**ANTI-CORROSIVE POTENTIAL OF NAPHTHALENE‐2‐CARBOHYDRAZIDE DERIVED COMPOUND AS CORROSION INHIBITOR IN ACIDIC MEDIUM**

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**REG NO: 2017/241202**

**DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY**

**UNIVERSITY OF NIGERIA, NSUKKA**

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# **TITLE PAGE**

**UNIVERSITY OF NIGERIA, NSUKKA**

**FACULTY OF PHYSICAL SCIENCES**

**DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY**

**ANTI-CORROSIVE POTENTIAL OF NAPHTHALENE‐2‐CARBOHYDRAZIDE DERIVED COMPOUND AS CORROSION INHIBITOR IN ACIDIC MEDIUM**

**A PROJECT SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF SCIENCE (B.Sc.) DEGREE IN INDUSTRIAL CHEMISTRY**

**BY**

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**REG NO: 2017/241202**

**SUPERVISOR: DR. C. U. IBEJI**

**CERTIFICATION**

This is to certify that the work reported herein by **UZOBUENYI NNAEMEKA STEPHEN**

with the registration number **2017/241202** is satisfactory and was carried out under our supervision. This project has been approved for the Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, University of Nigeria, Nsukka having met the requirement for the award of the Bachelor of Science (B.Sc.) Degree.

…………………………… ……………………………

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**ABSTRACT**

This study investigated the potential of of naphthalene‐2‐carbohydrazide derived compound as corrosion inhibitor against mild steel degradation in aggressive acidic medium of 1 M HCl by employing the techniques of gravimetric and surface morphology. The gravimetric study reveals an improvement in the inhibition efficiency with inhibitor concentration increase, attaining a maximum efficiency of 74 % at 303 K at a concentration of 0.0005 M but decreases with temperature rise attaining inhibition efficiency of 44.21% at 363K. The adsorption process was best described by Freundlich adsorption isotherm. The enthalpy (ΔH≠) values are all positive which stipulates endothermic nature of the adsorption process. Conversely, the entropy (ΔS\*) values were all negatives and large which signifies an association. The negative values of (-7.6 to -9.4 kJ/mol) obtained in this study posits a spontaneous adsorption process which involves physisorption. Hence, the derivative of naphthalene‐2‐carbohydrazide compound could serve as a good potential corrosion inhibitor in acidic medium in low temperature environment but fairly usable in an elevated temperature of 363 K.

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**CHAPTER ONE**

**1.0 INTRODUCTION**

**1.1 Background of the Study**

Over the years, most industries such as; petroleum, food, power production, chemical and electrochemical have found tremendous usage of iron and its alloys as construction materials. This is due to their high thermal and mechanical stability, ease of fabrication and joining, and low cost. However, these materials get gradually degraded upon its exposure to the environment as a result of chemical or/and electrochemical reactions with the environment (Verma *et al.,* 2016).

Various industrial operations employ the use of hydrochloric acid solution as an acid wash solution (cleaning, pickling, descaling) for rust and scale removal from mild steel surface. This most often results to severe metallic corrosion (Elemike *et al.,* 2017). The most effective method to prevent the severe attack of the acid on the metal and alloys is the use of an additive.

Several additives, have in recent times, been employed to prevent the corrosion of metals and its alloys. Although, organic compounds which possess electron rich functional groups along with π-electrons inside their frameworks have exhibited exceptional corrosion inhibition efficiency in such acid media (Aouniti *et al.,* 2016).

Reported studies reveals existing results show that, organic inhibitors adsorbed on the metallic surface either by physical or chemical adsorption or by both and eventually a protective layer is formed (Odewole *et al.,* 2021; Habeeb *et al.,* 2018, Asegbeloyin *et al.,* 2015). Organic molecules having N, O and S donor sites, unsaturated π-bonds, planar and conjugated aromatic rings are considered as effective adsorption centers, because of their capability to donate available lone pair of electrons or acceptance of electrons in their low energy empty orbitals (Goyal *et al.,* 2018). Thus, compounds containing both nitrogen (N) and oxygen (O) in their structural unit exhibits greater inhibition performance compare to those possessing only one of these heteroatoms (Singh *et al.,* 2019).

