.28 ± 0.1	94.8 ± 4.3	71.7 ± 7.8	73.8 ± 0.1
8	732.0 ± 3.0	1.65 ± 0.05	112.4 ± 1.4	172.2 ± 1.4	81.0 ± 0.2
10	664.0 ± 4.0	1.72 ± 0.05	157.8 ± 4.2	69.9 ± 0.5	80.2 ± 0.6
ED					
Concentration (μM)	$-E_{\text{corr}}$ (mV)	j_{corr} ($\mu\text{A cm}^{-2}$)	$-\beta_c$ (mV dec^{-1})	$-\beta_a$ (mV dec^{-1})	IE%

Blank	768.1 ± 1.1	749.8 ± 0.0	115.1 ± 5.2	313.0 ± 3.0	-
1_{ED}	800.5 ± 1.5	94.5 ± 2.3	11.1 ± 0.6	87.7 ± 6.8	87.4 ± 0.3
2_{ED}	790.1 ± 2.1	89.2 ± 0.7	3.9 ± 0.3	88.1 ± 3.3	88.1 ± 0.1
Concentration (μM)	$-E_{\text{corr}}$ (mV)	j_{corr} (mAcm^{-2})	$-\beta_c$ (mVdec^{-1})	β_a (mVdec^{-1})	IE%
0	700 ± 4.0	6.37 ± 0.2	494.5 ± 14.9	67.4 ± 8.2	-
2a					
2	720 ± 12.0	4.58 ± 0.3	373.9 ± 58.4	115.3 ± 13.5	28.2 ± 1.7
4	704 ± 4.0	3.88 ± 0.1	216.2 ± 2.0	237.6 ± 3.5	39.1 ± 0.2
6	662 ± 6.0	3.28 ± 0.05	364.9 ± 67.0	127.4 ± 3.4	50.0 ± 0.8
8	608 ± 4.0	2.65 ± 0.05	321.6 ± 0.3	198.4 ± 11.0	58.3 ± 2.0
10	652 ± 0.0	1.53 ± 0.1	115.1 ± 50.3	36.6 ± 4.0	76.1 ± 1.3
2 (in solution)					
2	672 ± 0.0	1.82 ± 0.20	95.5 ± 4.9	90.6 ± 7.6	71.5 ± 2.3
4	751 ± 0.0	1.10 ± 0.04	192.7 ± 20.5	615.4 ± 162.3	82.7 ± 1.1
6	704 ± 0.0	1.17 ± 0.03	52.1 ± 4.9	59.3 ± 2.5	81.6 ± 0.02
8	720 ± 4.0	1.46 ± 0.03	69.6 ± 1.4	41.1 ± 1.2	77.1 ± 1.1
10	728 ± 4.0	1.67 ± 0.02	88.5 ± 3.7	54.7 ± 1.1	73.8 ± 1.0

The subscript ED represents electrodeposited.

Table 4.2: Potentiodynamic polarization data for **3**, **4**, rGONS (3 mg) mixed with **3** or **4** and rGONS-**3**($\pi\pi$) and rGONS-**4**($\pi\pi$) in 1 M HCl

System	$-E_{\text{corr}}$ (mV)	j_{corr} (μAcm^{-2})	$-\beta_c$ (mVdec $^{-1}$)	β_a (mVdec $^{-1}$)	IE%
Blank	765.4 ± 1.4	749.8 ± 6.1	109.9 ± 19.3	310.1 ± 11.1	0.0 ± 0.0
Complex 3					
3a (2 μM)	801.3 ± 0.3	154.5 ± 8.3	28.3 ± 5.8	185.8 ± 8.5	79.4 ± 1.1
3b (4 μM)	802.0 ± 0.5	90.0 ± 9.8	15.8 ± 2.3	110.6 ± 16.1	88.0 ± 1.3
3c (6 μM)	798.7 ± 1.7	69.7 ± 15.7	5.6 ± 1.1	49.3 ± 3.4	90.7 ± 2.1
3d (8 μM)	806.1 ± 0.8	51.7 ± 19.5	8.7 ± 1.2	40.0 ± 4.8	93.1 ± 2.6
3e (10 μM)	811.0 ± 2.2	26.2 ± 9.0	5.7 ± 0.9	28.6 ± 6.2	96.5 ± 1.2
Complex 4					
4a (2 μM)	804.1 ± 0.0	133.7 ± 21.2	41.0 ± 1.4	203.3 ± 33.7	81.8 ± 3.2
4b (4 μM)	806.0 ± 0.0	88.6 ± 6.9	18.1 ± 4.6	101.1 ± 11.2	88.3 ± 0.8
4c (6 μM)	800.0 ± 0.6	69.5 ± 10.3	8.4 ± 2.4	208.3 ± 10.6	91.0 ± 1.1
4d (8 μM)	809.2 ± 0.0	47.2 ± 14.2	9.9 ± 3.3	82.1 ± 2.2	93.7 ± 1.9
4e (10 μM)	817.1 ± 0.6	23.0 ± 5.0	5.0 ± 0.5	35.3 ± 5.3	96.9 ± 0.7
rGONS	744.8 ± 0.4	614.1 ± 13.5	6.3 ± 1.3	69.1 ± 12.6	18.1 ± 1.8
rGONS-3					
rGONS- 3a	750.1 ± 0.0	95.5 ± 26.5	30.9 ± 3.0	43.8 ± 4.3	87.3 ± 3.5
rGONS- 3b	757.0 ± 0.6	57.9 ± 12.9	20.0 ± 6.2	34.3 ± 3.4	92.3 ± 1.7
rGONS- 3c	763.0 ± 0.1	33.4 ± 7.2	17.7 ± 3.1	21.5 ± 1.2	95.6 ± 0.9

rGONS-3d	768.0 ± 0.3	25.4 ± 8.9	13.6 ± 2.8	23.2 ± 2.3	96.6 ± 1.2
rGONS-3e	781.0 ± 0.0	14.1 ± 2.4	9.0 ± 1.6	14.0 ± 3.3	97.4 ± 0.4
rGONS-3($\pi\pi$)	770.7 ± 1.3	358 ± 4.6	21.0 ± 0.8	38.1 ± 1.1	52.2 ± 0.6
rGONS-4					
rGONS-4a	768.4 ± 0.0	45.2 ± 0.5	31.1 ± 1.2	52.1 ± 5.8	91.2 ± 2.7
rGONS-4b	773.8 ± .07	31.7 ± 0.3	18.6 ± 5.5	34.1 ± 5.2	94.3 ± 1.5
rGONS-4c	778.1 ± 0.8	20.5 ± 0.5	14.1 ± 1.1	23.1 ± 3.1	95.6 ± 1.6
rGONS-4d	781.3 ± 0.3	17.3 ± 0.9	7.2 ± 2.3	15.3 ± 2.9	97.5 ± 0.3
rGONS-4e	785.5 ± 0.0	10.5 ± 0.2	7.0 ± 0.0	11.0 ± 0.0	98.1 ± 0.5
rGONS-4($\pi\pi$)	777.7 ± 3.0	328.4 ± 12.7	23.3 ± 3.2	17.8 ± 4.3	56.2 ± 1.7

The following letters stand for the following: a = 2 μ M, b = 4 μ M, c = 6 μ M, d = 8 μ M
and e = 10 μ M.

Table 4.3: Polarization polarization data for **5_H₂**, **5_Co** and **5_Ga** in 1 M HCl.

Concentration (μM)	$-E_{\text{corr}}$ (mV)	j_{corr} (mAcm^{-2})	$-\beta_c$ (mVdec^{-1})	β_a (mVdec^{-1})	IE%
0	762.0 ± 2.0	200.9 ± 15.4	500.0 ± 76.3	312.3 ± 22.7	-
5_H₂					
2 μM	710.0 ± 5.8	63.2 ± 5.2	148.5 ± 7.6	81.6 ± 9.5	68.5 ± 1.2
4 μM	722.2 ± 4.0	42.8 ± 3.5	101.0 ± 3.1	56.0 ± 3.0	78.7 ± 0.1
6 μM	724.0 ± 6.0	26.1 ± 1.6	61.5 ± 4.2	34.7 ± 7.2	87.0 ± 0.2
8 μM	720.0 ± 4.0	19.9 ± 0.9	45.9 ± 5.0	28.4 ± 2.7	90.1 ± 0.3
10 μM	760.1 ± 4.0	13.5 ± 1.4	33.7 ± 1.9	20.0 ± 0.4	93.3 ± 0.2
5_Ga					
2 μM	712.0 ± 3.3	111.0 ± 4.5	274.6 ± 15.7	133.4 ± 9.4	44.7 ± 1.9
4 μM	713.4 ± 2.7	91.5 ± 5.1	207.0 ± 4.0	109.2 ± 5.3	54.5 ± 0.8
6 μM	716.6 ± 4.4	80.6 ± 2.6	183.3 ± 3.2	117.0 ± 1.3	59.9 ± 1.6
8 μM	706.5 ± 1.6	66.0 ± 8.2	148.6 ± 7.8	106.9 ± 11.2	67.2 ± 1.5
10 μM	736.5 ± 4.2	60.9 ± 6.3	140.8 ± 8.4	91.7 ± 1.7	69.7 ± 0.7
5_Co					

2 μ M	711.1 $\pm$ 3.1	90.2 $\pm$ 2.0	201.3 $\pm$ 6.9	105.3 $\pm$ 5.2	55.0 $\pm$ 2.4
4 μ M	756.3 $\pm$ 4.1	66.0 $\pm$ 1.8	135.7 $\pm$ 8.6	68.9 $\pm$ 2.9	67.2 $\pm$ 1.5
6 μ M	748.0 $\pm$ 0.0	45.4 $\pm$ 3.6	106.8 $\pm$ 7.5	60.4 $\pm$ 8.1	77.3 $\pm$ 0.0
8 μ M	736.6 $\pm$ 5.6	29.0 $\pm$ 1.4	68.4 $\pm$ 4.8	38.4 $\pm$ 7.8	85.5 $\pm$ 0.0
10 μ M	768.0 $\pm$ 2.0	24.3 $\pm$ 1.1	56.4 $\pm$ 5.7	31.9 $\pm$ 5.5	87.7 $\pm$ 0.0

Table 4.4: Polarization polarization data for **6** and **7** in 1 M HCl.

Concentration (μM)	$-E_{\text{corr}}$ (mV)	j_{corr} (mAcm^{-2})	$-\beta_c$ (μVdec^{-1})	β_a (μVdec^{-1})	IE%
0	763.5 ± 3.0	200.9 ± 13.2	311.8 ± 25.5	321.9 ± 33.6	-
6					
2	723.0 ± 1.0	47.4 ± 3.8	68.3 ± 11.6	110.7 ± 35.1	74.5 ± 1.9
4	730.5 ± 1.5	30.5 ± 2.0	40.7 ± 7.5	87.5 ± 18.8	82.8 ± 2.0
6	736.0 ± 0.0	26.0 ± 1.8	37.5 ± 2.8	60.6 ± 4.3	86.5 ± 0.5
8	740.5 ± 0.5	17.6 ± 1.2	24.5 ± 3.1	40.0 ± 7.7	91.0 ± 0.2
10	745.0 ± 1.0	14.9 ± 0.9	21.5 ± 5.7	34.6 ± 2.9	91.9 ± 0.7
7					
2	715.0 ± 1.0	64.4 ± 3.0	312.0 ± 12.6	117.9 ± 26.7	67.9 ± 0.6
4	720.0 ± 0.0	42.8 ± 2.6	219.0 ± 26.1	102.0 ± 18.2	76.9 ± 1.9
6	731.2 ± 0.8	29.9 ± 1.0	41.8 ± 4.3	68.5 ± 12.2	85.8 ± 0.7
8	737.2 ± 2.3	27.7 ± 0.5	40.3 ± 7.5	64.8 ± 29.5	86.8 ± 0.5
10	742.6 ± 1.5	26.3 ± 1.3	40.2 ± 1.9	62.8 ± 17.1	87.0 ± 0.1

4.5 Adsorption Isotherms

Considering that adsorption of inhibitor molecules onto the metal surface is the first step in the mechanism of corrosion inhibition [100], it is important to understand the adsorption behavior of organic molecules (inhibitors) on the metal surface. Thus, the adsorption of the studied corrosion inhibitors was investigated by subjecting the experimentally calculated surface coverage (θ) values to various adsorption isotherms such as El-Awady, Langmuir, Temkin and Freundlich isotherms. The values of equilibrium constants from the isotherm plots: Langmuir (K_L), Freundlich (K_F), Temkin (K_T), and El-Awady (K_{EI}) are presented in Tables 4.5-4.8.

4.5.1 Langmuir isotherm

Langmuir isotherm linear plots [101] are presented in Figure 4.6 for adsorption of the studied inhibitors on aluminum surface in 1.0 M hydrochloric acid solution.

$$C/\theta = C/K_L + C \quad 4.2$$

Equation 4.2 also is equation 1.15, where K_L is the Langmuir equilibrium constant, θ is the surface coverage and C represents the inhibitor concentration.

Langmuir adsorption isotherm was derived based on the assumption that the adsorption surface possesses sites with equivalent/similar energies of

adsorption, allowing maximum/saturated adsorption of solute molecules for adsorbent monolayer coverage [101]. It implies that molecules following Langmuir adsorption mechanism should have slope value of unity as predicted by Equation 4.2. The linear form of Langmuir adsorption isotherm used herein (equation 4.2) has C as the inhibitor concentration, θ is surface coverage ($\theta = \text{IE\%/100}$) [101] and K_L is the adsorption equilibrium constant obtained from Langmuir isotherm. Values of regression coefficient (R^2) 0.9871 for **1a** and 0.9971 for **1** were obtained from Langmuir isotherm plots, Figure 4.4a, hence the **1** shows better fit. The values of K_L were derived from the intercept of the plots, and the K_L values for **1a** and **1** are $5.0 \times 10^5 \text{ M}^{-1}$ and $1.0 \times 10^6 \text{ M}^{-1}$ respectively, Table 4.5; these are large and positive indicating strong adsorption onto the metal surface. Thus **1** performed better than **1a**. Thermodynamically, equilibrium constant value less than unity suggests unfavorable process; equal to zero suggests the process is in dynamic equilibrium and more than unity suggests a favorable process. Thus the equilibrium constant values obtained for the studied inhibitors suggest they adsorbed favorably onto the metal surface. The Langmuir isotherm predicts a slope value of unity but 1.20 and 1.10 M are obtained, Table 4.5. Though these values are very close to unity, the Langmuir isotherm does not give the best explanation to the adsorption profiles of the studied inhibitors onto the metal surface. The theoretical derivation of the Langmuir isotherm assumes that the adsorbent (herein the metal) surface is homogeneous, implying that the adsorption surface sites should possess similar energy as discussed above.

Values of regression coefficient (R^2) 0.8505 for **2a** and 0.9497 for **2** were obtained from Langmuir isotherm plots, Figure 4.6b, suggesting the Pc fits better. The values of K_L were derived from the intercept of the plots, and the K_L values for **2a** and **2** are $1.4 \times 10^5 \text{ M}^{-1}$ and $1.3 \times 10^5 \text{ M}^{-1}$ respectively, Table 4.5; these are large and positive indicating strong adsorption onto the metal surface. The Langmuir isotherm predicts a slope value of unity but 0.8 and 1.1 M are obtained.

The values of K_L are positive and large for **3** and **4**, a good indication of strong attractive interactions, Table 4.6. Langmuir isotherm gave slope values of 0.98 and 0.99 for **3**, **4** and rGONS_**3** which are close to theoretical value of unity, Figure 4.6c and rGONS_**4** has slope value of unity as predicted by equation 4.2. This implies that the adsorption data of **3**, **4**, rGONS_**3** and rGONS_**4** followed the Langmuir isotherm.

Figure 4.6d presents the plot of Langmuir isotherm for adsorption of **5**_H₂, **5**_Ga and **5**_Co on aluminum and shows linear fits with R^2 values of 0.9992, 0.9955 and 0.9962 respectively. The plots gave values of slope 0.97, 1.23 and 0.94 respectively for **5**_H₂, **5**_Ga and **5**_Co which are close to unity and in agreement with theory, Table 4.7. Langmuir isotherm ideally depicts or accounts for chemisorption processes, this can be ascertained for adsorption of **5**_H₂, **5**_Ga and **5**_Co on aluminum by considering the obtained adsorption parameter (K_L) values obtained from intercepts of Langmuir plots.

Values of regression coefficient (R^2) 0.9989 for **6** and 0.9982 for **7** were obtained from Langmuir isotherm plots, Figure 4.6e, suggesting that **6** fits better. The values of K_L were derived from the intercept of the plots, and the K_L values

for **6** and **7** are $1.4 \times 10^6 \text{ M}^{-1}$ and $5.0 \times 10^5 \text{ M}^{-1}$ respectively, Table 4.8; these are large and positive indicating strong adsorption onto the metal surface. The Langmuir isotherm predicts a slope value of unity but 1.02 and 1.05 M are obtained, Table 4.8.

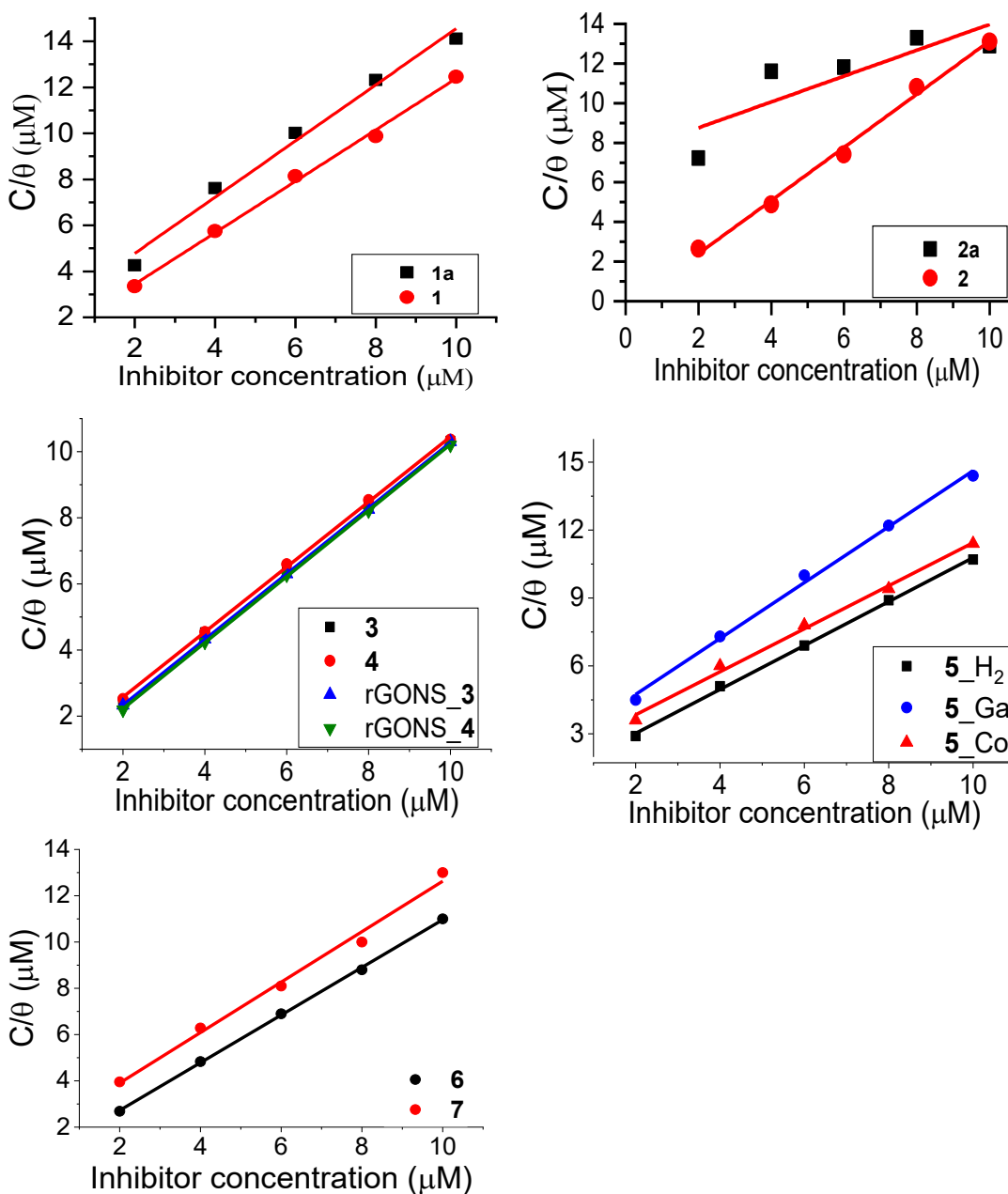


Figure 4.6: Langmuir isotherm plots at 28 °C

4.5.2 Freundlich isotherm

The Freundlich isotherm models adsorption of molecules on heterogeneous surfaces and the linear form used herein, equation 4.3, has C as the inhibitor concentration, θ is surface coverage (calculated as described above), “ n ” is Freundlich heterogeneity constant and K_F is the adsorption equilibrium constant obtained from Freundlich isotherm. Equations 4.3 and 1.16 are the same.

$$\ln \theta = \ln K_F + \frac{1}{n} \cdot \ln C \quad 4.3$$

Respectively, the values of K_F and “ n ” for the studied compounds are derived from the intercepts and slopes of Figure 4.7 plots (Equation 4.3). Freundlich isotherm plots gave R^2 values of 0.9728 and 0.9725 for adsorption data plots of **1a** and **1** respectively, showing a better fit for the Pc. The equilibrium constant (K_F) calculated from the Freundlich plots are 13.1 and 7.7 M^{-1} , respectively for **1a** and **1**, Table 4.5. Thus the equilibrium constant values obtained for the studied inhibitors suggest they adsorbed favorably onto the metal surface. The slope of the Freundlich plot (Figure 4.7a, Equation 4.3) allows the determination of an adsorption parameter (n) which gives a measure of the inhibitor adsorption layer [5]. Values of the Freundlich adsorption parameter (n) were calculated as 3.9 and 5.1 M respectively for the adsorption of **1a** and **1** on the metal surface, suggesting multilayer adsorption which is consistent with physisorption. The incorporation of benzothiazole moiety (**1a**) in a Pc ring to give **1**, therefore, did not cause a change in adsorption mechanism.

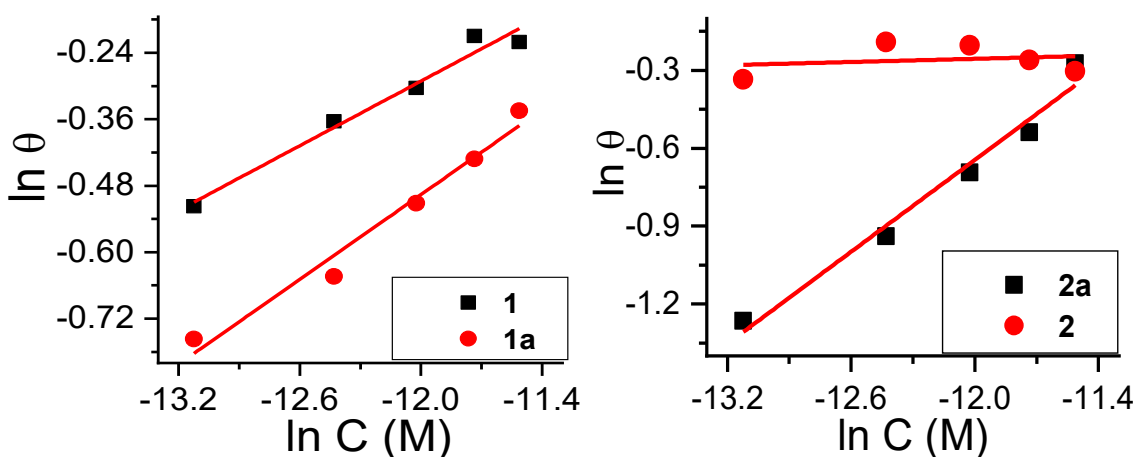
Freundlich isotherm plots gave R^2 values of 0.9754 and 0.0429 for adsorption data plots of **2a** and **2** respectively, showing a better fit for the phthalonitrile. The equilibrium constant (K_F) calculated from the Freundlich plots are 1.1×10^3 and 1.0 M^{-1} , respectively for **2a** and **2**. Thermodynamically, the equilibrium constant values obtained for **2a** and **2** suggest they adsorbed favorably onto the metal surface. The slope of the Freundlich plot (Figure 4.7b, Equation 4.3) gave Freundlich adsorption parameter (n) as 1.7 and 48.8 M respectively for the adsorption of **2a** and **2** on the metal surface. These values are positive suggesting attractive molecular lateral interactions [101]. The incorporation of benzothiazole moiety (**2a**) in a Pc ring to give **2**, though made the Pc substituent bulky, there seems not to be a change in adsorption mechanism.

Adsorption capacity values from Freundlich isotherm gave values of K_F for **3**, **4**, rGONS_3 and rGONS_4 which are greater than unity, suggesting strong adsorption of the inhibitors on metal surface, Table 4.6. The adsorption parameter, n , values are greater than unity, Table 4.6. These suggest multilayer adsorption due physisorption mechanism exhibited by **3**, **4**, rGONS_3 and rGONS_4. Freundlich plots for these corrosion inhibitors are shown in Fig. 4.7c.

Plots presented in Figure 4.7d are those of Freundlich isotherm for **5_H2**, **5_Ga** and **5_Co** adsorption on aluminum in 1.0 M hydrochloric acid solution. The correlation coefficient (R^2) of 0.9917, 0.9988 and 0.9936 respectively for **5_H2**, **5_Ga** and **5_Co** suggest good linear fits of the adsorption data to the isotherm. The Freundlich adsorption parameter (n) has values greater than unity,

suggesting many adsorption layers of **5**_{H₂}, **5**_{Ga} and **5**_{Co} molecules which is characteristic of physisorption, Table 4.7. Values of equilibrium adsorption constants obtained from intercepts of Freundlich plots (K_F) are greater than unity, indicating favorable adsorption interactions between inhibitor molecules and the aluminum surface.

K_F values greater than unity for **6** and **7** which are calculated from Freundlich isotherm, suggest strong adsorption of the inhibitors on metal surface, Table 4.8. The slopes of Freundlich isotherm plots gave adsorption parameter values, n , that are greater than unity. These suggest multilayer adsorption due physisorption mechanism exhibited by **6** and **7**. Figure 4.7e shows Freundlich plots of **6** and **7**.



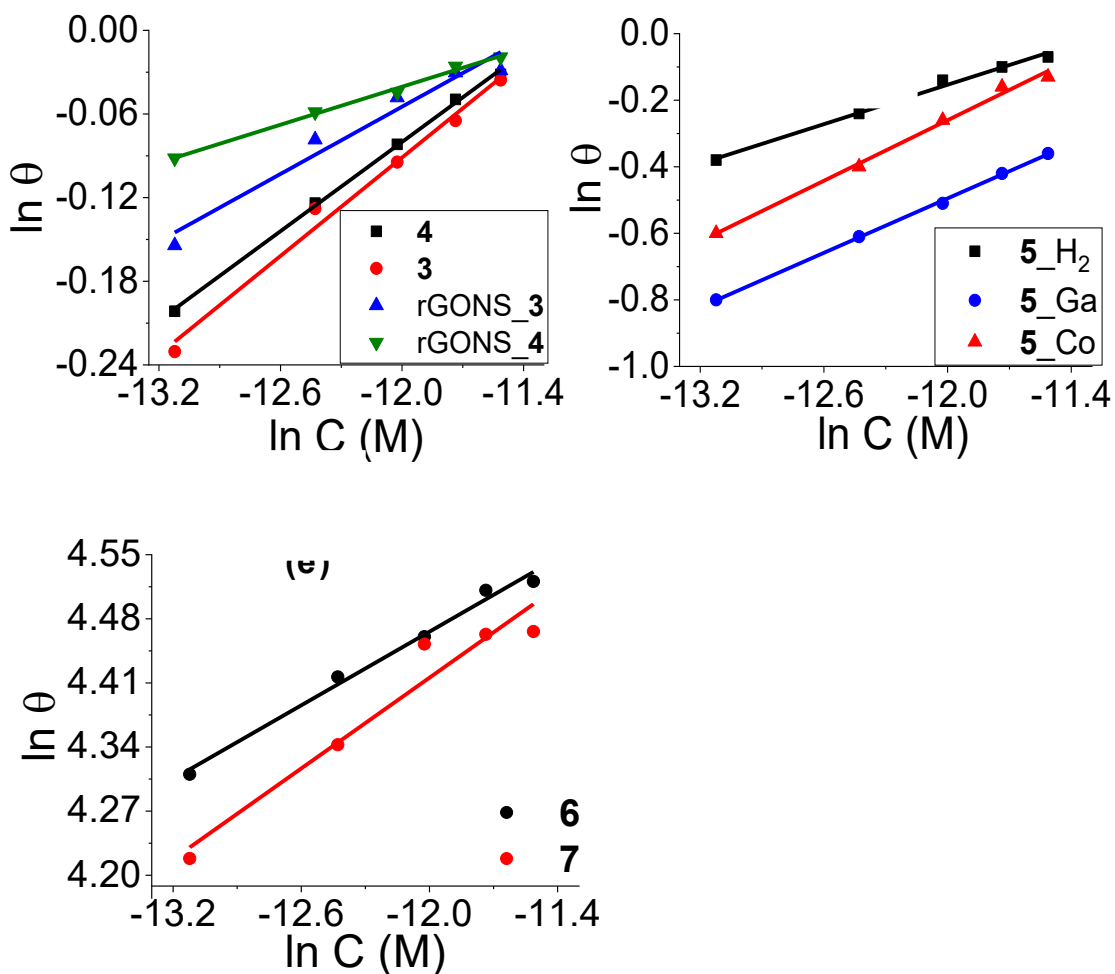


Figure 4.7: Freundlich isotherm plots at 28 °C.

4.5.3 Temkin isotherm

The Temkin isotherm model is based on adsorption of molecules on heterogeneous surfaces with adsorption sites possessing logarithmic energies from the equation reported earlier [102]. The linear form used herein (Equation 4.4) has C as the inhibitor concentration, θ is surface coverage (calculated as described above), “ f ” is Temkin heterogeneity constant and K_T is the adsorption equilibrium constant obtained from Temkin isotherm.

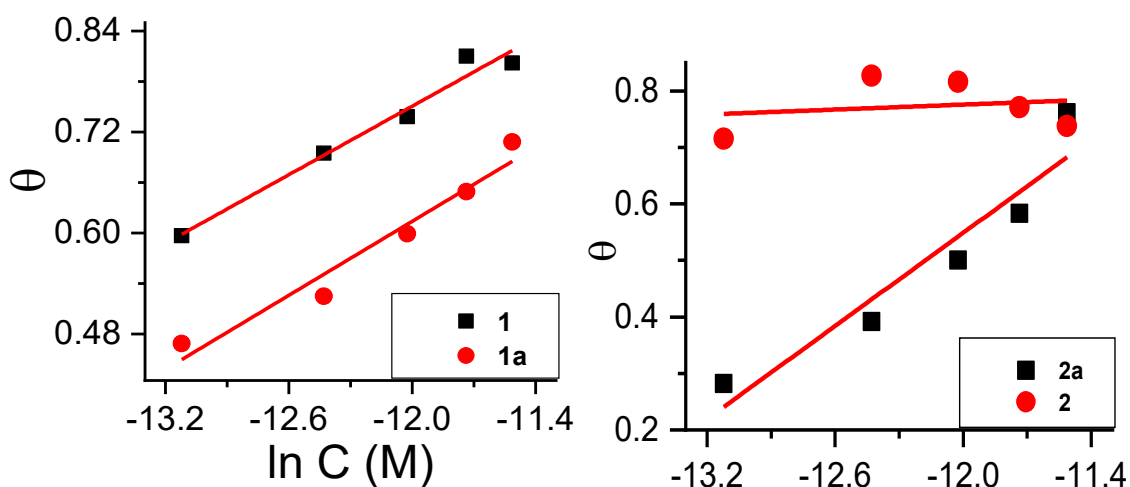
$$\theta = \frac{1}{f} (\ln K_T + \ln C) \quad 4.4$$

The values of K_T and “ f ” were derived from the intercepts and slopes of Figure 4.8 plots (Equation 4.4) respectively for the studied molecules. Temkin equilibrium constant (K_T) values calculated for **1a** and **1** are 1.07×10^7 and $4.1 \times 10^7 \text{ M}^{-1}$, respectively, these values are large and suggest favorable adsorption of the inhibitors on the metal surface in 1.0 M hydrochloric acid solution, Table 4.5. Temkin adsorption parameters (f) of 6.8 and 7.4 M, respectively, for **1a** and **1** are more than unity and positive suggesting the presence of attractive molecular interactions, supporting multilayer adsorption of the inhibitor molecules due to physisorption, as was the case with Freundlich adsorption discussed above.

Temkin equilibrium constant (K_T) values calculated for **2** and **2a** are 1.9×10^{28} and $1.2 \times 10^6 \text{ M}^{-1}$, respectively, these values are more than unity and suggest favorable adsorption of the inhibitors on the metal surface in 1.0 M hydrochloric acid solution, Table 4.5. Temkin adsorption parameters (f) of 68.5 and 3.6 M, respectively, for **2** and **2a** are more than unity and positive suggesting the presence of attractive molecular interactions, supporting multilayer adsorption of the inhibitor molecules due to physisorption.

Temkin adsorption parameter (f) values are 9.7 M^{-1} , 10.5 M^{-1} , 13.6 M^{-1} and 23.3 M^{-1} respectively for **3**, **4**, rGONS_3 and rGONS_4, Table 4.6. These values are greater than unity due to multilayer adsorption necessitated by physical adsorption mechanism. Large values of Temkin equilibrium adsorption constants (K_T) indicate strong interactions between inhibitor molecules and the metal surface.

Figure 4.8d presents the plots of Temkin isotherm for adsorption of **5**_H₂, **5**_Ga and **5**_Co on aluminum in 1.0 M hydrochloric acid solution. The correlation coefficient (R^2) values of obtained from these plots are 0.9944, 0.9939 and 0.9899 respectively for **5**_H₂, **5**_Ga and **5**_Co suggesting very good linear fits of the adsorption data to the isotherm. The values of Temkin adsorption parameter (f) are 6.4, 6.5 and 4.7 for **5**_H₂, **5**_Ga and **5**_Co respectively, and are greater than unity suggesting many adsorption layers of the inhibitor molecules which is characteristic of physisorption. K_T is greater than unity for **5**_H₂, **5**_Ga, **5**_Co, **6** and **7** which are calculated from Temkin isotherm, suggesting strong adsorption of the inhibitors on metal surface, Tables 4.7 and 4.8. Temkin adsorption parameter (f) values that are greater than unity, these suggest multilayer adsorption due physisorption mechanism exhibited by **5**_H₂, **5**_Ga, **5**_Co, **6** and **7**.



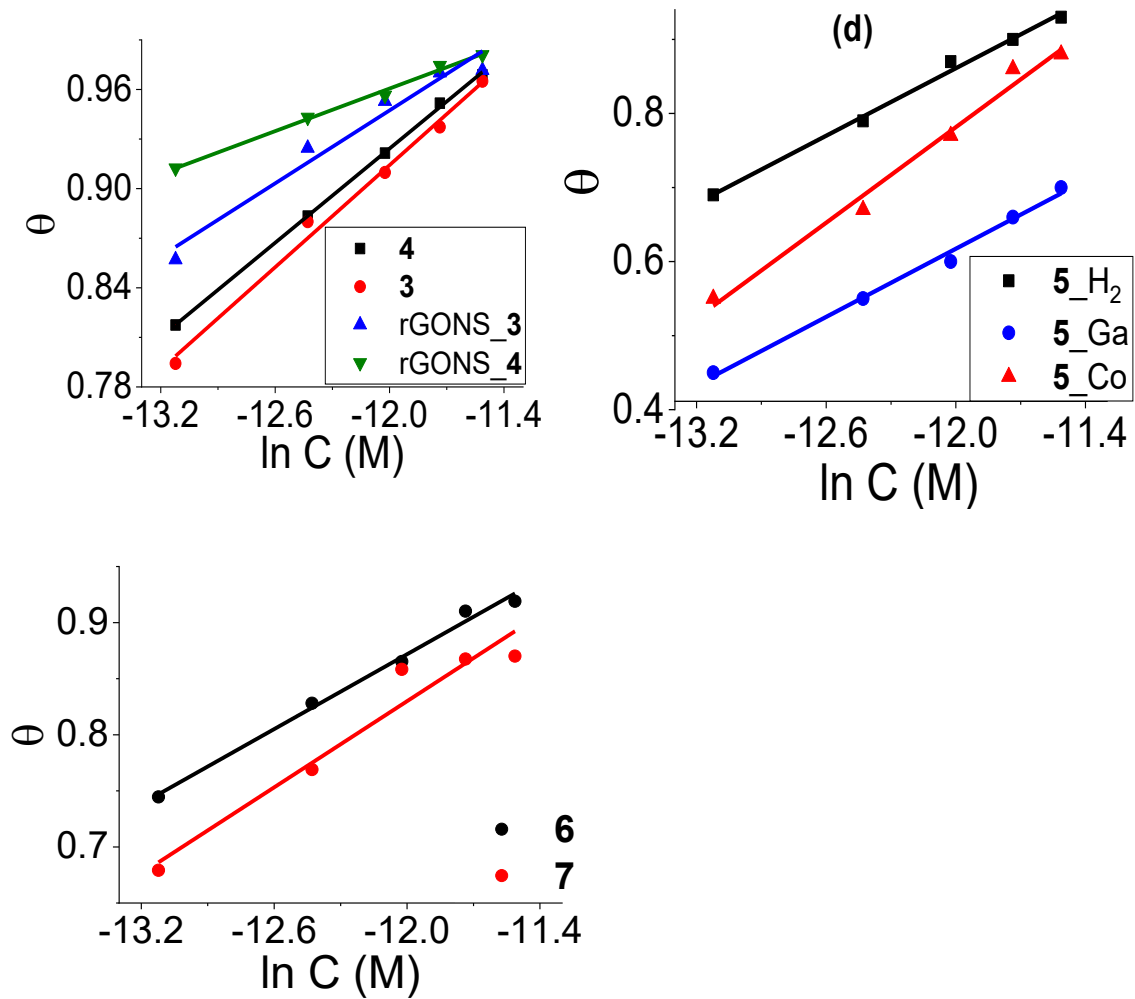


Figure 4.8: Temkin isotherm plots at 28 °C.

4.5.4 El-Awady isotherm

The adsorption model of the El-Awady isotherm characterizes the adsorption sites on the surface [103] and the linear form used (Equation 4.5) has C as the inhibitor concentration, θ is surface coverage, “ Y_{EI} ” is El-Awady heterogeneity constant and K_{EI} is the adsorption equilibrium constant obtained from El-Awady isotherm. The values of K_{EI} and “ Y_{EI} ” were derived respectively from the

intercepts and slopes of Equation 4.5 plots for the studied molecules. Equation 4.5 is the same with equation 1.18.

$$\ln \left[\frac{\theta}{(1 - \theta)} \right] = \ln K_{\text{El}} + Y_{\text{El}} \ln C \quad 4.5$$

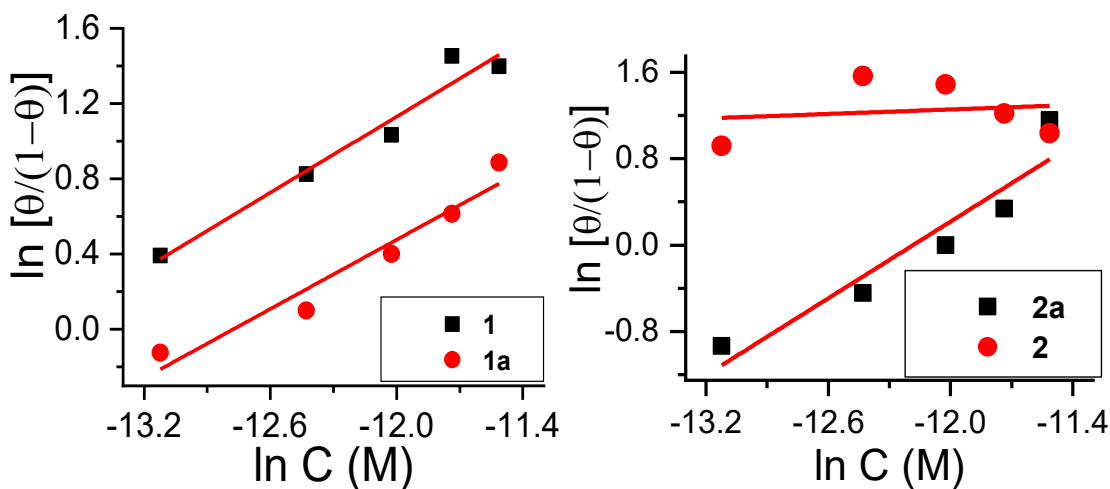
El-Awady plots for the adsorption data of **1a** and **1** onto the metal in 1.0 M hydrochloric acid solution are presented in Figure 4.9a. The equilibrium constants from the El-Awady plots (K_{El}) were calculated from the intercepts of the plots to give 2.5×10^3 and $1.0 \times 10^4 \text{ M}^{-1}$, respectively for **1a** and **1**, Table 4.5. These values are more than unity suggesting favorable adsorption. **1a** and **1** have El-Awady adsorption parameter (Y_{El}) values calculated from slopes of El-Awady plots as 0.6 M^{-1} and 0.7 M^{-1} , respectively (Table 4.5). These intrinsic adsorption parameters give a measure of the adsorbed inhibitor layers [5], suggesting that they are less than one inhibitor molecule thick on the metal surface, which is characteristic of chemisorption.

El-Awady plots for the adsorption data of **2a** and **2** onto the metal in 1.0 M hydrochloric acid solution are presented in Figure 4.9b. The equilibrium constants from the El-Awady plots (K_{El}) were calculated from the intercepts of the plots to give 1.8×10^6 and 8.0 M^{-1} , respectively for **2a** and **2**, Table 4.5. These values are more than unity suggesting favorable adsorption. **2a** and **2** have El-Awady adsorption parameter (Y_{El}) values calculated from slopes of El-Awady plots as 1.2 M^{-1} and -0.1 M^{-1} , respectively. The negative Y_{El} value for **2** suggests lateral repulsive interactions amongst **2** molecules likely occurred and steric hindrance very likely affected its adsorption, causing a drop in inhibition efficiency at higher concentrations. These intrinsic adsorption parameters give a measure

of the adsorbed inhibitor layers [5], suggesting adsorption layer of **2a** is unity and **2** has less than one inhibitor molecule thick on the metal surface, which characterize chemisorption.

The values of El-Awady equilibrium constants (K_{EI}) for **3**, **4**, rGONS_3 and rGONS_4 are greater than unity, suggesting strong metal/inhibitor interaction, Table 4.6. Y_{EI} obtained values suggest multilayer adsorption (or physisorption) because of calculated values of Y_{EI} which are greater than unity. The adsorption parameters for **3**, **4**, rGONS_3 and rGONS_4 were obtained from plots shown in Fig. 4.9c.

The values of El-Awady equilibrium constants (K_{EI}) for **5**_H₂, **5**_Co, **5**_Ga, **6** and **7** are greater than unity, suggesting strong metal/inhibitor interaction and Y_{EI} obtained values are less than unity in some cases and suggest chemisorption, Tables 4.7 and 4.8.