**1.2. Corrosion**

Corrosion is the dissolution of a metal or the alloy from the pure metallic form to the oxidized state due to its interaction with the corrosive environment by direct chemical reactions (Ani *et al.,* 2020).Corrosion is the irreversible reaction of an interlayer (polymer, metal, concrete, wood, or ceramic) with the environment leading to ingestion or dissolution of the environmental component material (Mahmood *et al.,* 2018). It constitutes an environmental threat with economic, preservation and safety consequences in several fields such as manufacturing, chemicals, automobiles, mechatronics, metallurgy, and medical applications. New approaches and techniques such as coatings, defensive bushings, cathodic/anodic protection, and sealants are being employed to counter these hazardous phenomena. However, the outcome of studies investigated on anti-corrosion textile applications in the aforementioned engineering fields showed the use of corrosion inhibitors to be the most facile approach to protect the degradation of metals and alloys in corrosive media (Chen *et al.,* 2022).

**1.2.1 Types of corrosion**

The tendency of a metal to corrode depends on its grain structure, composition formed upon alloying, or the temperature of a metal surface developed upon deformation during fabrication (Chen *et al.,* 2022). The various kinds of corrosion which depend on the media surrounding the material are outline below;

i. **Uniform corrosion:** A corrosive attack that occurs continuously over the entire surface or a significant percentage of the overall area is described as uniform corrosion.

**ii. Galvanic corrosion:** Bimetallic corrosion is also known as an electrochemical phase in which a metal corrodes over another metal with which it comes into contact in the presence of an electrolyte. When two separate metals are dipped in a conductive solution and electrically connected, galvanic corrosion occurs.

**iii. Pitting corrosion:** A localized type of corrosion that creates cavities or “holes” in a substance. Pitting is known as more risky than uniform corrosion damage because the identification, estimation and configuration of it is tougher. The pit is also filled by corrosion products.

**iv. Stress corrosion cracking:** The growth of a crack formed in a corrosive setting is referred to as stress corrosion cracking (SCC). It can result in an unforeseen and unexpected failure of metal alloys that are normally ductile under tensile stress, especially at high temperatures. SCC is very solvent-specific and certain alloys can be subject to SCC only if subjected to a limited number of chemical conditions. The chemical environment that causes SCC for a particular alloy is often the one that causes mild corrosion to the metal.

**v. Corrosion fatigue:** It occurs in a corrosive fatigue environment. It is the mechanical weakening of a material under corrosion and cyclical loading operating jointly. Almost all engineering systems undergo some form of alternate stress and are subjected to hazardous conditions throughout their lifespan.

vi. **Intergranular corrosion:** IGC, also known as intergranular attack (IGA), is a type of corrosion in which the boundaries of crystalline materials are more susceptible to erosion than the interiors.

vii. **Crevice corrosion:** Refers to a localized attack on a surface of metal at a distance of a fracture between two joining plates, or directly adjacent to it. Between two metals or one metal and non-metallic material the gap or crevice may be formed. Both metals are corrosion resistant outside the gap or without the gap.

**viii. Filiform corrosion:** It is a particular type of corrosion which occurs in the form of randomly dispersed filaments under some thin coatings. Corrosion of filiforms is often referred to as “underfilm corrosion”. Filiform corrosion is observed on surfaces of painted steel, magnesium, and aluminum with thin layers of tin, silver, gold, phosphate, enamel and varnish.

**ix. Erosion corrosion:** Material surface deterioration due to mechanical activity, often by impaction of material, slurry abrasion, particles trapped in fast-flowing liquid or gas, bubbles or droplets, cavitation.

**x. Fretting corrosion:** Corrosion impact on touch surface asperities is referred to. In the presence of repetitive relative surface movement, for instance, by vibration, this harm is incurred under load.

**1.2.2 Mechanism of Corrosion**

The corrosion of metal is a localized electrochemical reduction–oxidation reaction which occurs on the surface of the metal, in which electrons are released due to metal dissolution and transferred to a different location on the surface to reduce hydrogen ions. This process leads to the gradual metal deterioration and its eventual damage. In order to understand the underlying principles of corrosion in carbon steel/HCl solution systems. The iron corrosion process can be divided into two half electrochemical reactions, which entails both the cathodic and anodic reaction (Wu *et al.,* 2013). The overall chemical reaction of iron immersed in HCl solutions is depicted in Equation (1), while the anodic reactions of iron immersed in aqueous solutions and aqueous solutions containing Cl- ions are summarized as shown in Equations (2)–(7) (Yadav and Quraishi, 2012).