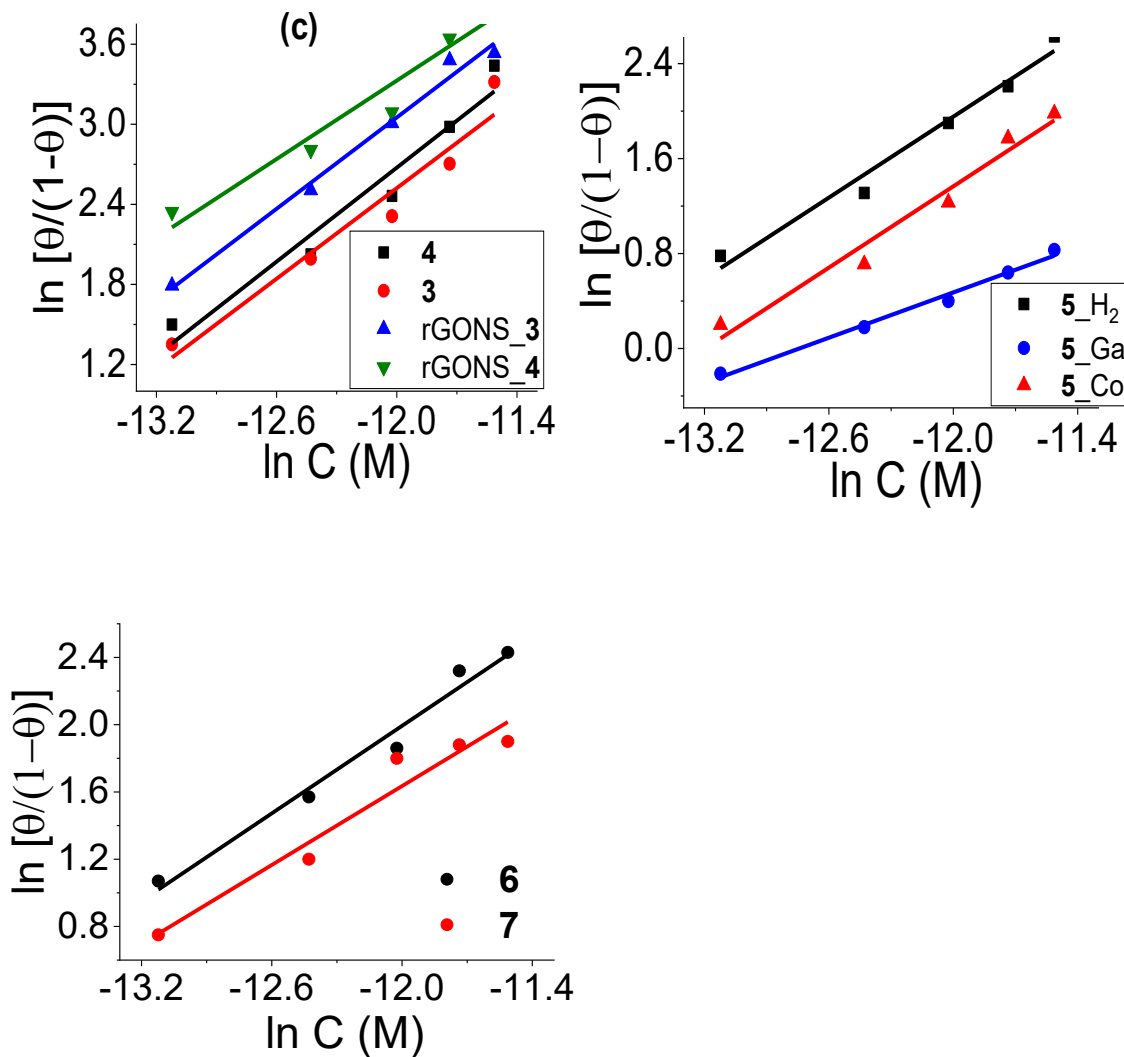


Figure 4.9: El-Awady isotherm plots at 28 °C.

4.5.5 Free energy

Free energies of adsorption (ΔG_{ads}^0) values were calculated from the various equilibrium constants (Equation 4.6).

$$\Delta G_{\text{ads}}^0 = -RT \ln(55.5 \times K_{\text{ads}}) \quad 4.6$$

Values of ΔG_{ads}^0 around -20 kJmol^{-1} or less (in magnitude) are consistent with physisorption, and those around -40 kJmol^{-1} or more (in magnitude) are due to

chemisorption as reported earlier [4]. The various values of ΔG_{ads}^0 calculated from the four isotherms studied for the corrosion inhibitors are presented in Tables 4.5 to 4.8.

1a has ΔG_{ads}^0 values as follows: -42.9 kJ/mol (Langmuir), -16.5 kJ/mol (Freundlich), -50.6 kJ/mol (Temkin) and -29.6 kJ/mol (El-Awady). In a similar manner ΔG_{ads}^0 values for **1** are as follows: -44.6 kJ/mol (Langmuir), -15.2 kJ/mol (Freundlich), -53.9 (Temkin) and -33.1 kJ/mol (El-Awady), Table 4.5. Langmuir and Temkin isotherms predict chemisorption for the studied inhibitors on aluminum in 1.0 M hydrochloric acid solution because the calculated ΔG_{ads}^0 values are more than -40 kJ/mol. Physisorption is depicted to be followed by Freundlich isotherm for the studied inhibitors considering that ΔG_{ads}^0 values less than -20 kJ/mol were calculated. ΔG_{ads}^0 values of the studied inhibitors are between -20 kJ/mol and -40 kJ/mol from calculations made using El-Awady parameters, suggesting competitive physisorption and chemisorption. Negative signs of the calculated values support spontaneous processes therefore favorable adsorption of the inhibitors. Different adsorption mechanisms predicted from ΔG_{ads}^0 values for the studied inhibitors, suggest that corrosion inhibition is a complex process. This assertion is supported by findings reported for the following corrosion inhibitors: cashew nut testa tannin, pyridinium-ionic liquid, isatin derivatives, clozapine and pyridine Schiff base derivatives [104–107].

Determined equilibrium constant values from the isotherm plots were used to calculate the values of free energy of adsorption (ΔG_{ads}^0) and found to be -39.8 kJ/mol (Langmuir), -18.0 kJ/mol (Freundlich), -45.1 kJ/mol (Temkin) and -46.1

kJ/mol (El-Awady) for **2a**. These values depict chemisorption (Langmuir, Temkin and El-Awady) and physisorption (Freundlich). Given that the Freundlich, Temkin and El-Awady isotherms best described **2a** adsorption onto the metal surface, a comprehensive adsorption (chemisorption/physisorption) mechanism took place during the corrosion inhibition process. Similarly, ΔG_{ads}^0 values are found to be -39.5 kJ/mol (Langmuir), -10.0 kJ/mol (Freundlich), -173.0 kJ/mol (Temkin) and -15.3 kJ/mol (El-Awady) for **2**, depicting comprehensive adsorption (chemisorption/physisorption) for Langmuir, physisorption (Freundlich and El-Awady) and chemisorption (Temkin). It can be concluded therefore that comprehensive adsorption took place during the corrosion inhibition process in the presence of **2**.

Calculated free energy of adsorption (ΔG_{ads}^0) values for **3**, **4**, rGONS_3 and rGONS_4 presented in Table 4.6, have values suggesting chemisorption from Langmuir, Temkin and El-Awady isotherms but Freundlich isotherm suggest physisorption.

ΔG_{ads}^0 values for **5_H₂**, **5_Ga** and **5_Co** (for Langmuir isotherm) were determined to be -44.6 kJ/mol, -42.9 kJ/mol and -42.9 kJ/mol, respectively, which are consistent with chemisorption. The ΔG_{ads}^0 values for Freundlich are less than -20 kJ/mol values suggesting physisorption. Values of ΔG for Temkin are -53.8 kJ/mol, -50.1 kJ/mol and -49.2 kJ/mol, while the negative signs indicate that the adsorption processes are spontaneous, their magnitudes (greater than -40 kJ/mol) indicate the mechanisms involved are chemisorption processes. It is difficult to explain why Temkin isotherm predicts chemisorption mechanism for

5_Co but it has lowest inhibition efficiency values compared to **5**_H₂ and **5**_Ga. The calculated ΔG_{ads}^0 values for El-Awady are -42.9 kJ/mol and -47.8 kJ/mol for **5**_H₂ and **5**_Co respectively, -30.4 kJ/mol and for **5**_Ga. This suggests chemisorption for **5**_H₂ and **5**_Co, and competitive physisorption and chemisorption for **5**_Ga. The observed difference in adsorption mechanism for **5**_Ga can be ascribed to the effect of attached axial ligand (Cl) to the central metal and heavy atom effect due to the presence of gallium. Values of free adsorption energy, from Langmuir, Temkin and El-Awady isotherms, indicate **5**_H₂ was most adsorbed onto the metal surface, **5**_Co was more adsorbed and **5**_Ga was the least adsorbed.

ΔG_{ads}^0 values for **6** and **7** were determined to be -25.3 kJmol⁻¹ and -26.0 kJmol⁻¹ (Freundlich) which are consistent with competitive adsorption, -59.7 kJmol⁻¹ and -56.3 kJmol⁻¹ (Temkin) values show chemisorption, El-Awady reveals chemisorption for **6** which has -41.1 kJmol⁻¹ and competitive adsorption for **7** which has -37.6 kJmol⁻¹. Negative signs of the calculated Gibbs free adsorption energy values indicate spontaneity of the adsorption processes of studied inhibitors. Free energy values calculated from Temkin and El-Awady plots reflect inhibitor performances exhibited by the studied molecules (**6**>**7**).

Table 4.5: Adsorption parameters for **1a**, **1**, **2a** and **2**. See footnote for more definitions.

	K_L	K_F	K_T	K_{EI}	Slope of Langmuir plot	n (F)	f (T)	Y (EL)	ΔG_{adsL} (kJmol ⁻¹)	ΔG_{adsF} (kJmol ⁻¹)	ΔG_{adsT} (kJmol ⁻¹)	ΔG_{adsEI} (kJmol ⁻¹)
						(M)	(M)	(M ⁻¹)				
1a	5.0×10^5	13.1	1.07×10^7	2.5×10^3	1.20	3.9	6.8	0.6	-42.9	-16.5	-50.6	-29.6
1	1.0×10^6	7.7	4.1×10^7	1.0×10^4	1.10	5.1	7.4	0.7	-44.6	-15.2	-53.9	-33.1
2a	1.4×10^5	1.1×10^3	1.2×10^6	1.8×10^6	0.78	1.7	3.6	1.2	-39.8	-18.0	-45.1	-46.1
2	1.3×10^5	1.0	1.9×10^{28}	8.0	1.06	48.8	68.5	-0.1	-39.5	-10.0	-173.0	-15.3

ΔG_{adsL} for Langmuir; ΔG_{adsF} and n(F) for Freundlich; ΔG_{adsT} and f(T) for Temkin; ΔG_{adsEI} and Y(EL) for EI-Awady.

Table 4.6: Adsorption parameters for **3**, rGONS + **3**, **4** and rGONS + **4**. See footnote for more definitions.

	K_L	K_F	K_T	K_{EI}	Slope of Langmuir plot	n (F) (M)	f (T) (M)	Y (EL) (M ⁻¹)	ΔG_{adsL} (kJmol ⁻¹)	ΔG_{adsF} (kJmol ⁻¹)	ΔG_{adsT} (kJmol ⁻¹)	ΔG_{adsEI} (kJmol ⁻¹)
3	1.7×10^6	3.7	1.2×10^9	9.9×10^6	0.98	8.5	9.7	1.1	-45.9	-13.4	-62.3	-50.4
rGONS_3	1.7×10^6	3.3	2.7×10^9	1.7×10^6	0.98	9.4	10.5	1.2	-45.9	-13.1	-64.4	-52.0
4	3.3×10^6	2.5	6.3×10^{10}	1.9×10^7	0.99	12.4	13.6	1.1	-47.6	-12.3	-72.3	-51.9
rGONS_4	5.0×10^6	1.7	8.1×10^{14}	3.6×10^8	1.0	22.0	23.3	1.0	-48.7	-11.3	-96.0	-47.8

ΔG_{adsL} for Langmuir; ΔG_{adsF} and n(F) for Freundlich; ΔG_{adsT} and f(T) for Temkin; ΔG_{adsEI} and Y(EL) for El-Awady.

Table 4.7: Adsorption parameters for **5_H₂**, **5_Ga**, and **5_Co**. See footnote for more definitions.

	K_L	K_F	K_T	K_{El}	Slope of Langmuir plot	n (F)	f (T)	Y (EL)	ΔG_{adsL} (kJmol ⁻¹)	ΔG_{adsF} (kJmol ⁻¹)	ΔG_{adsT} (kJmol ⁻¹)	ΔG_{adsEl} (kJmol ⁻¹)
5_H ₂	1.0×10^6	8.96	3.9×10^7	0.6×10^7	0.97	5.1	6.4	1.14	-44.6	-15.5	-53.8	-49.2
5_Ga	5.0×10^5	16.2	0.9×10^7	3.3×10^3	1.23	3.7	6.5	0.64	-42.9	-17.0	-50.1	-30.4
5_Co	5.0×10^5	29.5	0.6×10^7	3.5×10^6	0.94	3.3	4.7	1.14	-42.9	-18.5	-49.2	-47.8

ΔG_{adsL} for Langmuir; ΔG_{adsF} and n(F) for Freundlich; ΔG_{adsT} and f(T) for Temkin; ΔG_{adsEl} and Y(EL) for El-Awady.

Table 4.8: Adsorption parameters for **6** and **7**. See footnote for more definitions.

	K_L	K_F	K_T	K_{El}	Slope of Langmuir plot	n (F)	f (T)	Y (EL)	ΔG_{adsL} (kJmol ⁻¹)	ΔG_{adsF} (kJmol ⁻¹)	ΔG_{adsT} (kJmol ⁻¹)	ΔG_{adsEl} (kJmol ⁻¹)
6	1.4×10^6	434.3	4.2×10^8	2.4×10^5	1.02	7.5	9.0	0.9	-45.5	-25.3	-59.7	-41.1
7	5.0×10^5	600.0	1.1×10^8	0.6×10^5	1.05	6.1	7.8	0.8	-42.9	-26.0	-56.3	-37.6

ΔG_{adsL} for Langmuir; ΔG_{adsF} and n(F) for Freundlich; ΔG_{adsT} and f(T) for Temkin; ΔG_{adsEl} and Y(EL) for El-Awady.

4.5.6 Experimental/theoretical inhibition efficiency values compared

Values of inhibition efficiency are calculated and presented in Tables 4.1 to 4.4.

Inhibition efficiency values versus concentration plots for El-Awady, Freundlich, Langmuir and Temkin isotherms when compared with experimentally determined values are presented in Figure 4.10. El-Awady, Freundlich and Temkin isotherms gave very good descriptions of **1a** and **1** adsorption on aluminum in 1.0 M hydrochloric acid solution as shown in Figure 4.10, while Langmuir were not appropriate.

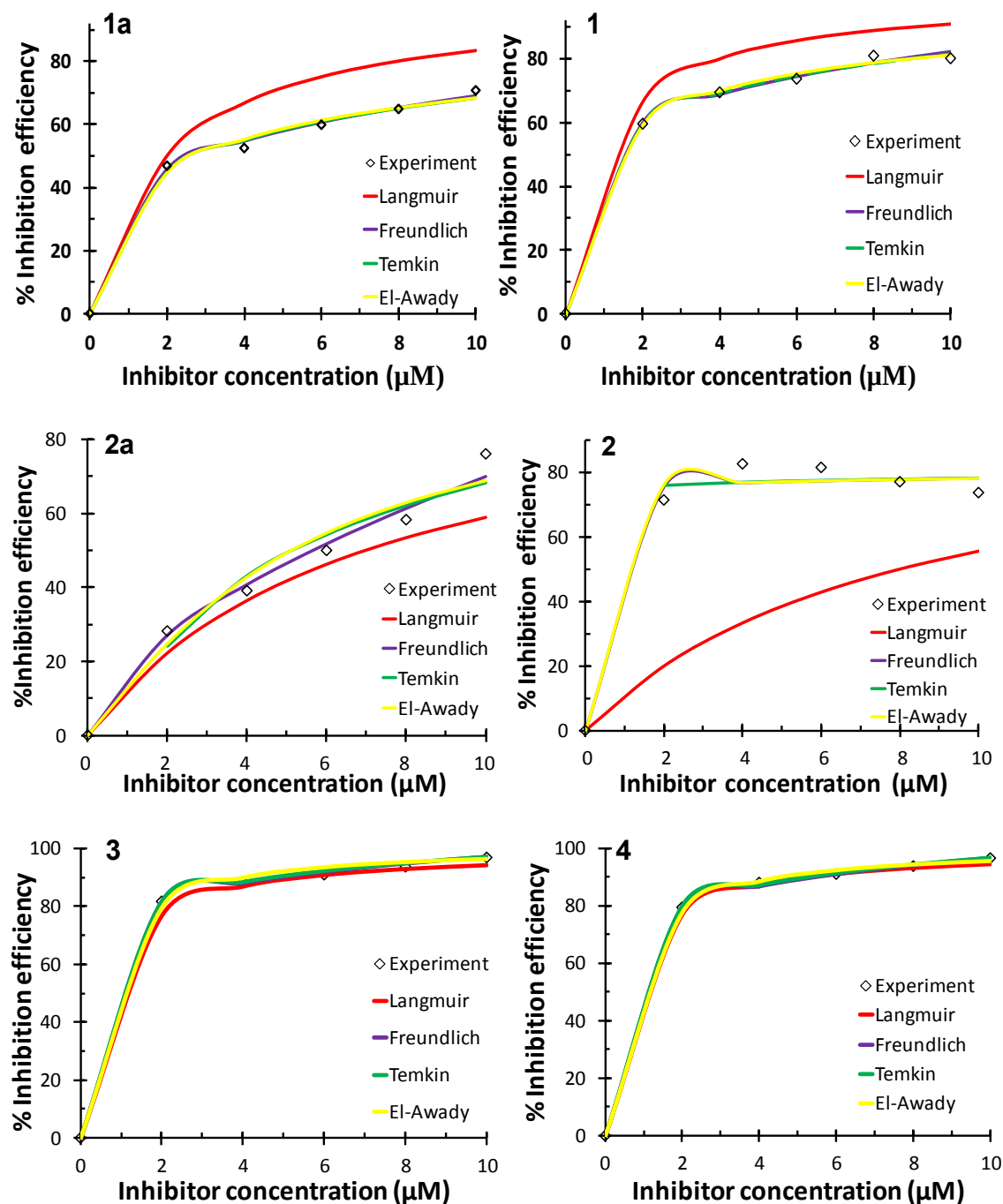
Figures 4.10 reveals that the Freundlich, Temkin and El-Awady isotherms gave the best descriptions/fits to adsorption profiles of **2a** and **2** in 1.0 M hydrochloric acid solution, Langmuir did not give good fits. These are shown in plots of Fig. 4.10.

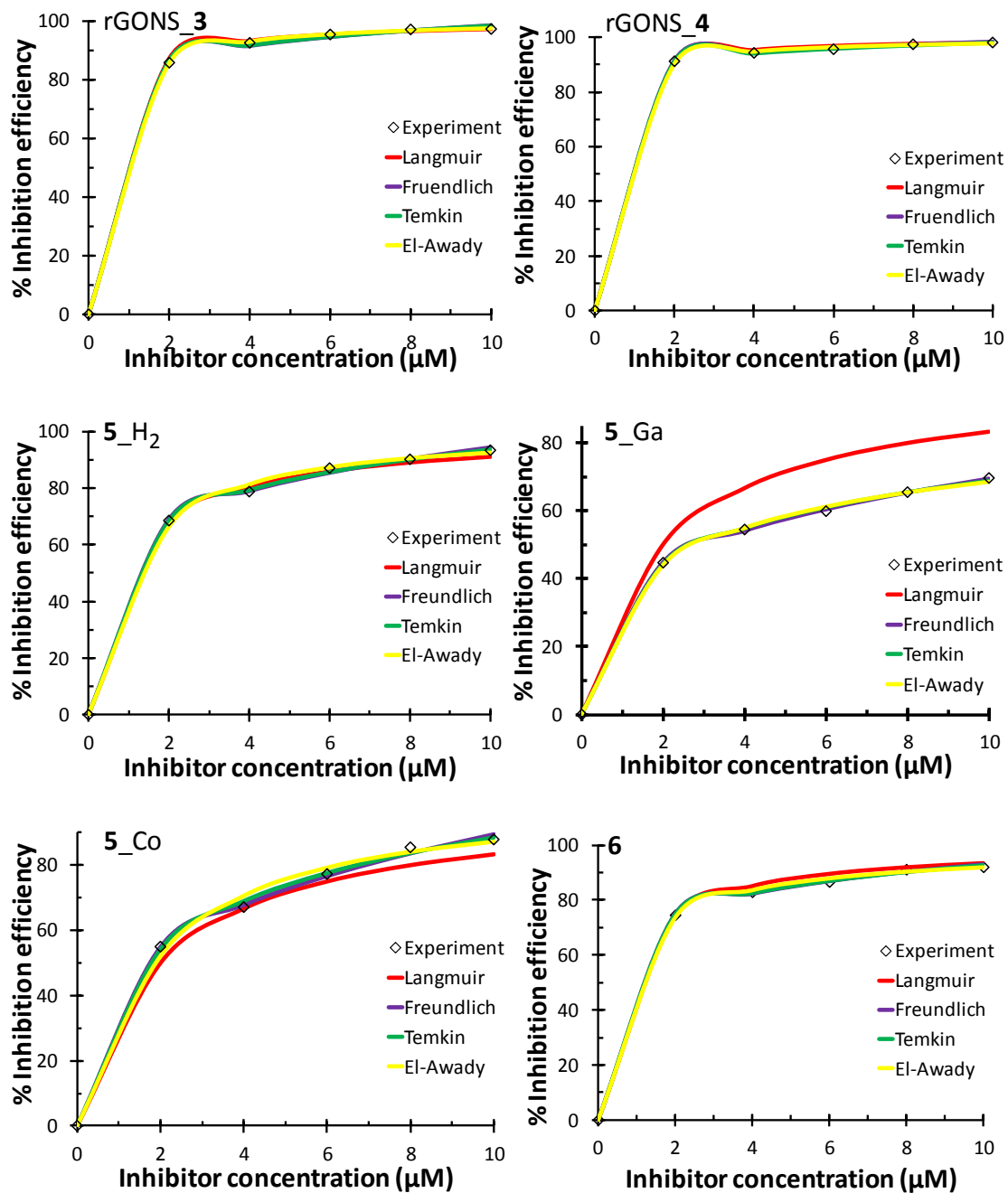
The tested isotherms, Langmuir, Freundlich, Temkin and El-Awady, gave good description of the adsorption of **3**, **4**, rGONS_3 and rGONS_4 as Fig. 4.10 shows.

Fig. 4.10 shows that Langmuir isotherm well described the adsorption process of **5**_H₂ only but could not for **5**_Ga and **5**_Co. El-Awady, Freundlich and Temkin isotherms however, describe the adsorption processes of **5**_H₂, **5**_Ga and **5**_Co well.

Studied isotherms gave very good descriptions of **6** but **7** has El-Awady, Freundlich and Temkin isotherms describing its adsorption on aluminum in 1.0 M

hydrochloric acid solution as shown in Figure 4.10, while Langmuir was not appropriate for **1a**, **1**, **2a**, **2**, **5_Ga**, **5_Co** and **7**.





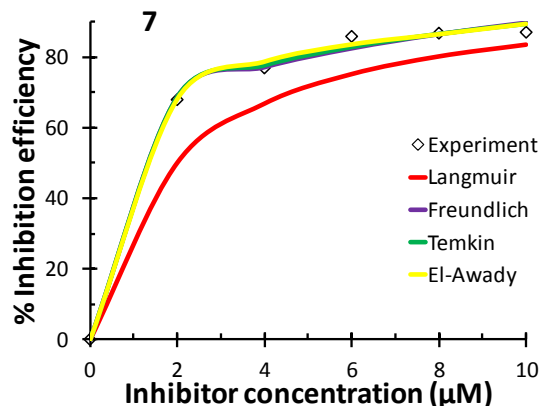


Figure 4.10: Comparison of experimental and theoretical inhibition efficiency values of studied corrosion inhibitors at 28 °C.

4.6 Electrochemical Impedance Spectroscopy (EIS)

Nyquist plots are presented in Figure 4.11 for aluminum in 1.0 M hydrochloric acid solution with and without corrosion inhibitors. Large capacitive curves are apparent at high frequency followed by inductive curves at low frequency values. In the presence of the inhibitors, the capacitive curve diameters are larger than that of the blank solution and increases with inhibitor concentration. This indicates that the impedance of the inhibited substrate increased in the presence of the inhibitors. Similar analogy was posited earlier by Li et al. [108].

Adsorption of $H^+_{(ads)}$ or inhibitor molecules on the electrode surface are involved in the relaxation process believed to cause the inductive curves at low frequency curves [108]. The inductive curve in Nyquist plots (Figure 4.11) therefore may be closely related to the existence of a passive film on aluminum [109].

Analyses of the impedance data were performed using equivalent circuit shown in Figure 4.11. The solution resistance (R_s), charge transfer resistance (R_t or R_{ct}), constant phase element (CPE), the inductive resistance (R_L) and inductance (L) are introduced to simulate the inductive curves. Selected impedance parameter (R_{ct}) and inhibition efficiency values from the fitting of the EIS data are presented in Tables 4.9–4.12. This is because R_{ct} was used in the calculation of inhibition efficiency, presented in equation 4.7 from EIS data [89]:

$$IE\% = \left(\frac{R_{ct}^{inh} - R_{ct}^0}{R_{ct}^{inh}} \right) \times 100 \quad 4.7$$

where resistances to charge transfer without or with inhibitor, respectively are represented by R_{ct}^0 and R_{ct}^{inh} .

The highest R_{ct} values obtained for studied corrosion inhibitors are found to increase with inhibitor concentration and in excellent agreement with results from polarization experiments. The inhibition efficiency values are higher for the electrodeposited corrosion inhibitors, Table 4.9.

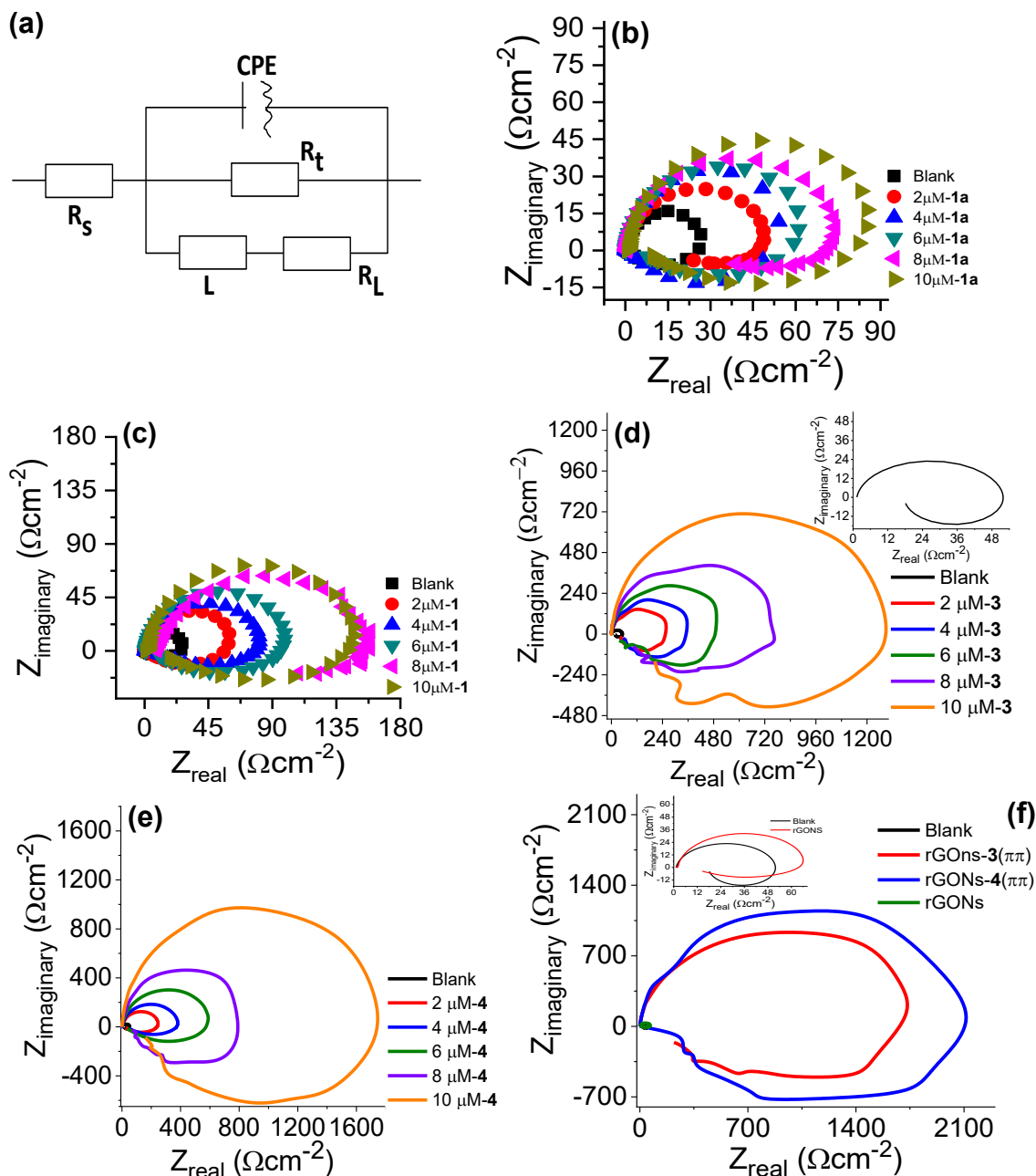


Figure 4.11: Nyquist plots of aluminum in 1.0 M HCl without and with equivalent circuit used to fit EIS data for selected corrosion inhibitors.

Bode plots presented in Figure 4.12 are for aluminium corrosion in 1.0 M HCl solution without and containing selected corrosion inhibitors. Observed trend in Figure 4.12 shows higher impedance modulus values than in the blank solution at the low to medium frequency range. The trend is such that increase in R_{CT} (Figure 4.11) also caused impedance modulus values to rise in the low to medium frequency range. That is, impedance modulus values found to increase with inhibitor concentration, suggesting better corrosion inhibition. Similar observation was reported earlier [110].

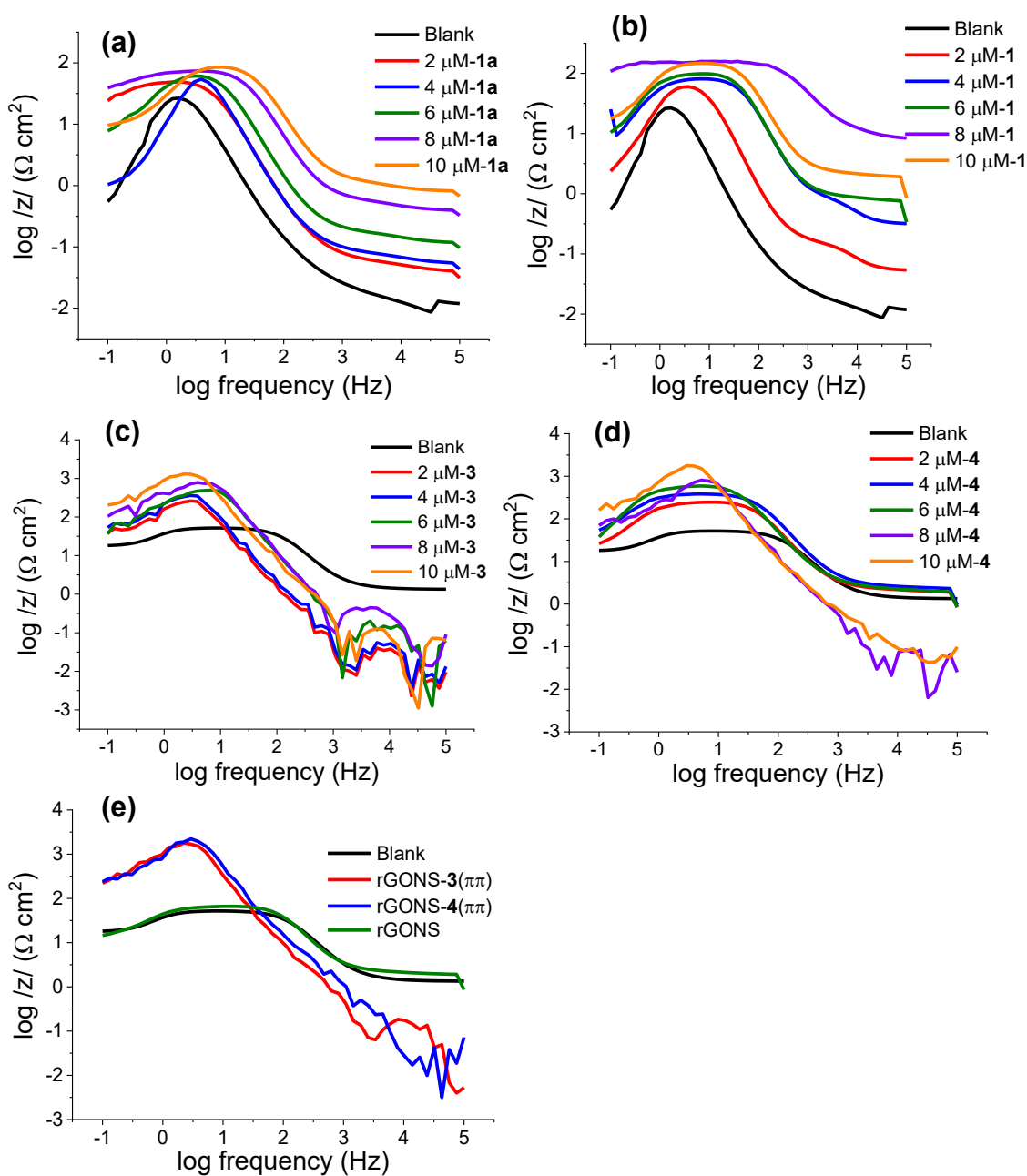


Figure 4.12: Bode plots of aluminum in 1.0 M HCl without and with selected corrosion inhibitors.

Table 4.9: Parameters from EIS data fitting for aluminum in 1.0 M hydrochloric acid in the absence and presence of **1a** and **1**.

Concentration (μM)	R_t (Ωcm^2)	IE%
Blank	26.6 ± 0.16	–
1a		
2	48.81 ± 0.65	45.5 ± 0.4
4	54.22 ± 1.76	50.9 ± 1.3
6	61.15 ± 0.37	58.6 ± 2.1
8	72.91 ± 2.10	63.5 ± 0.8
10	85.09 ± 1.83	68.7 ± 0.5
1		
2	59.52 ± 0.58	55.3 ± 0.7
4	85.24 ± 4.39	68.7 ± 1.8
6	114.92 ± 16.26	76.4 ± 3.2
8	157.4 ± 0.36	83.1 ± 0.14
10	140.87 ± 3.78	81.1 ± 0.62
Electrodeposited		
Blank (uncoated Al)	27.2 ± 3.1	0.0
1 _{ED}	152 ± 4.4	82.1 ± 2.6
2 _{ED}	197 ± 8.4	86.1 ± 0.1

The subscript ED represents electrodeposited.

Table 4.10: EIS parameters for aluminium in 1.0 M hydrochloric acid in the absence and presence of **3**, **4**, rGONS, rGONS + **3** and rGONS + **4**.

System	Inhibitor	Rct (Ω .cm ²)	IE %
Blank (uncoated Al)		53.2 $\pm$ 1.4	0.0
3	2 μ M	264.6 $\pm$ 3.7	79.9 $\pm$ 0.2
	4 μ M	364.2 $\pm$ 3.2	85.4 $\pm$ 0.3
	6 μ M	509.8 $\pm$ 12.8	89.6 $\pm$ 0.0
	8 μ M	705.4 $\pm$ 13.1	92.5 $\pm$ 0.1
	10 μ M	1200.9 $\pm$ 3.9	95.6 $\pm$ 0.1
4	2 μ M	248.0 $\pm$ 7.9	78.4 $\pm$ 0.3
	4 μ M	392.3 $\pm$ 18.5	86.4 $\pm$ 0.3
	6 μ M	580.6 $\pm$ 8.0	90.8 $\pm$ 0.1
	8 μ M	812.6 $\pm$ 19.8	93.5 $\pm$ 0.1
	10 μ M	1361.8 $\pm$ 59.2	96.1 $\pm$ 0.1
rGONS	rGONS	67.6 $\pm$ 3.4	21.3 $\pm$ 1.8
	rGONS- 3 ($\pi\pi$)	1722.9 $\pm$ 59.4	96.9 $\pm$ 0.0
	rGONS- 4 ($\pi\pi$)	2105.0 $\pm$ 113.8	97.5 $\pm$ 0.0

Table 4.11: EIS parameters for aluminum in 1.0 M hydrochloric acid in the absence and presence of **5**_H₂, **5**_Ga and **5**_Co.

Concentration (μM)	R_{ct} (Ωcm^2)	IE%
Blank	56.6 ± 4.8	–
5 _H ₂		
2	203.5 ± 12.9	72.2 ± 0.6
4	269.2 ± 8.1	79.0 ± 1.1
6	339.7 ± 17.8	83.3 ± 0.5
8	486.0 ± 6.1	88.4 ± 0.9
10	598.7 ± 22.2	90.5 ± 0.4
5 _Ga		
2	95.6 ± 6.4	40.8 ± 1.0
4	108.0 ± 6.0	47.6 ± 1.5
6	128.8 ± 6.5	56.1 ± 1.5
8	138.8 ± 5.6	59.2 ± 1.7
10	153.2 ± 16.4	63.1 ± 0.7
5 _Co		
2	108.1 ± 7.3	47.6 ± 0.8
4	151.7 ± 10.4	62.7 ± 0.6
6	213.0 ± 8.6	73.4 ± 3.2
8	346.4 ± 8.8	83.7 ± 1.0
10	416.1 ± 12.1	80.4 ± 0.7

Table 4.12: EIS parameters for aluminum in 1.0 M hydrochloric acid in the absence and presence of **6** and **7**.

Inhibitor	Concentration (μM)	R_{ct} (Ωcm^2)	IE (%)
Blank		56.6 ± 4.8	0.0
6	2	183.4 ± 1.6	69.1 ± 2.3
	4	295.2 ± 3.3	81.7 ± 2.7
	6	389.6 ± 10.4	85.5 ± 0.9
	8	661.7 ± 11.1	91.4 ± 0.5
	10	686.6 ± 16.5	91.8 ± 0.5
7	2	160.5 ± 6.5	64.7 ± 1.5
	4	203.2 ± 17.3	71.1 ± 0.1
	6	273.5 ± 18.1	79.3 ± 0.4
	8	300.2 ± 17.5	81.1 ± 0.4
	10	310.1 ± 29.7	81.7 ± 0.2

4.7 Conclusion for the chapter

Electrochemical and surface characterization techniques were used in the studies. Electrochemical measurements from OCP and polarization techniques revealed the compounds **1a** and **1** are mixed-type corrosion inhibitors with predominant cathodic behavior. **2a**, **2**, **5**_{H₂}, **5**_{Co} and **5**_{Ga} are mixed-type corrosion inhibitors with predominant anodic behavior and anodic behavior exhibited by rGONS, **6** and **7**.

Chapter Five

Surface Analyses and Quantum Chemical Studies

Chapter five discusses the surface analyses of aluminium before and after corrosion in the absence and presence of corrosion inhibitors. Furthermore, this chapter presents the results from computational studies.

5. Surface analyses

5.1 Fourier-transform infrared (FTIR) spectroscopy

5.1.1 Complexes 1, 2, 5, 6 and 7

Al (before corrosion) coupons earlier preserved in a desiccator were scratched, metal powder obtained from doing so was employed for FTIR measurements. The metal surfaces after exposure to HCl solution in the absence (Al_{corr}) and presence of inhibitors, were carefully removed by scraping with a clean stainless steel blade, and care was taken to avoid contamination during the collection of the corrosion products. The obtained powders were employed for FTIR. The FTIR spectra of tested inhibitors, **1a** and **1** (as examples), are shown in Figure 5.1.

Vibrational peak around 3100 cm^{-1} seen in the infrared spectrum for corroded aluminum (labelled as Al_{corr} in Figure 5.1) can be ascribed to the signals of aluminum hydroxides: $\text{Al}(\text{OH})_3$, AlO.OH and hydrated aluminum ($\text{Al-H}_2\text{O}$) [111]. This indicates that the metal surface composed of oxides of aluminum form a protective thin film. Interestingly the infrared spectrum of corroded aluminum in the presence of **1a**, scrapped from Al and labelled as **1a**_{corr}, shows a reduction in the intensity of the peak at 3100 cm^{-1} (shifted to 3300 cm^{-1}), Figure 5.1. In a

similar manner, the infrared spectrum of corroded aluminum in the presence of **1**_{corr} shows a further decrease in the intensity of the peak at 3100 cm⁻¹ (shifted to 3300 cm⁻¹), and this provides evidence of improved metal corrosion retardation than **1a**. A peak seen at 1162 cm⁻¹ in corroded aluminum was earlier ascribed to aluminum oxyhydroxide (γ - AlO.OH) [112], this peak was absent after corrosion in the presence of the inhibitors, this is a good indication of effective protection of the metal from corrosion.

Vibrational signals characteristic of phthalonitriles and ascribed to C–N moieties [113] appeared in the spectrum of **1a** at 2231 cm⁻¹ (before corrosion), as Figure 5.1 shows and this peak disappeared after corrosion, suggesting the involvement of the C–N groups as adsorption sites for **1a** onto the metal surface. Vibrational signals for **1a** at 1534 cm⁻¹ (–CN), 1424 cm⁻¹ (–CH₂), 1279 cm⁻¹ (C–H), 1077 cm⁻¹ (C=C and –CN) and 910–720 cm⁻¹ (aromatic C=C and C–H) have been ascribed earlier [114–117]. After corrosion, these vibrational signals disappeared which indicates good **1a**/aluminum adsorption interaction. The assignment of 751 cm⁻¹ to C–S–C vibration is consistent with the report of Omaka and co-workers [117] for benzothiazole moiety. The disappearance of this signal after corrosion is a good indication that corrosion inhibition by **1a** is due to adsorption onto metal surface. Formation of **1a**-aluminum complex as thin film covering metal surface is thus evidenced by FTIR.

The infrared spectra of **1** (before) and **1**_{corr} (**1** scrapped from Al metal after corrosion), are shown in Figure 5.1. Vibrational signals seen in the 1796–2647 cm⁻¹ range ascribed to Ar-CN vibrations [118–120], appear after metal corrosion

in the presence of **1** (that is **1**_{corr}). Infrared spectra of corroded aluminum and **1** (before corrosion) show that these vibrational signals were absent, revealing the role of the phthalocyanine structure of **1** in the corrosion inhibition adsorption process. These indicate that **1** possesses very high electron density due to the presence of de-localized electrons in the rich (condensed) aromatic structure shown in Table 1.4, which imparts on it good corrosion inhibition character. Formation of **1**-aluminum complex as thin film covering metal surface is thus evidenced by FTIR. Similar infrared spectra changes were observed for **2a**, **2**, **5**_H₂, **5**_Co, **5**_Ga, **6** and **7**.

Herein, an attempt has been made to estimate corrosion inhibition efficiency using FTIR peak intensities (transmittance values). Using the technique of FTIR peak intensities (transmittance values) and bearing in mind the relationship between transmittance and absorbance (Equation 5.1), then, Equation 5.2 applies:

$$\text{Absorbance (A)} = 2 \log(\%T) \quad 5.1$$

$$IE\% = \frac{A_0 - A_x}{A_0} \times 100 \quad 5.2$$

where A_0 represents the absorbance of the infrared peak (at 3100 cm^{-1} for Al alone) for corroded aluminum in the absence of inhibitor, A_x represents the absorbance of the infrared peak for corroded aluminum in the presence of an inhibitor. The inhibition performance values of 98.2% and 99.5% respectively for **1a** and **1** (as examples) indicating that **1** protected metal surface better than **1a** in hydrochloric acid solution.