(i) HCl solutions (overall chemical reaction):

(ii) Aqueous solutions (oxidative dissolution):

(iii) Aqueous solutions containing Cl- ions (oxidative dissolution):

The Equations indicates that iron tends to dissolute and lose two electrons to the electrolyte, which simultaneously produces free electrons that can travel through the metal, upon exposure of iron to the above solutions. [FeOH]ads and [FeClOH]ads are the adsorbed intermediates, each of which is involved in the rate determining step of Fe dissolution according to mechanisms (ii) and (iii). The presence of Cl- ions does not exclude dissolution through the [FeOH]ads intermediate in chloride free acid media, as the two mechanisms can proceed simultaneously (Chen *et al.,* 2022).

Conversely, for an acidic solution, the electric potential is caused by the accumulation of excess electrons generated in the anode, which can be neutralized at the cathodic site by the reduction of H+ to form hydrogen gas. This process can be presented as follows (Equations (8)–(10)).

This overall process involved in corrosion of iron is depicted in Figure 1.1



**Figure 1.1: Mechanism of corrosion process**

**1.2.3 Consequences of corrosion**

Recently, corrosion becomes the utmost destructive and stimulating challenges faced with industries across the globes. Some of the consequences includes;

i. Huge economic losses

ii. Environmental degradation

iii. Explosion resulting to loss of infrastructures, injuries and deaths in severe cases.

**1.3. History of inhibitors**

Inhibitors have found large application in several industrial systems and commercial applications, some of which includes cooling systems, refinery units, pipelines, chemicals, oil and gas production units, boilers and water processing, paints, pigments, lubricants (Ani *et al.,* 2020). In the nineteenth century, there were proof of inhibitors application. In this period, the processes that entails acid pickling, acidified oil wells, and cooling systems employed the use of this inhibitors which were majorly chromate, phosphate, arsenic compounds. These were found to be highly toxic and hazardous to the environment and therefore not suitable for use. This gave rise to researchers to develop environmentally friendly and natural products such as plant extracts, essential oil, and purified compounds to obtain environmentally friendly corrosion inhibitors (Dariva and Galio, 2014). The first evidence of natural product as corrosion inhibitor was in the 1930s when extracts of Chelidonium majus (Celadine) and other plants were used for the first time in H2SO4 pickling baths (Raja and Sethuraman, 2008). However, in the 1950s and 1960s, there was a significant development in technology for the study of corrosion inhibitors as the application of electrochemistry has also improved (Dariva and Galio, 2014).

**1.3.1 Synthetic corrosion inhibitors**

Organic inhibitors which possess heteroatoms, such as oxygen, nitrogen, and sulphur, have been proven via experimental and computational approach to behave as effective and efficient inhibitors in corrosive environments (Verma *et al.,* 2018). The active site for the process of adsorption on the metal surface are O, N, and S, with the inhibition efficiency in the sequence O < N < S < P (Aouniti *et al.,* 2016). The use of organic compounds containing oxygen, sulphur, and especially nitrogen to mitigate corrosion attack on metals has been well documented (Odewole *et al,* 2021; Verma *et al.,* 2018). Literature reveals that most organic inhibitors are adsorbed on the surface of the metal via displacement of water molecules on the surface and forms a compact barrier. The presence of nonbonded (lone pair) and p-electrons in inhibitor moiety enhance the transfer of electron from the inhibitor molecule to the metal. A coordination covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed (Saha *et al.,* 2015). The strength of the chemisorption bond depends upon the electron density on the donor atom of the functional group and also the polarizability of the group. Replacement of an H atom attached to a C atom in the ring by a substituent group (–NH2, –NO2, –CHO, or –COOH) improves inhibition (Kadhim *et al.,* 2021).