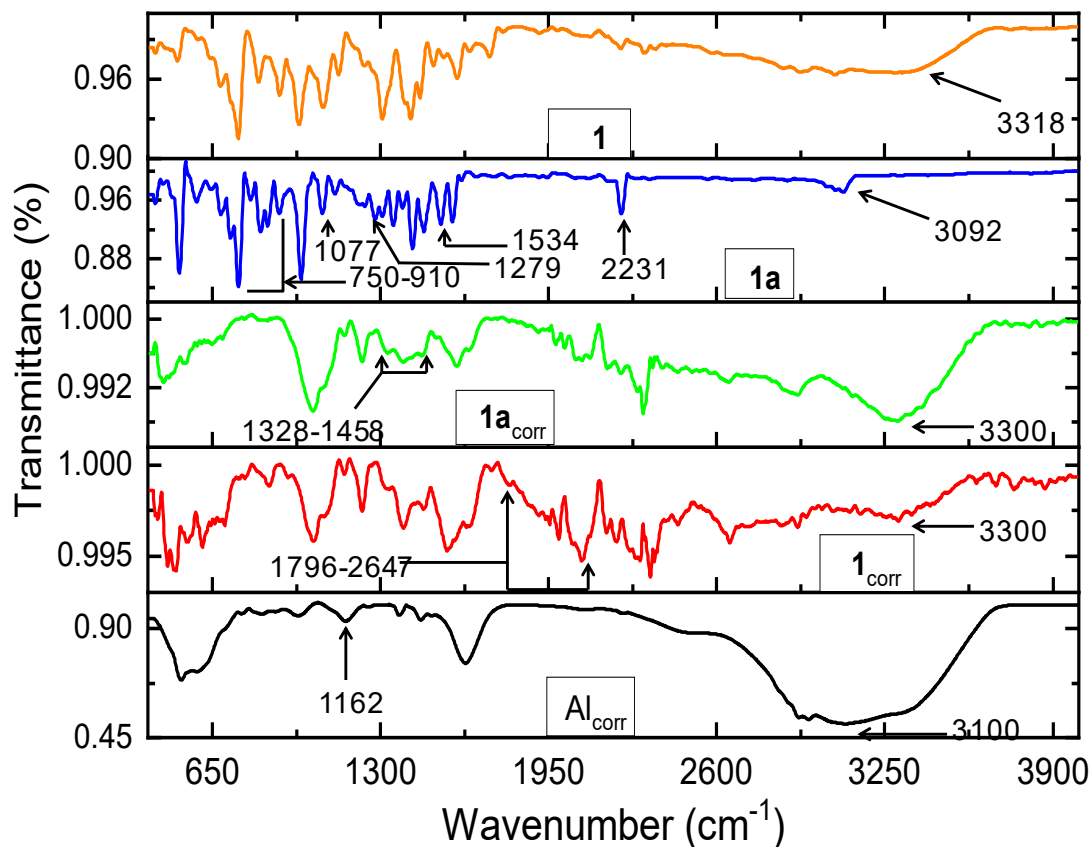
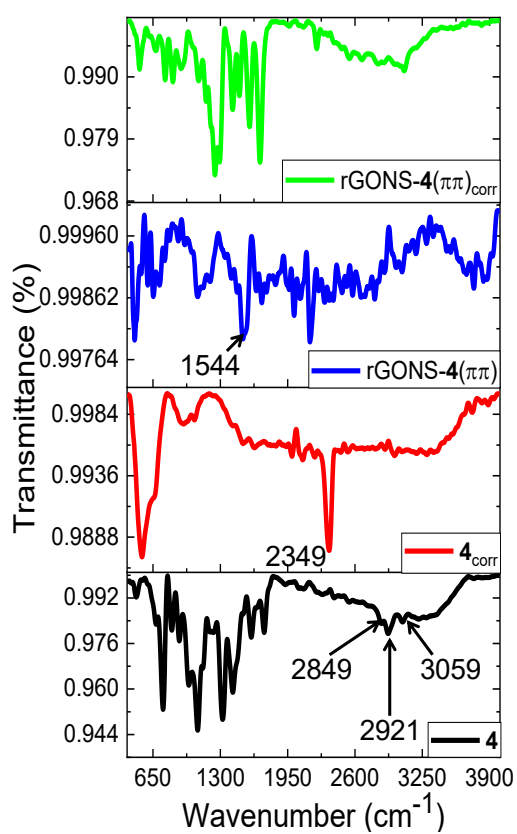
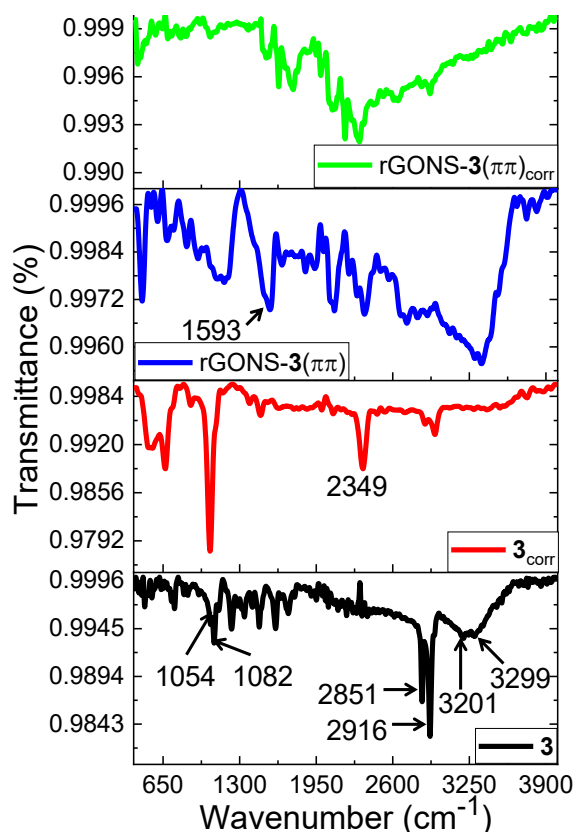


Figure 5.1: Infrared spectra of corroded aluminum in the absence of inhibitor (Al_{corr}), corroded aluminum in the presence of inhibitors scrapped from Al ($\mathbf{1a}_{\text{corr}}$ and $\mathbf{1}_{\text{corr}}$), and the inhibitors ($\mathbf{1a}$ and $\mathbf{1}$).

5.1.2 rGONS, 3 and 4

For infrared analyses, powder samples of **3**, **4**, rGONS-**3**($\pi\pi$) and rGONS-**4**($\pi\pi$) were used directly. Also scrapped powders from Al after corrosion in the presence of the inhibitors ($\mathbf{3}_{\text{corr}}$, $\mathbf{4}_{\text{corr}}$, rGONS $_{\text{corr}}$, rGONS-**3**($\pi\pi$) $_{\text{corr}}$ and rGONS-**4**($\pi\pi$) $_{\text{corr}}$) were used to obtain infrared spectra presented in Figure 5.2. Analyses

of FTIR spectrum of **3** showed peaks at 3299 cm^{-1} and 3201 cm^{-1} (very weak signal at 3059 cm^{-1} for **4**) which can be ascribed to aromatic C-H vibrations [121]. These signals became weak (or disappeared) after corrosion, for **3** and **4** alone. Very strong signals observed for **3** spectra at 2916 cm^{-1} and 2851 cm^{-1} are consistent with aliphatic C-H vibrations of the long chain alkyl CH_2 units [122]. Signals at 2849 cm^{-1} for **4**, can be ascribed to N-H deformation [123]. After metal immersion, the peaks due to the Pcs are difficult to identify since they will overlap with peaks for Al. A prominent peak at 2349 cm^{-1} formed after metal immersion and corresponds to aromatic C=C vibrations [122] for both **3**_{corr} and **4**_{corr}. These vibrations are strong following immersion, suggesting change in the structure. Before corrosion, the reduced graphene oxide nanoparticles (rGONS) has the infrared spectrum presented in Figure 5.2, with a strong broad peak in the $3008\text{--}3600\text{ cm}^{-1}$ range which corresponds to O-H and N-H vibrations [124–126]. After immersion, metal surface thin film for rGONS_{corr} shows signals that shifted to 3059 cm^{-1} and 3367 cm^{-1} , respectively ascribed to O-H and N-H vibrations and the large peak due to corroded Al at 3100 cm^{-1} has disappeared. The conjugates have vibrational signals at 1593 cm^{-1} (rGONS-**3**($\pi\pi$)) and 1544 cm^{-1} (rGONS-**4**($\pi\pi$)) for aromatic C-H [127]. There is also a considerable shift in all vibrations following immersion in HCl. It has been explained that shifts in FTIR peaks can be directly correlated with the level of specific molecular interactions, such as hydrogen bonding and dipole–dipole interaction [127].



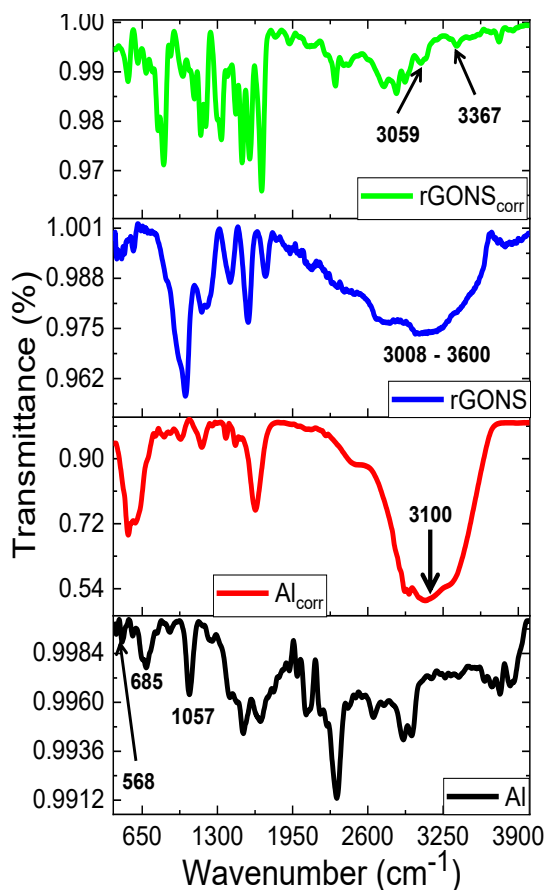


Figure 5.2: FTIR spectra of **3**, **4**, rGONS, rGONS-**3**($\pi\pi$) and rGONS-**4**($\pi\pi$) (before corrosion), and the corresponding spectra of **3**_{corr}, **4**_{corr} and rGONS_{corr}, rGONS-**3**($\pi\pi$)_{corr} and rGONS-**4**($\pi\pi$)_{corr} (their adsorbed films on mild steel surface after corrosion).

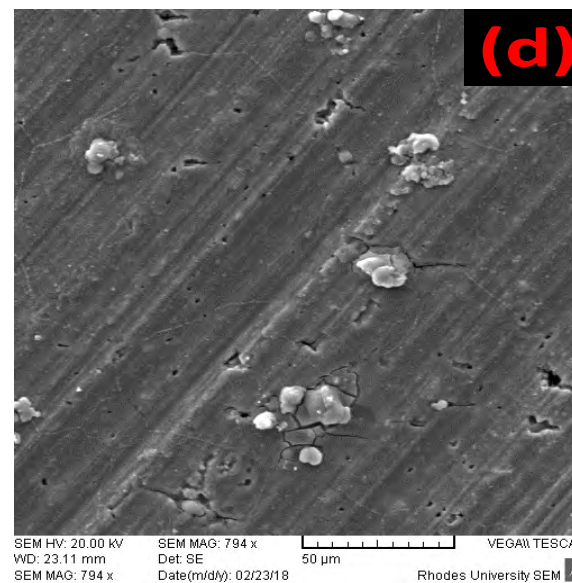
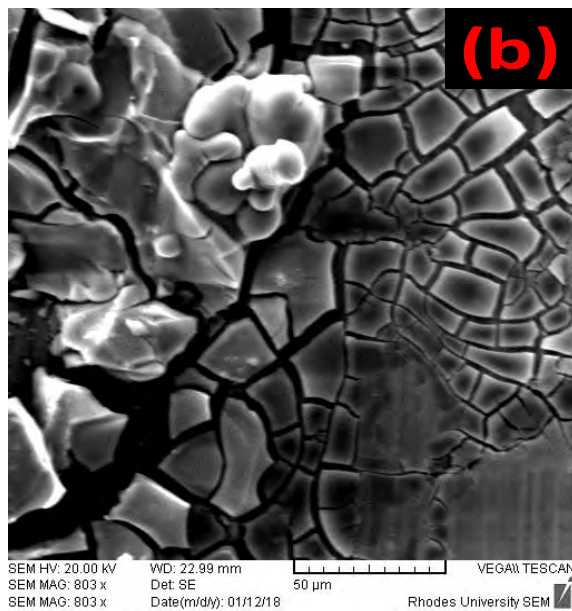
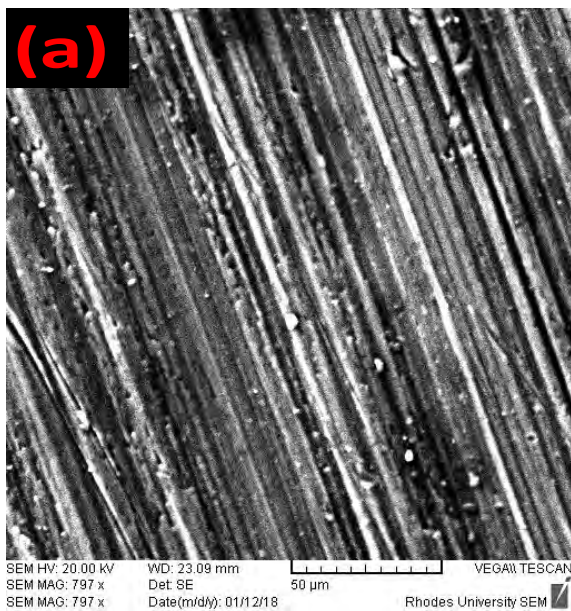
5.2 Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy

Figure 5.3 shows the SEM images, using **1** and **1a** as examples, of uncorroded aluminum, corroded aluminum in the absence of inhibitors and corroded aluminum in the presence of inhibitors. Earlier work [128] used SEM to characterize the

heterogeneous nature of aluminum surface, revealing the microstructure properties of the metal surface. Rosa and co-workers [129] reported the correlation between surface structure and corrosion resistance and their findings are supported an earlier work reported [130]. To this end therefore, the heterogeneity of the uncorroded metal surface adsorption sites is revealed in the SEM image presented in Figure 5.3a. Figure 5.3b reveals that after immersion in hydrochloric acid in the absence of inhibitor, the metal surface becomes corroded badly due to the attack of chloride ion. The formation of a white colored “flower-like” substance thought to be from the corrosion resistant aluminum oxide film, failed to protect the metal from the attack of chloride ion which agrees with an earlier report [131]. The corrosion attack on the metal surface decreased markedly in the presence of inhibitors (Figs. 5.3c,d), a strong indication that the presence of inhibitors protected the metal surface from Cl^- attacks effectively, hence, its use for aluminum corrosion inhibition is encouraged.

Fig. 5.3e shows SEM image of electrodeposited-2, before immersion in HCl. An amorphous surface with intrinsic platelet-like flakes covering the metal surface is observed. The electrodeposited-2 covering strongly adheres to the metal surface such that even after exposure to the corrosive medium, the metal is protected from acid attack as Fig. 5.3f shows. This is judged by the similarities of the images of the electrodeposited-2 before and after immersion in acid, showing that the observed surface is that of the phthalocyanine and not the metal. The electrodeposited aluminium surfaces of Figure 5.3f became more dense and rough necessitated by the formation of films, which in turn protected the metal to exposure to aggressive environments. This observation is in

agreement with earlier findings [132]. Amorphous and crystalline surfaces of electrodeposited benzothiazoles have been reported earlier [133].



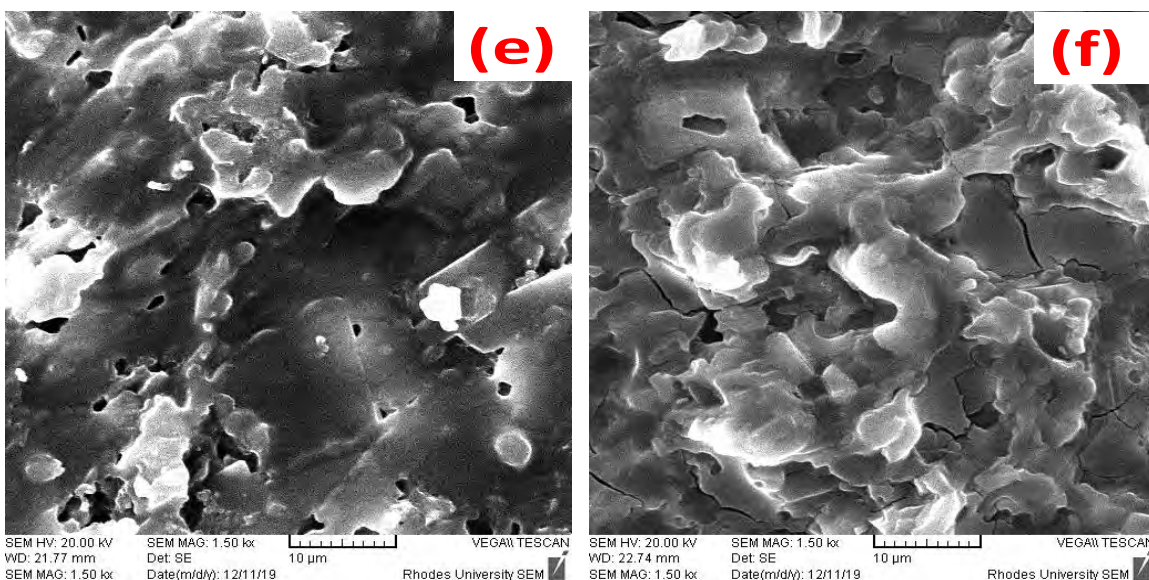


Figure 5.3: SEM images of (a) bare aluminum metal, (b) aluminum metal after immersion in 1.0 M HCl, (c) aluminum metal after immersion in 1.0 M HCl containing **1a**, and (d) aluminum metal after immersion in 1.0 M HCl containing **1**, Electrodeposited-**2** before (e) and after (f) immersion in HCl.

Energy dispersive X-ray (EDX) is discussed using **1** and **1a** as examples. Here high aluminum composition was revealed by EDX measurement for the uncorroded metal (Figure 5.4A) and small contents of carbon and oxygen. In the absence of the inhibitors, EDX shows very high contents of chlorine and oxygen, Figure 5.4B, for corroded Al. Figure 5.4D reveals the absence of chloride ion on the metal surface in the presence of **1**, suggesting effective protection of the metal from aggressive attacks of Cl^- . The absence of chlorine has been reported earlier for the use of phthalocyanines as corrosion inhibitors [93]. There is still some small amount of chloride ions for **1a** (Figure 5.4C). The EDX results therefore strongly support that the presence of Cl^- cause enhanced metal

corrosion and also the presence of electron rich compounds play effective roles by adsorbing on the metal surface, retarding metal corrosion. The metal surface protection was feasible possibly due to the formation of a film on the metal surface, leading to effective metal protection in hydrochloric acid solution by mainly **1**. The oxygen contents of the corroded metal surfaces clearly decreased in the presence of **1**, reflecting better corrosion inhibition than **1a**.

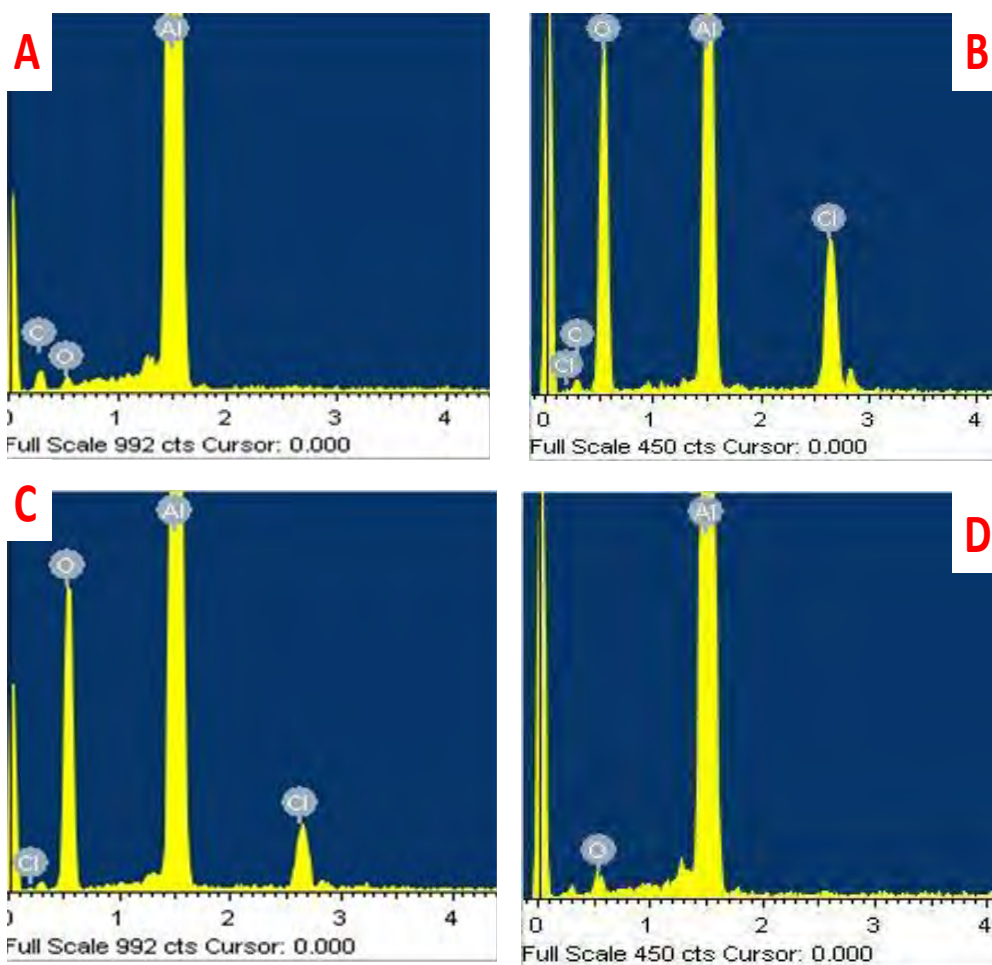


Figure 5.4: EDX of (A) bare aluminium metal, (B) aluminium metal after immersion in 1.0 M HCl, (C) aluminium metal after immersion in 1.0 M HCl containing 6.0 μ M **1a**, and (D) aluminium metal after immersion in 1.0 M HCl containing 6.0 μ M **1**.