The electron density in the metal at the point of attachment changes leading to inhibition of reactions at both cathodic or anodic sites. Electrons are lost at the cathode and are gained at the anode. Thus, corrosion is retarded. Straight chain amines containing between three and fourteen carbons have been examined. Inhibition increases with carbon number in the chain to about 10 carbons, but, with higher members, little increase or decrease in the ability to inhibit corrosion occurs. This is attributed to the decreasing solubility in aqueous solution with increasing length of the hydrocarbon chain. However, the presence of a hydrophilic functional group in the molecule would increase the solubility of the inhibitors (Kadhim *et al.,* 2021) The performance of an organic inhibitor is correlated to the chemical structure and physicochemical features of the compound such as functional groups, electron density at the donor atom, *p*-orbital character, and the electronic structure of the molecule (Verma *et al.,* 2021).

The inhibition could be due to adsorption of the molecules or ions on anodic and/or cathodic sites, increase in cathodic and/or anodic overvoltage, and the formation of a protective barrier film. Some factors that contribute to the action of inhibitors are chain length, size of the molecule, bonding, aromatic/conjugate, strength of bonding to the substrate, cross-linking ability, and solubility in the environment. The role of inhibitors is to form a barrier of one or more molecular layers against acid attack. This protective action is often associated with chemical and/or physical adsorption involving a variation in the charge of the adsorbed substance and charge transfer from one phase to another. Sulphur and/or nitrogen-containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitors (Rani and Basu, 2012).

**1.3.2 Acid corrosion inhibitors**

The synthesis and utilization of organic inhibitors essentially for iron and its alloys, like mild steel in acid cleaning industries and oil and gas fields, are highly anticipated. These organic inhibitors often times protects the surface of the metal via the mechanism of adsorption. The passivation from organic inhibitors has some merits over that of inorganic inhibitors. For instance, organic inhibitors passivate the surface of the metal uniformly which leads to maximum possible protection, whereas, the passive films on the metal surface by inorganic inhibitors are highly broken and porous, which eventually leads to localized corrosion of the metal surface (Goyal *et al.,* 2018). The availability of organic compounds in the acidic medium generally transforms the electrochemical nature of the acidic media.

**1.4. Mechanism of corrosion inhibition**

The interactions of organic inhibitors with the surface of metal entails donor acceptor interactions. Several inhibitors documented to have been employed are compounds that possess heteroatoms either in their aliphatic or aromatic ring(s) or in side chain. In aggressive acidic media, these heteroatoms with unshared electron pairs easily protonate and exist in their cationic forms (Verma *et al.,* 2015). Conversely, the surface of the metals becomes positively charged due to rapid oxidation of metallic elements in the aggressive solution and attracts the negatively charge counter ions such as chloride and sulphate ions of hydrochloric and sulphuric acids, which then adsorb on the metallic surface and make it negatively charged. This attraction is through electrostatic interactions (physisorption) (Verma *et al.,* 2016). However, as inhibitor molecules adhere onto the metallic surface through physisorption, further oxidation of surface metallic atoms results into the production of electrons that consume by protonating hydrogen and eliminate hydrogen gas. Thereby, cationic inhibitor molecules return their neutral form and heteroatoms with lone pairs of electrons can transfer their lone pair of electrons into the d-orbitals of the surface metal atoms that results into the phenomenon of chemisorption (Goyal *et al.,* 2018).

The adsorption tendency of organic inhibitors on the metallic surface depends upon numerous factors such as nature of corroding metal and corrosive medium, solution temperature and electronic structure of inhibitor molecules (Verma *et al.,* 2015).

**1.5 Techniques for Evaluating/Monitoring Inhibitor performance**

i. Weight loss or gravimetric measurements

ii. Electrochemical measurements: Some of this measurement includes; polarization resistance method and the impedance measurement

iii. Hydrogen monitoring

iv.Non-destructive testing (NDT) techniquessuch asultra-sonic, radiography, thermography, eddy current measurement

**v.** Analytical techniquessuch asiron counts, chloride counts, oxygen, conductivity and pH measurements, flow measurements and temperature

**1.5.1 Weight loss techniques**

Weight loss technique is also known as gravimetric techniques. It is the simplest and oldest method of all corrosion evaluation techniques. It entails exposing a specimen (coupon) of the material to the corrosive environment for a given duration, and measuring the resultant weight loss. The specimen, is first weighed, exposed into a specific environment, removed, and then cleaned and reweighed to estimate the amount of weight loss that has occurred over a specific period of time. The corrosion coupons could be in different shapes or forms such as; discs, rods, plates or of any convenient shape. The ease of the measurement this method offered is such that it forms the baseline method of measurement in many corrosions monitoring programs (Cottis and Abdullah, 2017).

**1.6 Adsorption Isotherm**

Adsorption isotherms are employed to describe adsorbent-adsorbate equilibrium relationship. In the process of adsorption, the adsorbate constitutes the bulk phase and is in contact with the surface of the adsorbent. If the adsorbate and adsorbent are contacted for too long, equilibrium may be established between the amounts of inhibitor molecules adsorbed and the amount remaining in the bulk phase. The equilibrium relationship is easily described using adsorption isotherm where a plot that relates the amount of adsorbate adsorbed to the equilibrium concentration of the inhibitor at a given temperature. This amount adsorbed (θ) is expressed as a function of inhibitor concentration (C) in the bulk medium and may be represented by the general form (Umoren *et al*., 2015).

### 1.6.1 Langmuir Adsorption Isotherm

This isotherm is the simplest and most useful isotherm for both physical and chemical adsorption. This model premise on the assumption that adsorption is limited to a monolayer surface coverage. Once a site is occupied, no further adsorption can take place in that site; the intermolecular attractive forces rapidly decrease as distance rises. Langmuir isotherm can be represented by the equation 1 (Gerengi *et al*., 2020)

(1)

where C is the concentration of inhibitor, is the surface coverage and Kads is the equilibrium constant of adsorption process. The equation requires that a plot of C/θ against C.

### 1.6.2 Freundlich Adsorption Isotherm

Freundlich Adsorption Isotherm is one of the foremost isotherms introduced to describe the adsorption isotherm. This is used to describe the adsorption characteristics of the heterogeneous surface, that is leading to multilayer adsorption. The stronger binding sites are occupied first, until adsorption energy is exponentially decreased upon the completion of adsorption process (Saadi *et al*., 2015). This isotherm is applicable at normal conditions of temperatures and pressure but fails at extreme conditions of temperature and pressure. Its equation is given below according to (Dim *et al.,* 2012).

(2)

Where C is the concentration of inhibitor, θ is the surface coverage, Kads is the equilibrium constant of adsorption process and n is adsorption intensity.

**1.7. Problem Statement**

Metallic materials are extensively used for constructional purposes especially in petroleum, oil and gas industries due to their cost-effectivity, prolonged existence and high thermal and metallic strength. However, most of the metals undergo corrosive degradation that results to huge safety threat, and economic losses. The global economy has been plunged to a loss of about 3.4% of the world GDP.

Owing to huge safety, fatality and economic losses, researchers across the globe have been developing, and advancing for effective measures to protect the metallic materials from corrosion. Among the several possible options, use of organic compounds is one of the best methods of corrosion mitigation due to their cost-effectiveness, high protection efficiency and

most importantly their environmental friendliness. Most of the effective organic inhibitors are those that contain polar functional groups in their molecular structures. Moreso, previous work have revealed conjugated pie bonds and heteroatoms in organic compounds are responsible for enhancement in the corrosion inhibition efficiency. The compound of interest used in this study which is naphthalene‐2‐carbohydrazide derived compound is rich in several conjugated pie bonds and hetero atoms, hence a potential corrosion inhibitor. However, studies on the use of naphthalene‐2‐carbohydrazide derived compounds as corrosion inhibitors are few in the literature. In addition, a perusal of literature reveals that corrosion inhibition efficiency of the compound of interest in this study have not been reported, hence the need for its usage in this study.

**1.8. Aim of the Study**

This study aims at investigating the anti-corrosive potentials of compound from naphthalene‐2‐carbohydrazide against the deterioration of mild steel immersed in 1 M hydrochloric acid solution through gravimetric (weight loss).