5.3 X-ray diffraction studies

The XRD patterns of the uncorroded aluminum surface, corroded aluminum surfaces in 1.0 M hydrochloric acid in the absence and presence of inhibitors are presented in Figure 5.5, using **1a** and **1** as examples. Uncorroded aluminum shows peak patterns at about $2\theta = 39.3, 45.5, 65.8, 78.8$ and 83.1° . These peaks correspond to aluminum signals of gibbsite [$\gamma\text{-Al}(\text{OH})_3$], bayerite [$\alpha\text{-Al}(\text{OH})_3$], alumina (Al_2O_3), boehmite (AlO.OH) and metastable alumina ($\chi\text{-Al}(\text{OH})_3$ and $\kappa\text{-Al}(\text{OH})_3$) [111, 134–136]. These diffraction peaks are indexed as orthorhombic phase of boehmite AlOOH (JCPDS number 00-021-1307) for $2\theta = 39.3$ and 65.8° , as cubic $\gamma\text{-Al}_2\text{O}_3$ (JCPDS number 00-001-1303) for $2\theta = 45.5^\circ$ and as face centered cubic aluminum (JCPDS number 004-0787) for $2\theta = 65.8$ and 78.8° . On comparison with diffraction peaks of metallic aluminum, peaks at $2\theta = 39.3, 45.5, 65.8, 78.8$ and 83.1° match well (JCPDS number 89-4037) [137–141].

Figure 5.5 presents the XRD patterns of corroded Al in the absence of inhibitors (Al_{corr}) with peaks at $2\theta = 39.8, 41.5, 46.0, 65.7, 78.8$ and 99.6° , revealing two new peaks at $2\theta = 41.5$ and 99.6° for corroded Al and the disappearance of the peak for uncorroded Al at $2\theta = 83.1^\circ$. Following protection with inhibitors (**1** and **1a**), the latter peak reappears.

Herein, therefore, a successful attempt has been made to estimate corrosion inhibition efficiency using XRD peak heights by the following equations 5.3 and 5.4:

$$IR = \frac{H_{wi}}{H_w} \quad 5.3$$

$$IE\% = \frac{IR_{wi} - IR_w}{IR_{wi}} \times 100 \quad 5.4$$

where IR represents relative corrosion rate, H_{wi} and H_w respectively stand for peak height ($2\theta = 99.6^\circ$) of corroded metal in the presence and absence of an inhibitor, respectively, IR_{wi} and IR_w are for the relative corrosion rates of the metal with inhibitor and without respectively. Calculated corrosion inhibition efficiency values are 51.3% and 70.3%, respectively for corroded metal in the presence of **1a** and **1** which corroborates trend of inhibition efficiency values calculated from the polarographic technique.

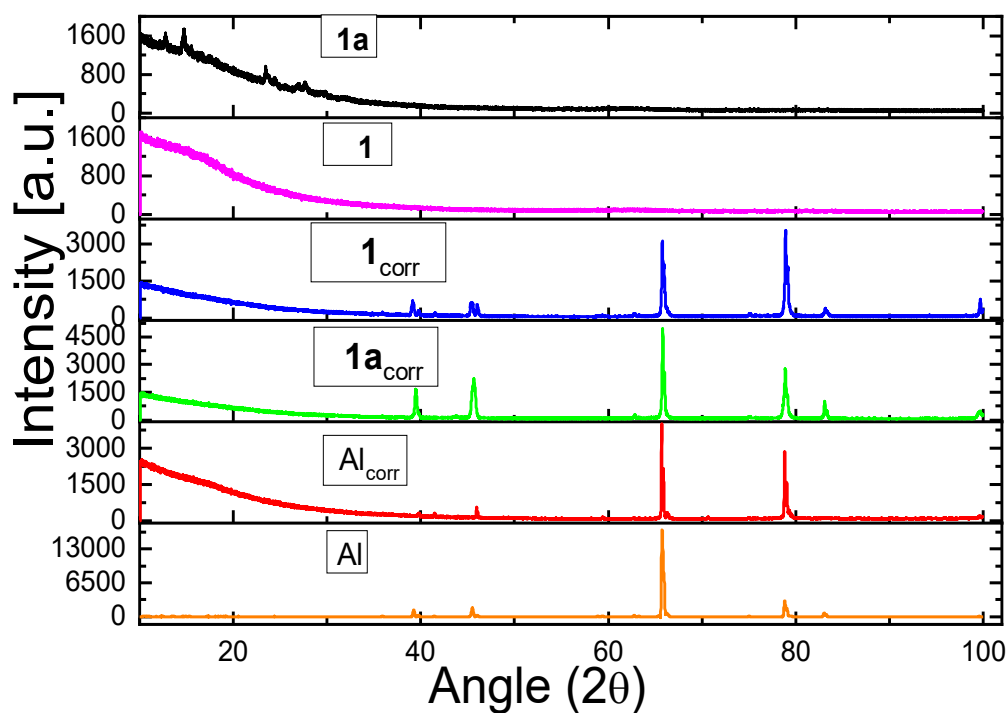


Figure 5.5: XRD patterns of: uncorroded aluminum metal (Al), aluminum metal after immersion in 1.0 M HCl (Al_{corr}), aluminum metal after immersion in 1.0 M HCl containing **1a** ($1a_{corr}$), aluminum metal after immersion in 1.0 M HCl containing **1** (1_{corr}) and inhibitors (**1** and **1a**).

5.4 Quantum Chemical Studies

5.4.1 **1a**, **2a**, **1** and **2**

The optimised structures of the studied corrosion inhibitors are shown together with the corresponding electron density surfaces of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the molecules in Figure 5.6 for **1a/1** and Figure 5.7 for **2a/2**.

The HOMO is localized mainly on the benzothiazole moiety, and the para-substituted thio-part of the phthalonitrile, suggesting that the adsorptive interactions of **1a** with the metal surface via π -electron donation to the empty d-orbitals predominantly occur in this region. The HOMO orbitals around the S-atom of the para-substituted thio-part of the phthalonitrile are σ -type, indicating that this group can interact with the empty p-orbitals of the metal. In contrast, the LUMO is localized mainly on the phthalonitrile, and the para-substituted thio-part of the phthalonitrile suggesting that this region of **1a** molecule can accept a charge from occupied orbitals of a metal. The HOMO and LUMO of **1** are localized mainly on the phthalocyanine ligand and the benzylic part of the benzothiazole substituents.

Explanations of the adsorption centers of inhibitor molecules onto metal surfaces have been done earlier using frontier molecular orbital (FMO) theory [120, 142]. From the HOMO plots shown in Fig. 5.7, it can be observed that for the neutral **2a** molecule, the HOMO is localized mainly on the benzothiazole moiety and the 4-phenoxy part of **2a** which are electron rich centres that can be actively involved in adsorptive interactions with metal surface. In contrast, the

LUMO is localized mainly on the phthalonitrile part of **2a** and can accept charge from occupied orbitals of a metal. The neutral form of **2** has its HOMO and LUMO localized mainly on the phthalocyanine ligand, Fig. 5.7.

The following molecular parameters: the HOMO energy (E_{HOMO}), the LUMO energy (E_{LUMO}), the energy gap (ΔE), global hardness (η), global softness (δ), global electronegativity (χ), and fraction of electron transferred from inhibitor to metal (ΔN) are presented in Table 5.1. The derived parameters, ΔE ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), η , χ , and ΔN were calculated and were helpful in explaining the performance of compounds as corrosion inhibitors [5].

Interactions which occur when corrosion inhibitors adsorb on aluminum surface are such that the electron donating abilities of the inhibitor molecules to the metal surface (acceptor) are enhanced by high E_{HOMO} value. Calculated E_{HOMO} values for the inhibitors, as shown in Table 5.1, reveal that **1** has the higher E_{HOMO} which is consistent with its better inhibition efficiency and corresponds to enhanced donor ability. Complex **1** has lower E_{LUMO} value than **1a** supporting better electron accepting ability from the metal, which improves adsorption property of inhibitor molecule onto the metal and translates to higher inhibition efficiency. The adsorption and corrosion inhibition properties of an organic compound are related to donor-acceptor abilities which favor both forward and backward donation of electrons and appear to affect inhibitive potential as aforementioned for the calculated E_{HOMO} and E_{LUMO} values. The same applies to **2a** and **2**, Table 5.2.

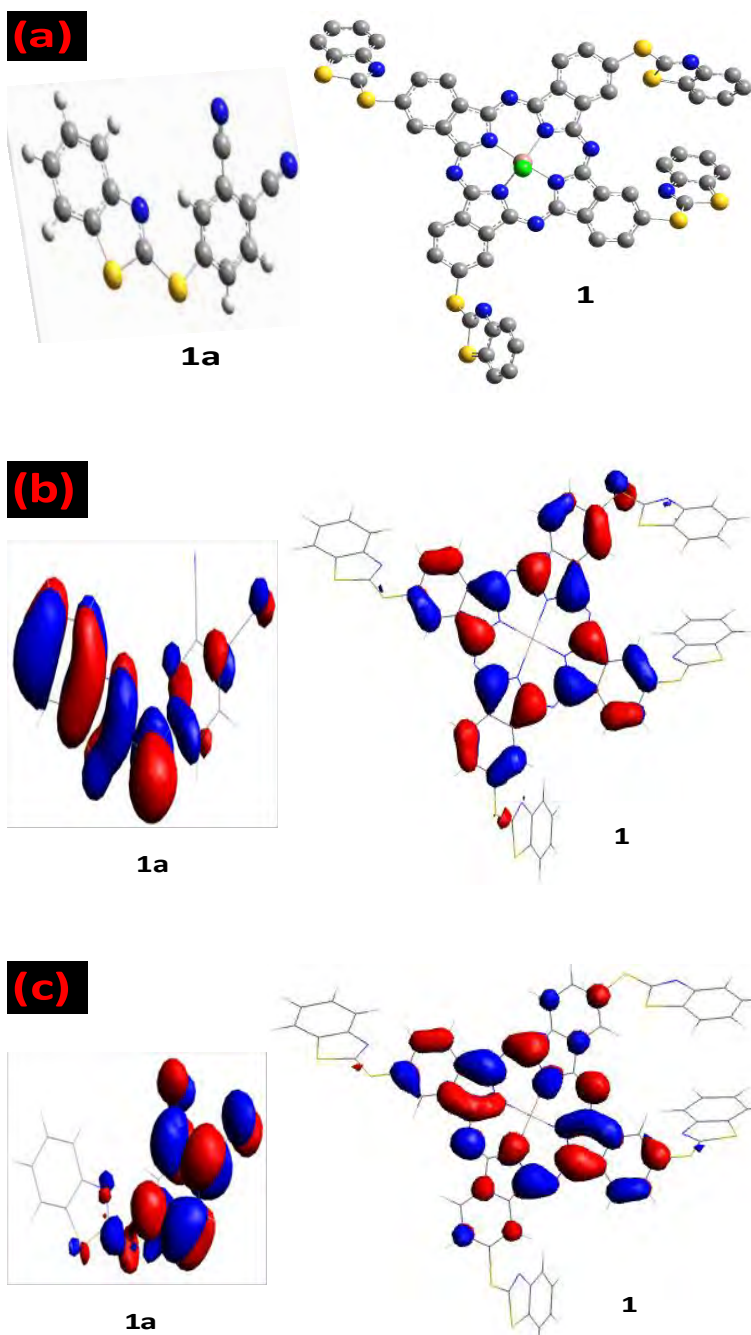


Figure 5.6: Gas phase optimised structures of studied molecules at B3LYP/6-31++G(d,p) level (a), lowest unoccupied molecular orbitals (LUMO) (b), and highest occupied molecular orbitals (HOMO) (c).

Results presented in Table 5.1 indicate that **1** has higher reactivity than **1a**, hence better corrosion inhibition performance, because of its lower values of ΔE and η and higher value of δ . The lower value of χ for **1** translates to a poor grip of molecular electrons and corresponds to the better tendency of releasing electrons during intermolecular interactions. This is same for **2a** and **2**, Table 5.2. It was earlier reported [120] that higher ΔN (less negative) value suggest better electron donating ability, a property known to retard metal oxidation process. From the foregoing, higher ΔN value which corresponds to better corrosion inhibition performance of metallated phthalocyanine inhibitor corroborates higher inhibition performance presented in Tables 5.1 and 5.2. Negative ΔN value was calculated for an aluminum corrosion inhibitor, ethylenediaminetetraacetic acid (EDTA), and the report posited that EDTA donated electrons to the metal surface [143]. ΔN value less than 3.6 has been reported to affect the electron donation by the inhibitor in a way that increased electron donation to the metal surface increase inhibition efficiency [144–146].

Table 5.1. Quantum chemical parameters for **1** and **1a** obtained at B3LYP/6-31++(d,p) level.

Inhibitor Molecule	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	η (eV)	χ (eV)	ΔN	δ (eV)
1	-6.12	-3.66	2.46	1.23	4.89	-0.83	0.81
1a	-8.14	-2.56	5.59	2.79	5.35	-1.06	0.36

Table 5.2. Quantum chemical parameters for **2** and **2a** obtained at the B3LYP/6-31G(d) level of theory.

Molecule	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	η (eV)	χ (eV)	ΔN	δ (eV)
Neutral (water)							
2	-5.330	-3.281	2.050	1.025	4.306	-0.525	0.976
2a	-6.067	-2.047	4.019	2.010	4.057	-0.206	0.498
Protonated (water)							
2 + H⁺	-5.354	-3.296	2.058	1.029	4.325	-0.532	0.972
2 + 2H⁺ (opp)	-5.385	-3.342	2.043	1.022	4.364	-0.555	0.978
2 + 2H⁺ (adj)	-5.424	-3.606	1.818	0.909	4.515	-0.707	1.100
2 + 3H⁺	-5.461	-3.380	2.080	1.041	4.421	-0.572	0.961
2 + 4H⁺	-5.506	-3.420	2.086	1.043	4.463	-0.591	0.959
2a + H⁺	-6.873	-2.663	4.209	2.105	4.768	-0.365	0.475

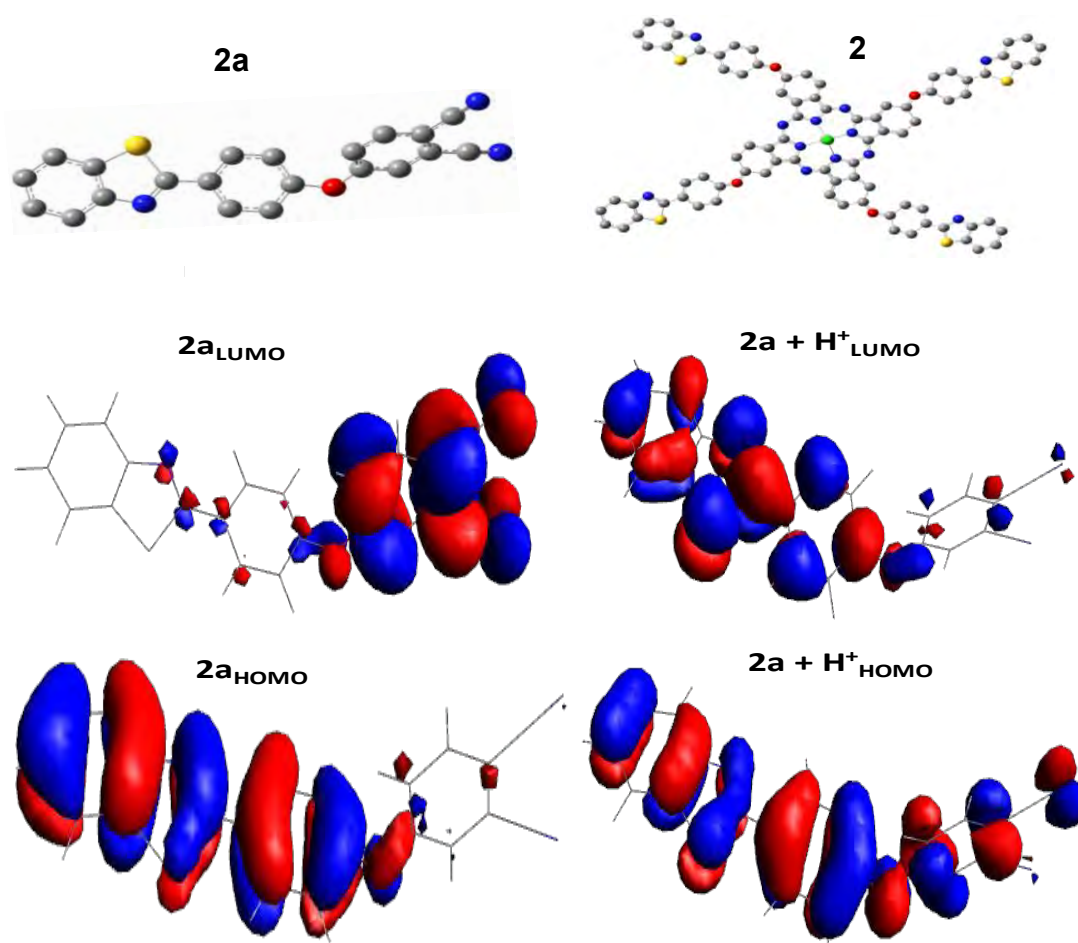


Figure 5.7: Optimized structures of studied molecules at B3LYP/6-31G(d) level of theory, HOMO and LUMO of neutral and protonated **2a** in water at the B3LYP/6-31G(d) level of theory.

5.4.2 Effect of Protonation

Table 5.2 presents some molecular parameters derived from theoretical calculations for the inhibitor molecules when solvated by water, using **2** and **2a** as examples. The donor-acceptor abilities of a molecule seems to positively correlate with its adsorption and corrosion inhibition properties.

Fig. 5.7 presents the optimized geometries, plots of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the molecules. The optimized structure of **2** presented in Fig. 5.7 illustrates the possible source of steric hinderance during adsorption onto the metal surface.

Earlier studies have shown that the nitrogen atom on the benzothiazole (**2a**) can be protonated [147, 148], and that the same should be the case with the four peripheral benzothiazole moieties of **2** providing scope for the addition of up to four protons [47, 149]. The mono-, opp-di-, adj-di-, tri- and tetra- protonated forms of a phthalocyanine have been reported by Bernstein and Lever [47]. The HOMOs and LUMOs of the protonated forms of **2a** and **2** are shown in Figs. 5.8. The HOMO plots of neutral and protonated **2a** in water are similar, so solvation of **2a** is unlikely to have a significant effect on the inhibition property of the phthalonitrile. The HOMOs and LUMOs of neutral **2** and various protonated species in water (Fig. 5.8) are localized on the phthalocyanine ring in a similar manner. This provides an indication that these species co-exist in acidic medium in a manner that would likely not significantly alter the inhibition properties.

The foregoing therefore supports that relative reactivities and corrosion inhibition performances can be assessed on the basis of the difference between the ΔE values (Table 5.2) of the solvated inhibitor molecules in their neutral and protonated states ($/\Delta E/$). The values obtained on this basis in water for **2a** and **2** are given by equations 5.5–5.10:

$$/\Delta E/_{2a_w+H^+}^{2a_w} = E_{2a_w} - E_{2a_w+H^+} = 0.19 \text{ eV} \quad 5.5$$

$$/\Delta E/_{2_w+H^+}^{2_w} = E_{2_w} - E_{2_w+H^+} = 0.008 \text{ eV} \quad 5.6$$

$$/ \Delta E /_{2_w+2H^+ (opp)}^{2_w} = E_{2_w} - E_{2_w+H^+ (opp)} = 0.007 \text{ eV} \quad 5.7$$

$$/ \Delta E /_{2_w+2H^+ (adj)}^{2_w} = E_{2_w} - E_{2_w+2H^+ (adj)} = 0.232 \text{ eV} \quad 5.8$$

$$/ \Delta E /_{2_w+3H^+}^{2_w} = E_{2_w} - E_{2_w+3H^+} = 0.03 \text{ eV} \quad 5.9$$

$$/ \Delta E /_{2_w+4H^+}^{2_w} = E_{2_w} - E_{2_w+4H^+} = 0.036 \text{ eV} \quad 5.10$$

where w = water, opp = opposite and adj = adjacent.

In previous studies, Gerengi and co-workers [150] have reported $/\Delta E/ = 0.552\text{eV}$ for the solvated neutral and protonated forms of 8-hydroxyquinoline (8HQ), and Haque et al. [99] have reported that ethyl 1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (THP-1) has $/\Delta E/ = 1.080 \text{ eV}$, while ethyl 2,6-bis(4-methoxyphenyl)-1-phenyl-4(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (THP-2) has $/\Delta E/ = 0.660 \text{ eV}$. The predicted $/\Delta E/$ values for **2a** and **2** suggest that the conversion of the solvated neutral forms to their solvated protonated forms is theoretically feasible (as judged by the smaller $/\Delta E/$ values) when a comparison is made for the values obtained previously for 8HQ, THP-1 and THP-2. This suggests that in 1.0 M hydrochloric acid solution, solvated neutral and protonated forms of **2a** and **2** are likely to co-exist in solution.

Calculated values for the solvated inhibitor molecules (neutral and protonated forms) as shown in Table 5.2, revealed that values of E_{LUMO} and ΔN are lower for the protonated species. These observed trends are found to cause better corrosion protection in agreement with earlier studies [5, 151], therefore adjudged by values of E_{LUMO} and ΔN , significant amount of protonated species of **2** would adsorb on the metal surface. Protonation of phthalocyanines in acid medium is

known to cause asymmetry [152] and explains the possible steric effect that led to the drop in inhibition efficiency when phthalocyanine concentration increased as Table 4.1 presents. Ledson and Twigg [153] earlier posited that steric effect arises when phthalocyanines are protonated.