**1.9. OBJECTIVES OF STUDY**

**The objectives of study are:**

**i.** To ascertain using gravimetric method, the effect of varying concentration (0.0001 to 0.0005 M) and temperature (303 K, 333 K and 363 K) on the inhibition efficiency of mild steel in 1 M HCl provided by naphthalene‐2‐carbohydrazide inhibitor.

**ii.** To determine the nature of the adsorption process employing isotherm models of Langmuir and Freundlich.

**iii.** To determine the thermodynamic parameters such as; enthalpy (ΔH≠), entropy (ΔS\*) and Gibbs free energy ( involved in the process.

**1.10 Scope of Study**

The scope of this study includes the following:

**i.** Gravimetric study of mild steel in 1 M hydrochloric acid media for 6 hours at temperatures of 303 K, 333 K and 363 K.

**ii.** To ascertain adsorption isotherms using Langmuir and freundlich isotherms

iii. To evaluate mechanism of inhibition by investigating the gibbs free energy and the thermodynamic parameters

**CHAPTER TWO**

**2.0 LITERATURE REVIEW**

**2.1 Review of related literature**

In the study of Ibrahim *et al.,* (2022), the authors employed acetophenone derivatives as corrosion inhibitors to retard corrosion of mild steel (MS) in acidic medium. They investigated the inhibition effect of 3-nitroacetophenone (3-NA) on the corrosion of MS in acidic medium (1M HCl) using weight loss measurements, electrochemical measurements, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and quantum chemistry analysis. They performed their study using different concentrations of inhibitors and at different temperatures. Their outcome indicated that the inhibition efficiency of 3-NA increases with an increase in inhibitor concentration and reaches to a maximum of 64% at inhibitor concentration of 250 ppm at 30°C. The result from their potentiodynamic polarization measurement indicated that 3-NA acts as mixed type indicator. The adsorption process was reported by the authors to followed the Langmuir adsorption isotherm. The results they obtained from their DFT study revealed that 3-NA performs fairly as corrosion inhibitor for MS in acidic medium.

Odewole *et al*., (2021) evaluated the anticorrosive potentials of two Schiff base derivatives namely 4-[(E)-[(2E)-3-(4- nitrophenyl)prop–2-en-1-ylidene]amino]benzenethiol (4-NPPABT) and 4-[(E)-[(2E)-3-(4-nitrophenyl)prop-2- en-1-ylidene]amino]cyclohexan-1-ol (4-NPPACH) on mild steel in 0.1 M HCl. They employed gravimetric and theoretical techniques. Their outcome reveals an enhancement in the inhibition efficiency with increase in inhibitor concentration, whereas they observe a decline in the inhibition efficiency as temperature rises. 4-NPPABT showed highest inhibition efficiency of 64.9% at the highest concentration. They revealed the adsorption mechanism of the inhibitors on mild steel occurs predominantly by physisorption. More so, they revealed micrograph obtained from scanning electron microscopy (SEM) indicated the surface coverage of the mild steel by the inhibitor molecules which retard the rate of corrosion.

Naciri *et al.,* (2020) studied the use of a novel 1,2,4-triazole derivative, namely 5-hexylsulfanyl-1,2,4-triazole (HST) in inhibiting the carbon steel corrosion in 1.0 M HCl using mass loss measurements, electrochemical, scanning electron microscopy coupled with X-ray detection (SEM-EDX), X-ray diffraction (XRD) and computational techniques. They found from the gravimetric study that the optimal concentration of HST is 10−3 M with highest inhibition efficiency attained at 97 %. Their outcome from mass loss and electrochemical impedance spectroscopy (EIS) shows increases in inhibition with increasing inhibitor concentration as potentiodynamic polarization (PDP) revealed the inhibitor behaved as a mixed inhibitor. The inhibitor they used mitigates corrosion at the temperature range of 298 K–338 K, with an inhibition efficiency of 89 % at 338 K. They reported the free Gibbs energy obtained from the Langmuir isotherm model suggests chemisorption.