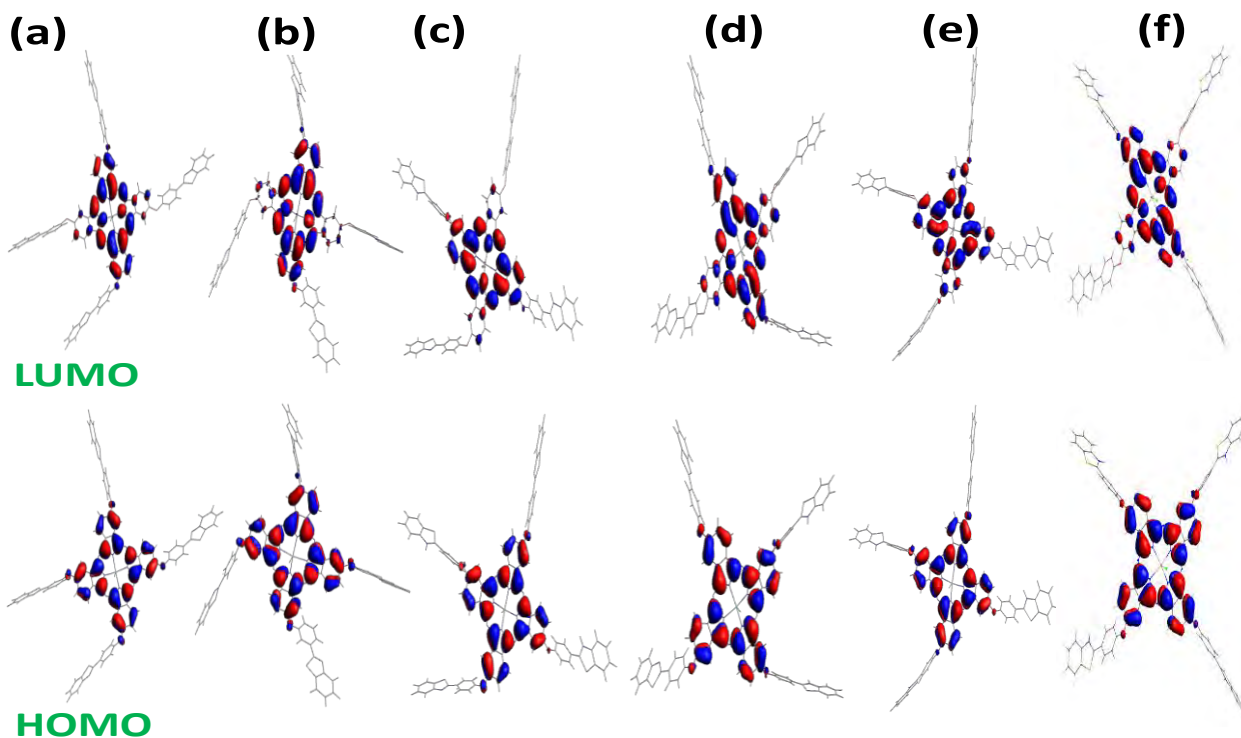


Figure 5.8: HOMO and LUMO of neutral (a), and mono- (b), opp-di- (c), adj-di- (d), tri- (e) and tetra- (f) protonated **2** in water at the B3LYP/6-31G(d) level of theory. Adj = adjacent; opp= opposite.

5.4.3 Effect of nanomaterial (rGONS)

The ball-type Pcs studied consist of a wide range of different isomers, since there is scope for different bridging alignments and the axial chloride ligands of the

central atom can be aligned in either opposite or parallel directions. Optimized structures of **3** and **4** are presented in Fig. 5.9. Earlier calculations [46, 50], used the **3ii** and **4ii** structures in DFT calculations to account for their nonlinear optical properties. In this study, we propose that the **3i** and **4i** structures provide an explanation for how a ball-type Pc with two axial chloride ligands can generate the observed adsorption characteristics. The letters “i” and “ii” are used to differentiate proposed structures of **3** and **4** showing conformational orientations of the axial chloride ligands, Figure 5.9.

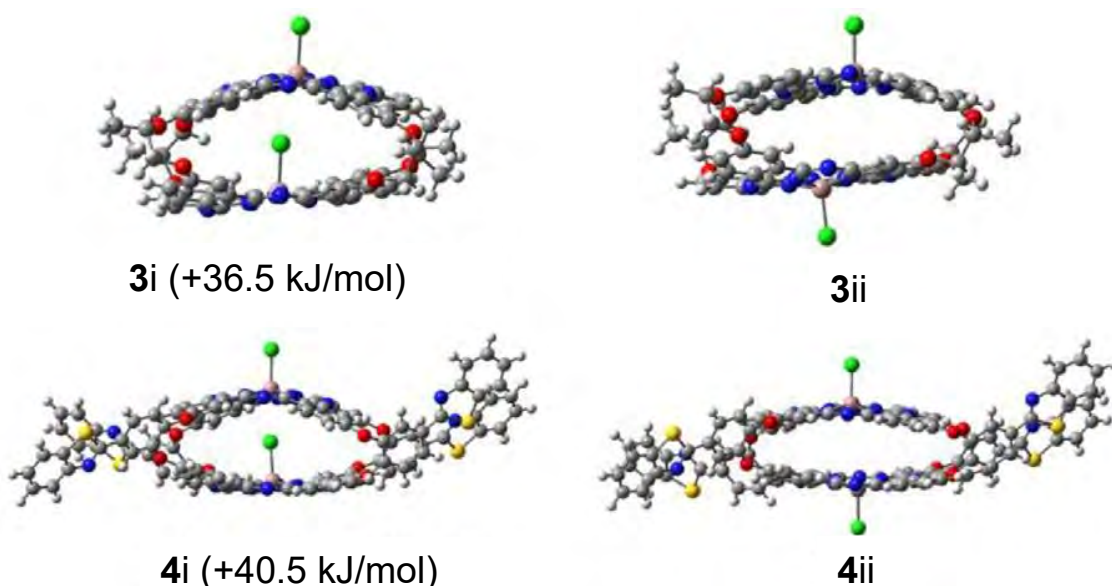


Fig. 5.9: Optimized model structures for **3** and **4** at the B3LYP/3–21G level of theory.

Geometry optimization calculations for sets of isomers with differing chloride axial ligand alignments but comparable bridging patterns predict that there is a 36.5 kJ/mol energy difference for **3i** and **3ii**. The flexible alkyl chains of **3** are replaced with methyls to simplify the calculation. In a similar manner, a 40.5 kJ/mol energy

difference is predicted between model structures **4i** to **4ii**. The cyclotetramerization reactions that are used to prepare the complexes are carried out in refluxing high boiling point solvents so both types of structure are expected to readily form. The presence of an axial chloride ligand in the central cage of **3i** and **4i** results in a near planar Pc ring that can readily interact with a near planar rGONS surface.

The optimized geometries of rGONS and **3a** were used to obtain the initial optimized geometry of the rGONS_**3i**($\pi\pi$) complex and a similar DFT approach then provided the optimized geometry of the rGONS_**3i**($\pi\pi$) complex, Fig. 5.10. The final converged geometry of the rGONS_**3i**($\pi\pi$) complex reveals a strong π - π stacking interaction between one of the Pc rings and the planar rGONS surface. A similar approach was used for rGONS_**4i**($\pi\pi$) (figure not shown), and interaction energies (Table 5.3) of -23.8 and -65.7 kJ/mol were predicted, respectively. The values are negative, and are consistent with exothermic and energetically favourable adsorptions of **3i** and **4i** onto the planar rGONS surface.

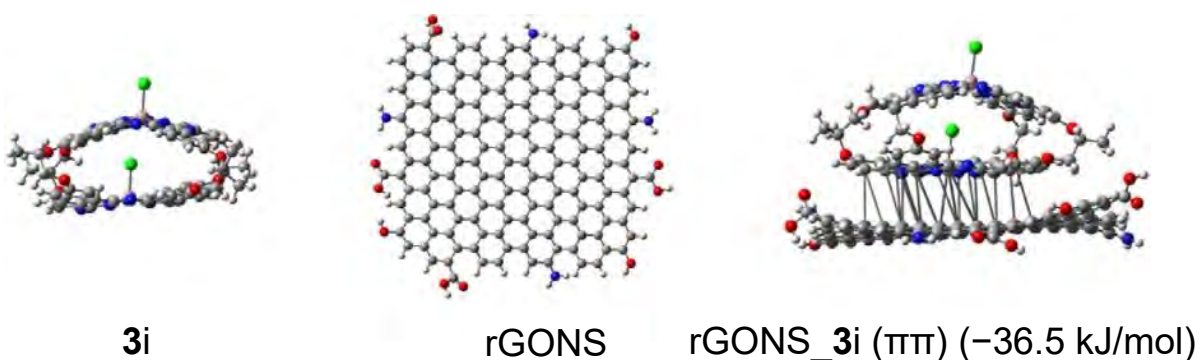


Figure 5.10: Optimized model structures for **3i**, rGONS and rGONS_**3i**($\pi\pi$) at the B3LYP/3-21G level of theory.

The frontier MOs of **3i** and **4i** also provide scope for adsorptive interactions with planar metal surfaces such that the occupied metal d-orbital electrons supply electrons to the frontier unoccupied MOs of **3i** and **4i**. Subsequently, the electron-rich frontier occupied MOs of **3i** and **4i** can interact with the frontier unoccupied MOs of other inhibitor molecules, thus generating more layers on the metal surface. Table 5.4 presents some molecular parameters. The E_{HOMO} and E_{LUMO} values reveal that **4i** has a higher electron donating property (E_{HOMO} value is most negative) than **3i**. The small energy gap values for rGONS does not imply the best inhibitor properties because of the scope for defects that have been reported previously [50, 51]. Values for the calculated energy gaps of rGONS_3i($\pi\pi$) and rGONS_4i($\pi\pi$) as in Table 5.4, decreased and suggests that the $\pi\pi$ reactivity of molecules and their corrosion inhibition performance can be assessed on this basis. rGONS_4i($\pi\pi$) has the lowest ΔE and η values, and highest δ value. This is consistent with the optimal corrosion inhibition performance exhibited in the electrochemical measurements.

Table 5.3. Energy values for **3a** and **4a** at semi-empirical level.

rGONS	-7203.63 a.u.	$E_{\text{interaction}}$	rGONS	-720.63 a.u.	$E_{\text{interaction}}$
3i	-9908.11 a.u.		4i	-12447.06 a.u.	
rGONS_3i	-17111.734 a.u.		rGONS_4i	-19650.686 a.u.	
rGONS_3i($\pi\pi$)	-17111.743 a.u.	-23.8 kJmol ⁻¹	rGONS_4i($\pi\pi$)	-19650.712 a.u.	-65.703 a.u.

Equation 5.11 shows how interaction energy was calculated.

$$E_{\text{interaction}} = E_{\text{complex}} - (E_{\text{rGONS}} + E_{\text{inhibitor}}) \quad 5.11$$

Table 5.4. Quantum chemical parameters for **3** and **4** at B3LYP/SDD level.

Molecule	E _{HOMO}	E _{LUMO}	ΔE	η	χ	ΔN	δ	
	(eV)	(eV)	(eV)	(eV)	(eV)		(eV)	
(in water)								
3i	-5.395	-3.475		1.920	0.960	4.435	-0.628	1.042
3ii	-5.478	-3.493		1.985	0.993	4.485	-0.422	1.008
4i	-5.545	-3.552		1.993	0.996	4.549	-0.662	1.004
4ii	-5.612	-3.583		2.029	1.014	4.597	-0.674	0.986
rGONS	-3.914	-3.673		0.242	0.121	3.794	-2.331	8.299
rGONS_ 3i (ππ)	-3.788	-3.416		0.372	0.186	3.602	-1.000	5.376
rGONS_ 4i (ππ)	-4.068	-3.806		0.263	0.131	3.937	-2.698	7.634

The letter “a” represents optimized structures of **3** and **4** showing conformational orientations of the axial chloride ligands pointing in the same direction and “b” pointing in different directions, Figure 5.9.

5.4.4 Effect of central metal:– 5_H₂, 5_Co and 5_Ga

The optimized structures for complexes **5** are presented in Figure 5.11 and show they can adsorb well on aluminium surface due to their good structural planarity properties. Figures 5.11b and 5.11c present the highest occupied molecular orbitals and lowest unoccupied molecular orbitals of the molecules studied which are localized on the phthalocyanine ligand. Consequently, complexation of the phthalocyanine cavity with cobalt and gallium resulted in changes in electron distributions of the studied molecules (Figs. 5.11b and 5.11c) and in-turn would affect their adsorption properties differently. Torsional angles measured from the optimized structures are presented in Table 5.5. Planarity can be adjudged to fulfil $\pm 0^\circ$ and $\pm 180^\circ$ conditions of the planes considered. Comparatively, inhibitor **5_Co** has the most torsional angles very close to the conditions and inhibitor **5_Ga** has most of its torsional angles deviate most from the conditions. The trend considering Pc planarity is **5_Co** > **5_H₂** > **5_Ga**. The low planarity of complex **5_Ga** explained why it was the worst performing for corrosion inhibition. Considering the torsional angles shown in Table 5.5, the studied molecules have very small deviations from the planarity conditions. It therefore suggests the studied inhibitors are planar, as Figure 5.11d shows the side views of the modeled phthalocyanines. Assertions herein are supported by earlier opinions Belghiti and co-workers [154].

Table 5.6 presents other molecular parameters calculated which can be used to explain molecular reactivity as it concerns corrosion inhibition. Lower η values

and higher values of δ calculated for compounds are in the order **5**_H₂ > **5**_Co > **5**_Ga and is in agreement with earlier findings [155].

Values of E_{HOMO} and E_{LUMO} calculated for the inhibitors are presented in Table 5.6 such that complex **5**_H₂ has the highest (most positive) E_{HOMO} , this trend accounts for best inhibition efficiency exhibited in the following order **5**_H₂ > **5**_Ga > **5**_Co. Though earlier reported [155] that more positive E_{HOMO} translates to better corrosion inhibition, very low R^2 value of Figure 5.12e suggests E_{HOMO} has minimal/negligible effect [156]. Complex **5**_H₂ has lowest E_{LUMO} and this trend supports better electron accepting ability from aluminium, improving its adsorption property in a way that it exhibited highest inhibition efficiency [155]. The trend of E_{LUMO} is **5**_H₂ > **5**_Co > **5**_Ga and corroborates results from electrochemical measurements. Figure 5.11e has R^2 value high enough to suggest E_{LUMO} has significant effect on inhibition performance [156]. Similar analogy shows that ΔE , though has the order **5**_Co > **5**_Ga > **5**_H₂, its effect on inhibition performances of studied molecules is minimal. Figure 5.11e shows trends for the relationships between inhibition efficiency and some molecular parameters (E_{HOMO} , E_{LUMO} and ΔE).

The numbering pattern in the optimized structures of **5**_H₂, **5**_Ga and **5**_Co, Figure 5.12, is used for discussion of results.

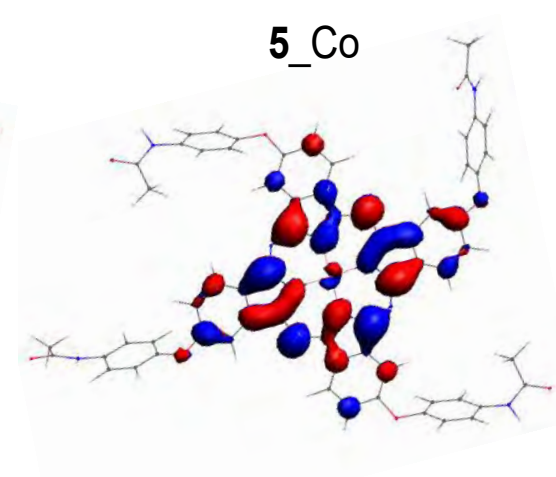
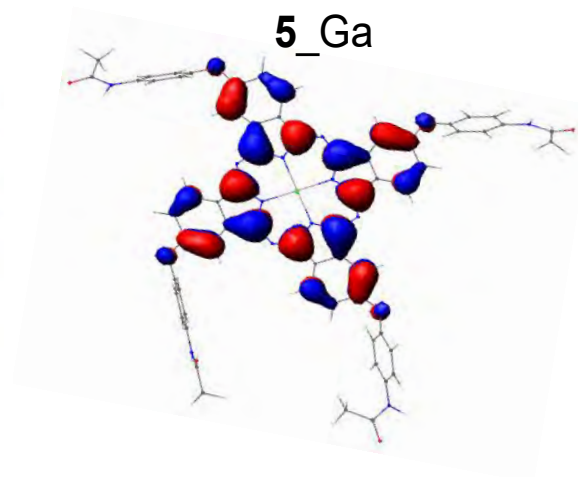
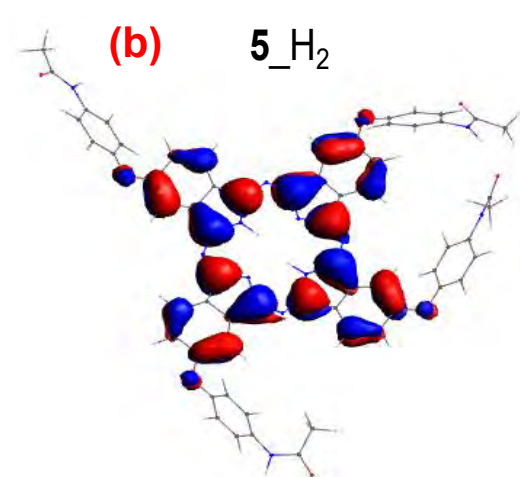
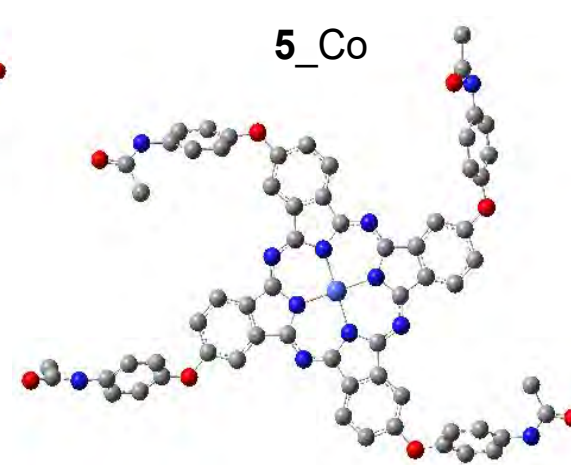
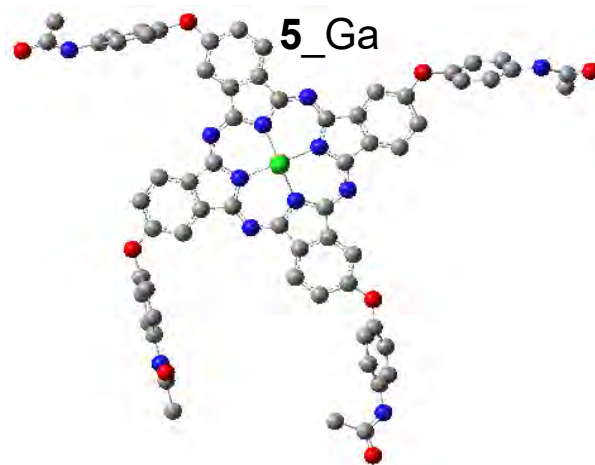
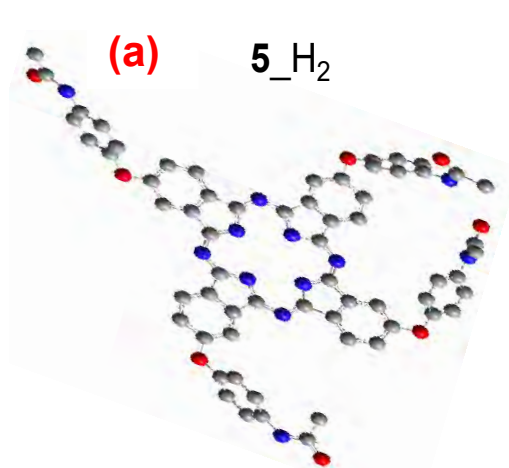
Table 5.5: Measured torsional angles of optimized structures of studied inhibitor molecules obtained at the B3LYP/6-31G(d) level of theory. The numbering is shown in Figure 5.12

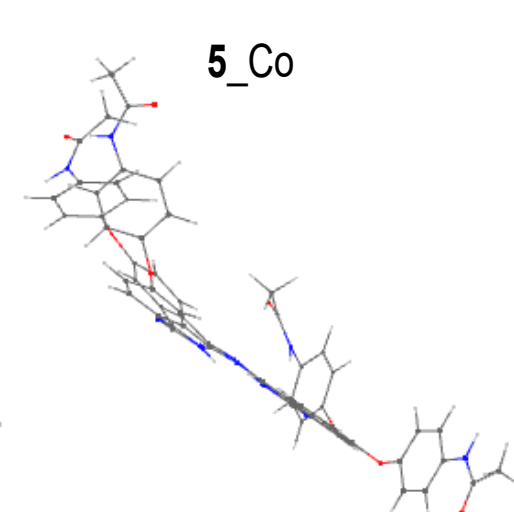
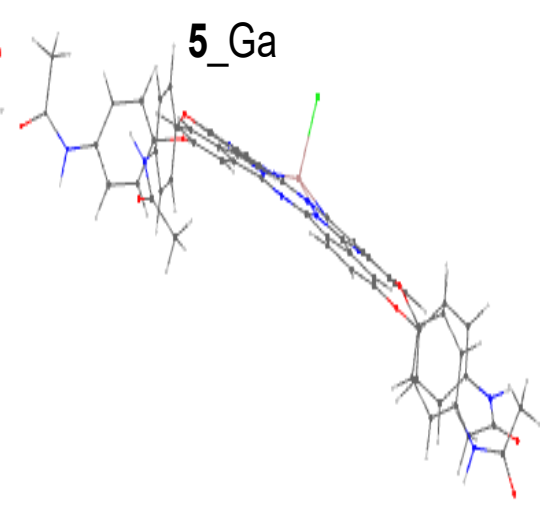
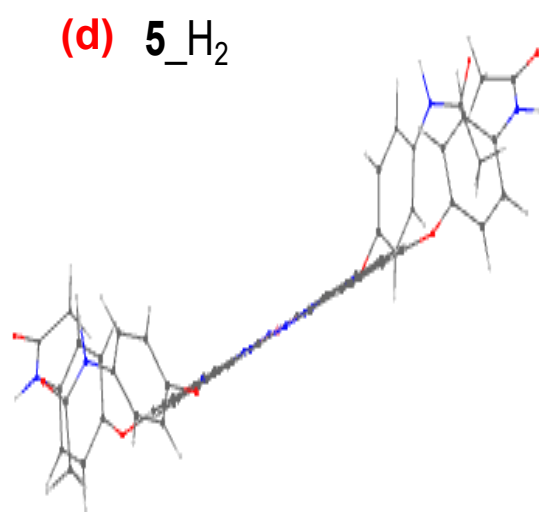
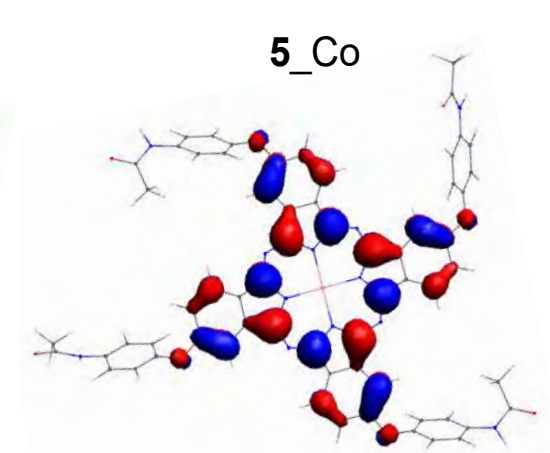
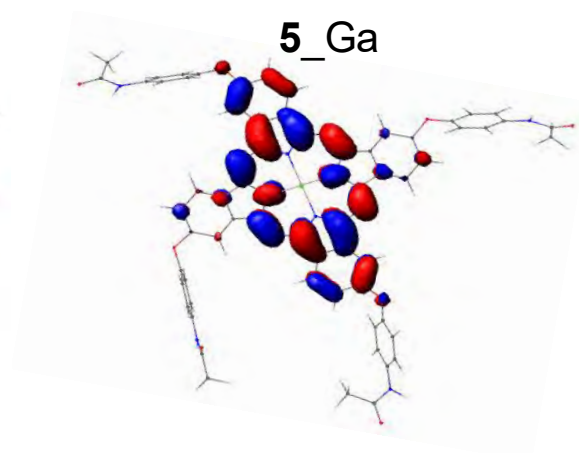
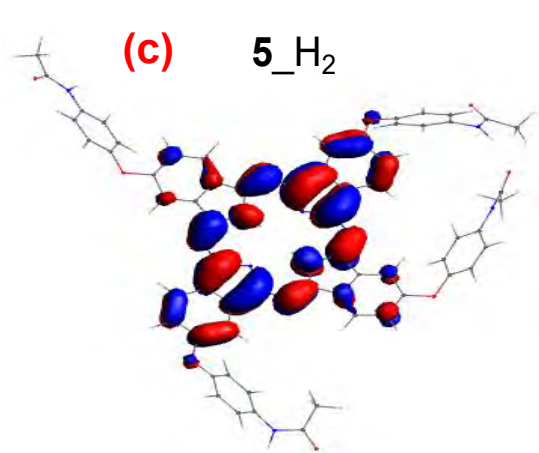
	5_H₂	5_Ga	5_Co
Torsional angles (°)			
N1 – C7 – N2 – C14	-176.9	177.6	–179.8
C7 – N2 – C14 – N3	176.6	–177.6	180.0
N2 – C14 – N3 – C15	–1.4	3.0	0.2
C14 – N3 – C15 – N4	1.4	-2.9	0.0
N3 – C15 – N4 – C22	–178.6	177.6	179.8
C15 – N4 – C22 – N5	179.6	–177.7	–180.0
N4 – C22 – N5 – C23	4.0	3.0	–0.2
C22 – N5 – C23 – N6	2.1	–2.9	–0.2
N5 – C23 – N6 – C30	179.1	177.6	–179.9
C23 – N6 – C30 – N7	170.8	–177.6	–180.0
N6 – C30 – N7 – C31	–0.0	2.9	0.2
C30 – N7 – C31 – N8	10.2	–3.0	0.0
N7 – C31 – N8 – C6	–174.7	177.6	179.9
C31 – N8 – C6 – N1	178.5	–177.6	–180.0
N8 – C6 – N1 – C7	–5.9	3.0	–0.2
C6 – N1 – C7 – N2	–4.6	–3.0	–0.0

Please see Figure 5.12 for numbered atoms of optimized structures

Table 5.6: Quantum chemical parameters for inhibitor molecules obtained at the B3LYP/6-31G(d) level of theory

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	η (eV)	χ (eV)	ΔN	δ (eV)
5 _H ₂	-4.42	-3.30	1.11	0.56	3.86	-0.56	1.78
5 _Ga	-5.31	-3.27	2.03	1.08	4.37	-0.53	0.93
5 _Co	-5.45	-3.29	2.17	1.02	4.29	-0.52	0.98





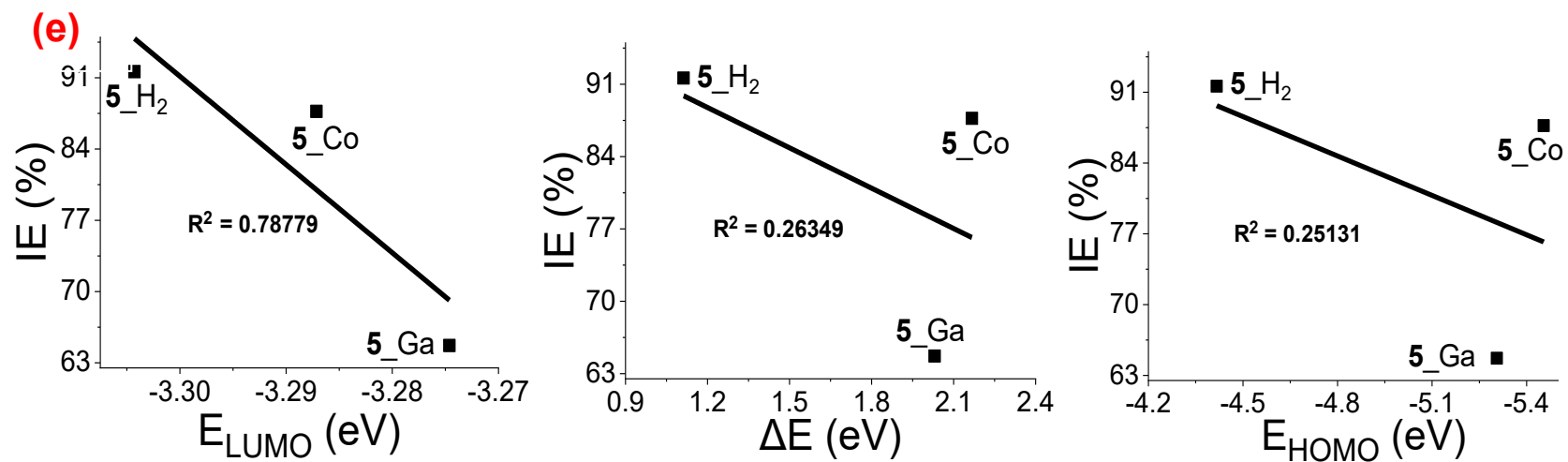
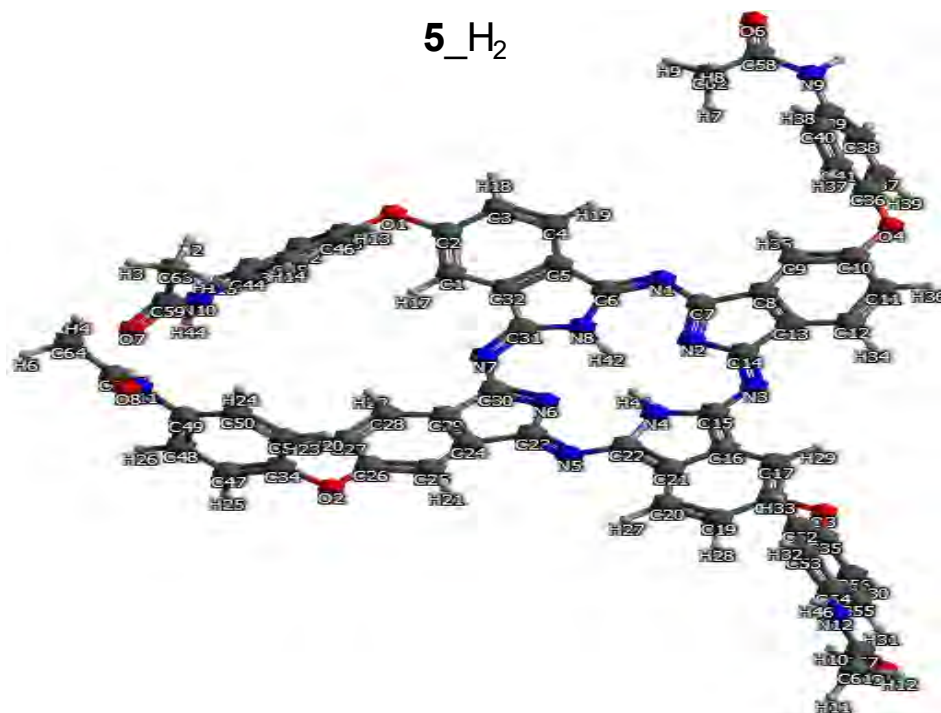
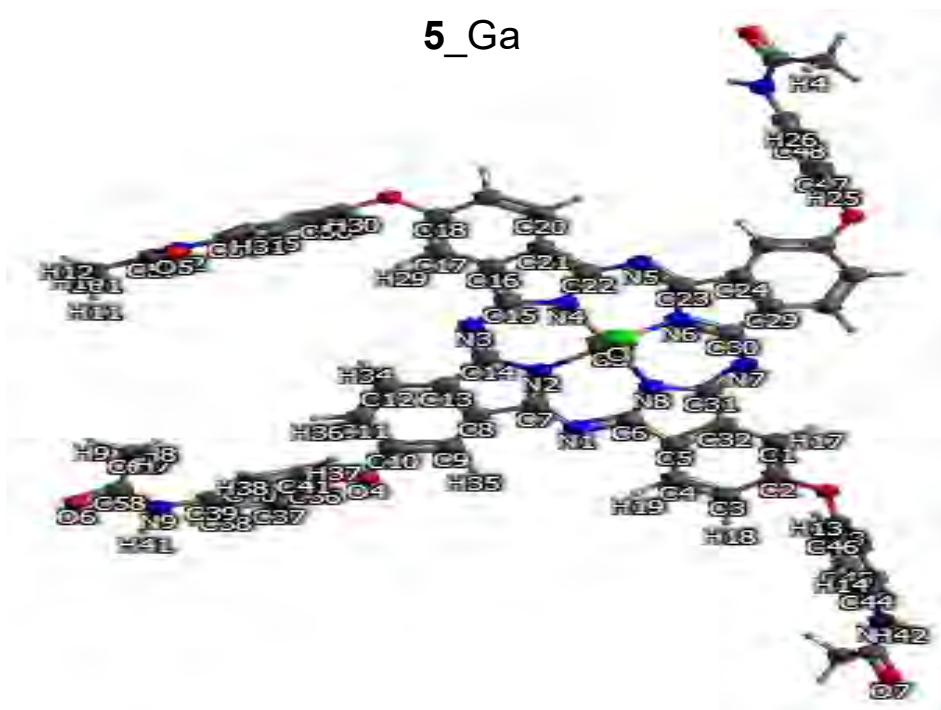


Fig. 5.11: Optimized structures of studied molecules at B3LYP/6-31G(d) level (a), HOMO graphics (b), LUMO graphics (c), side views of the modeled phthalocyanines (d) and correlation between inhibition efficiency and molecular parameters (E_{LUMO} , ΔE and E_{HOMO}) (e).

5_H₂



5_Ga



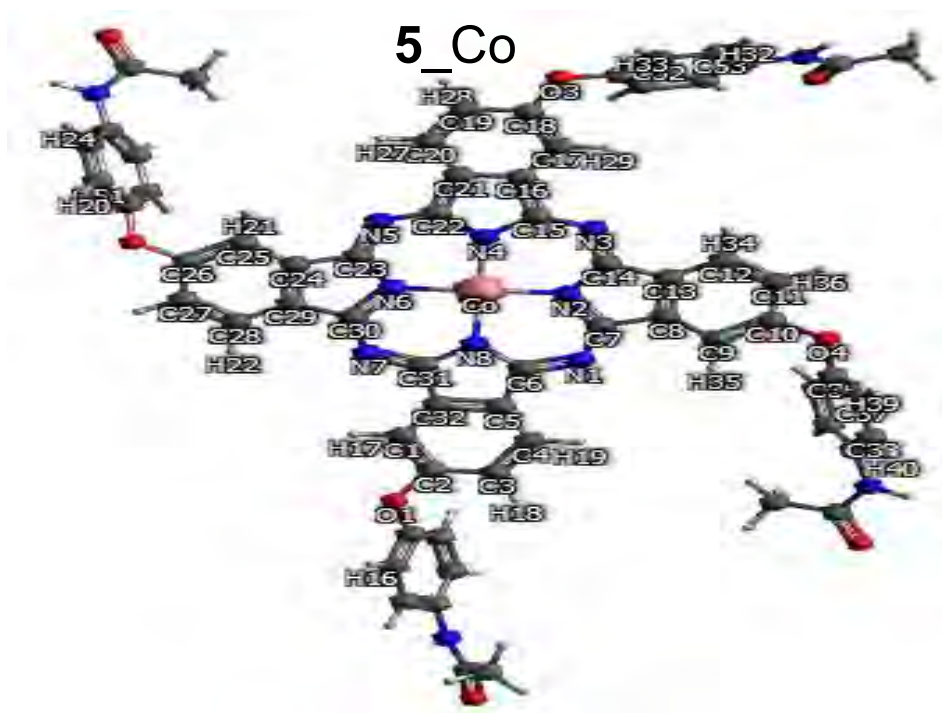


Figure 5.12: Numbered atoms for optimized structures of studied inhibitor molecules obtained at the B3LYP/6-31G(d) level of theory.

5.5 Inhibition mechanism

Aluminium surface coverage by thin films from inhibitor molecules adsorption forms metal-inhibitor complex, generally believed to passivate metal surface and lead to corrosion retardation by preventing further metal oxidation. As an example for the studied corrosion inhibitors, the ease of **6** and **7** adsorption is due to the presence of heteroatoms electron lone pairs, delocalized electrons of unsaturated and aromatic electron rich centers. Herein, this adsorption mechanism is proposed in Fig. 5.13. Obi-Egbedi and Obot [157] believe that this adsorption mechanism prevents corrosion products formation, consequently retarding metal corrosion. In

the corrosive environment (acid medium), the metal surface is positively charged which enables interaction with the electron-rich centers of **6** and **7**.

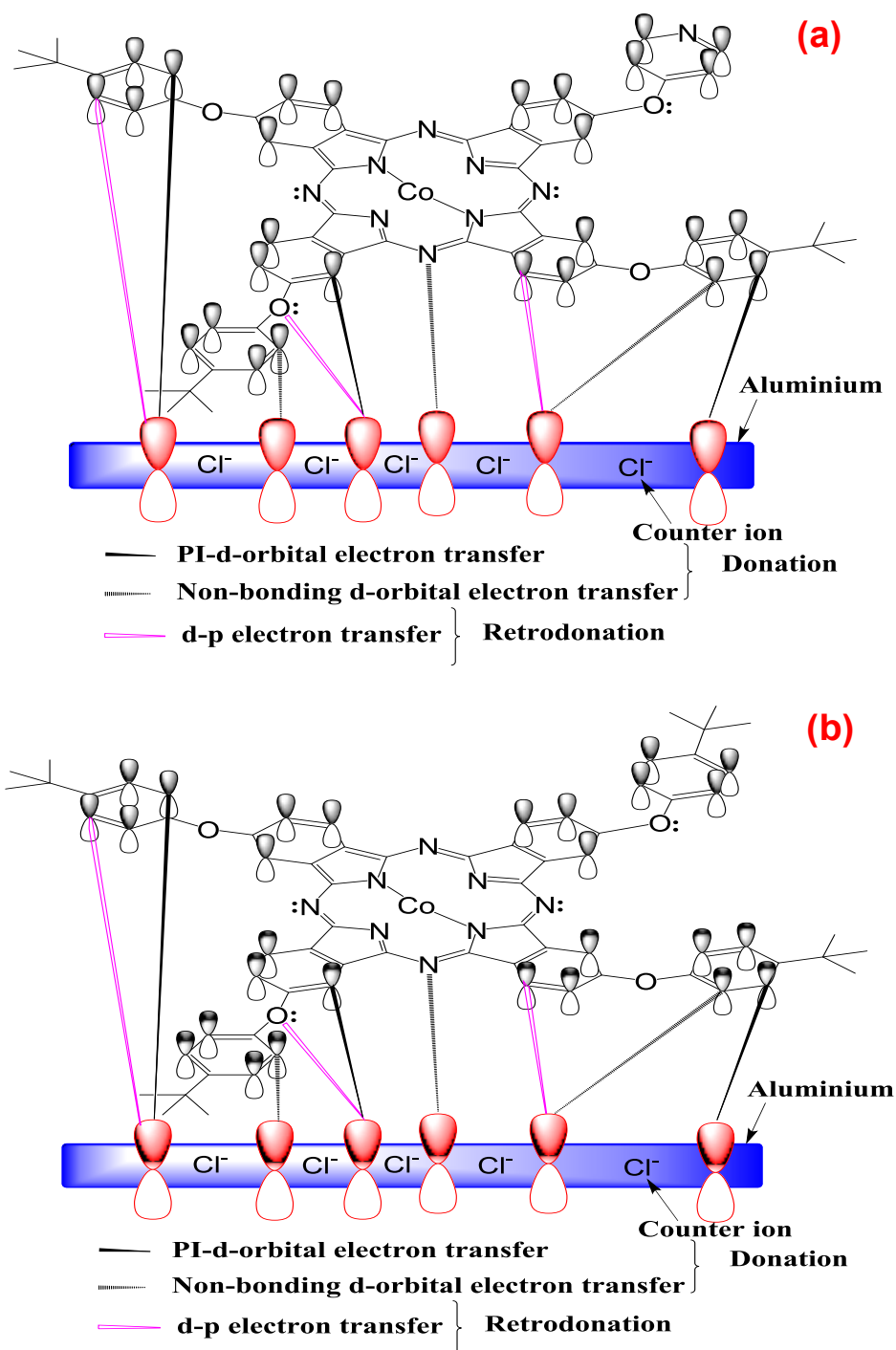


Figure 5.13: Adsorption mechanism proposed for inhibitor molecules on aluminium surface (a = **6** and b = **7**).

5.6 Conclusion for the chapter

FTIR spectroscopic, SEM and XRD techniques support strong passivation by the corrosion inhibitors which retarded acid corrosion. Smoother surfaces revealed by SEM are due to metal surface protection from acid corrosion by studied corrosion inhibitors. Representative inhibition mechanism shows corrosion inhibitors adsorb on the metal surface easily due to availability of intrinsic electron rich sites of the corrosion inhibitors and corroborates well computational studies.

Chapter Six

Summary, Conclusion and Recommendations

Chapter six summarizes the results presented in this work, concludes the research work and suggests a way forward.

6. Conclusion and Recommendations

6.1 Conclusion

Aluminum corrosion inhibition potentials of **1a** and **1** in 1.0 M hydrochloric acid solution suggest predominant cathodic characters with higher corrosion efficiency for **1** compared to **1a** due to the higher π conjugation in the former. Quantum chemical calculations strongly support the experimental results that demonstrate that the corrosion inhibition performance of the inhibitors is in the order **1** > **1a** thus supporting the conclusion that inhibitors containing more unsaturation in their molecular structures perform better. For similar reason, the corrosion inhibition behavior of **2** protected aluminium better than **2a** in 1.0 M hydrochloric acid solution. Quantum chemical calculations strongly support this analogy.

Reduced graphene oxide nanosheets (rGONS) could not effectively protect aluminium from corrosion alone. Ball type Pcs (**3** and **4**) showed promising corrosion inhibition properties and have synergistic protection effects with reduced graphene oxide nanosheets (rGONS).

Acetamidophenoxy derived MPcs have decreased corrosion protection such that the heavier the atom the more decreased the protection and the free base performed best of the three.

Studied tertbutylphenoxy-derived CoPcs (**6** and **7**) exhibited good corrosion inhibition properties in the acidic solution studied. The unsymmetric type (**6**), with more heteroatoms, gave better performance.

6.3 Contributions, Recommendation and Suggestion

This study has made remarkable contributions, amongst which are:

1. phthalocyanines with increased π -electron system would retard aluminium corrosion more in acidic environments;
2. phthalocyanines with much more π -electron system as the case of ball type Pcs would inhibit aluminium corrosion more than unsymmetric Pcs;
3. the nature of phthalocyanine substituents have significant effect on aluminium corrosion inhibition such that those containing more heteroatoms would decrease rate of corrosion more;
4. effect of nanomaterials, particularly those containing high π -electron system, have synergistic protection against aluminium corrosion;
5. effect of central metal was investigated, metalated acetamidophenoxy phthalocyanines have decreased corrosion protection than free base type such that increase in central metal size has significant reduced effect on aluminium corrosion protection; and
6. effect of symmetry affected aluminium corrosion inhibition in a way that unsymmetric type, with more heteroatoms, performs better than the symmetric type which has less heteroatoms.

Based on the findings of this study, the researcher recommends the use of phthalocyanines as good alternatives for inorganic corrosion inhibitors which are disfavoured due to environmental hazard shortcomings. The researcher suggests further corrosion inhibition study of Pcs designed to possess more heteroatoms such as nitrogen and sulphur more than those investigated herein, also which are water soluble.

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