Sehmi *et al.,* (2020) assessed the potential of two pyrazole carboxamides named 5-(4-(dimethylamino)phenyl)-3-phenyl-4,5-dihydro-1H-pyrazole-1-carboxamide DPC-1 and (E)-5-(4-(dimethylamino)phenyl)-3-(4-(dimethylamino)styryl)-4,5-dihydro-1H-pyrazole-1 carboxamide DPC-2 as corrosion inhibitor of mild steel in 1 M hydrochloride acid using weight loss measurements, Tafel polarization curves and electrochemical impedance spectroscopies (EIS). Their obtained results show that DPC-1 and DPC-2 are effective corrosion inhibitors in 1 M HCl solution. They reported the inhibition efficiency η (%) increases with the increase of inhibitors concentration to reach 84.56 % at 4 × 10-4 M and 80 % at 1.6 × 10−4 M for DPC-1 and DPC-2 at 303 K, respectively. The authors revealed the adsorption of synthesized pyrazoles on MS surface obeys the Langmuir adsorption isotherm with both inhibitors acting as a mixed-type inhibitor The SEM analysis they carried out shows the formation of protective organic film on steel surface. They further investigated the relationship between the inhibition performance of pyrazoles and their structural parameters using DFT calculations.

Alhaffar *et al.,* (2019) evaluated the performance of environmentally friendly novel synthesized isoxazolidine derivative namely 5-(4-dodecyloxy-3-methoxybenzyl)-2-methylisoxazolidine (DMBMI) as anticorrosion agent for carbon steel in 1 M HCl solution using gravimetric and electrochemical techniques. They investigated the kinetics parameters of the corrosion process and the thermodynamic data of adsorption of the organic molecule on the carbon steel surface

in order to characterize the performance of the studied compound as a corrosion inhibitor. They revealed corrosion inhibition efficacy is dependent on concentration and temperature, as they observed corrosion inhibition ability increases with increasing inhibitor concentration but decreases with temperature rise. They revealed the inhibitor to be anodic type from the outcome of their PDP study. They further documented an enhanced inhibition efficiency with the addition of KI. They revealed results from theoretical studies and surface analysis are in conformity and reveal that the O and N heteroatoms in the synthesized molecule are the interaction centers.

Verma *et al.,* (2018) investigated the effect of electron withdrawing nitro (–NO2) and electron releasing hydroxyl (–OH) groups on corrosion inhibition potentials of 5-arylaminomethylenepyrimidine-2,4,6-trione (AMP). They studied Four AMPs tagged AMP-1, AMP-2, AMP-3 and AMP-4 for their potential to inhibit mild steel corrosion in 1 M HCl employing experimental and theoretical approach. The outcome from their gravimetric study showed that inhibition efficiency of the studied inhibitors increases with increasing concentration. The results further revealed that that electron withdrawing nitro (–NO2) group decreases the inhibition efficiency of AMP, while electron donating hydroxyl (–OH) group increases the inhibition efficiency of AMP. Their SEM and AFM studies revealed that the studied compounds inhibit mild steel corrosion by adsorbing at the metal/electrolyte interface. They further documented the nature of adsorption process obeyed the Temkin adsorption isotherm. The outcome of their potentiodynamic polarization study revealed that studied inhibitors acted as mixed type inhibitors with predominant effect on cathodic reaction. They showed the order of interaction energies derived from Monte Carlo simulations is AMP-4 > AMP-3 > AMP-2 > AMP-1, which is in agreement with the order of inhibition efficiencies obtained from experimental measurements.

Mishra *et al.,* (2018) investigated the anti-corrosive performance of three 5-aminopyrazole carbonitriles (designated as AHPC, ANPC, and AMPC) on mild steel in 1M HCl medium using gravimetric, electrochemical, surface, and density functional theory (DFT) methods. They revealed from their gravimetric measurements that inhibition efficiency of the tested compounds increases on increasing their concentration and that AHPC, ANPC, and AMPC showed the highest efficiencies of 90.34%, 92.04%, and 95.45%, respectively, at 7.69 × 10−4 M concentration. They further documented from the outcome of their electrochemical studies that tested inhibitor molecules acted as mixed type corrosion inhibitors and also enhance charge transfer resistance for corrosion process. Surface morphological studies carried out by the authors using SEM and AFM revealed that AHPC, ANPC, and AMPC molecules adsorbed and form surface protective film.

Al-Baghdadi *et al.,* (2018) evaluated the inhibitive effects of five carbazole derivatives (CZs) on mild steel corrosion and bio corrosion in 1 M HCl and microbial environments using weight loss measurements, electrochemical techniques, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques. They found that results of both weight loss and electrochemical techniques showed all the compounds inhibit both the acid induced corrosion and microbial corrosion and their inhibition efficiencies increase with increase in concentration. They reported the nature of adsorption process obeyed Langmuir isotherm and occur mainly via physisorption. They further revealed the outcome of the analyses from SEM images and EDX indicated that the studied compounds adsorbed on mild steel surface and form protective film that shield the surface from direct effect of corrosion in acidic and SRB media and that potentiodynamic polarization measurements revealed that the studied CZs are mixed-type corrosion inhibitors with predominantly cathodic inhibitive effects.

Murmu *et al.,* (2018) studied the corrosion inhibitive performance of two double condensed Schiff bases;4-(4-((pridin-2yl)methyleneamino)phenoxy)-N-((pyridin-2-yl)methylene)benzenamine (PMB) and 4-(4-(4-((pridin-2-yl)methyleneamino)phenoxy)phenoxy)-N-((pyridin-2yl)methylene)benzenamine (PPMB) on mild steel in 1 MHCl medium by gravimetric and electrochemical measurements. Their study revealed the higher inhibition efficiency of PPMB to that of PMB; and exhibited 93% inhibition efficiency at 5.0 mmol L-1 HCl solution. Their outcome shows that corrosion rate reduces with increasing inhibitor concentration. They reported that the adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm and that the obtained values revealed the predominant chemisorptions property of both the inhibitor molecules. Their surface morphology study revealed from micrographs from field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) and atomic force microscopy (AFM) demonstrated the adsorption of inhibitor molecules on the mild steel surfaces. Their results obtained from experimental and computational method are in good accordant with each other.

Gupta *et al.,* (2016) synthesized three Schiff' bases (SBs) namely, 2-amino-6 (2-hydroxybenzelideneamino) hexanoic acid (SB-1), 2-amino-6-(4-methoxybenzelideneamino) hexanoic acid (SB-2) and 2-amino-6-((4-dimethylamino)benzylideneamino) hexanoic acid (SB-3) and evaluated them as corrosion inhibitors for mild steel in 1 M HCl solution using weight loss, electrochemical, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy methods. The results showed that inhibition efficiency increases with the increasing concentration. Among the studied SBs, the SB-3 showed maximum inhibition efficiency of 95.6% at 400 mgL−1 concentrations. Potentiodynamic polarization study revealed that the investigated SBs act as cathodic type inhibitors. Adsorption of the SBs on mild steel surface obeys the Langmuir adsorption isotherms. The negative sign of suggests that the SBs adsorbed spontaneously on the surface. The weight loss and electrochemical results were well supported by SEM, EDX and AFM analyses.

**CHAPTER THREE**

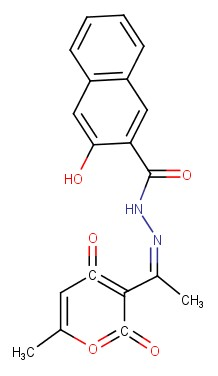
**3.1. EXPERIMENTALS**

### 3.1.1 Materials/Apparatus

Varying grades of abrasive paper, drug nylon, water bath (Leaidal Medical), measuring cylinder, hand gloves, nose masks, forceps, funnel, spatula, volumetric flask (1000 ml), scissors, electrical weighing balance (ATOM), beakers (100 ml), desiccator, syringe, brush.

**3.1.2 Reagents**

37 % HCl (Hydrochloric acid), acetone, ethanol, distilled water, calcium chloride (CaCl2), Valine dipeptide derivatives. All the chemicals used were of good quality and no further purifications were carried on before use. Concentrated HCl, ethanol, acetone, CaCl2 (desiccant) and distilled water, were purchased from Joe–Chem. Ventures, Nsukka, Enugu State.



**Fig 3.1:** Structure of carbohydrazide derivative; 3‐hydroxy‐N'‐[(1Z)‐1‐(6‐methyl‐2,4‐dioxo‐1lambda3‐pyran‐3‐yl)ethylidene]naphthalene‐2‐carbohydrazide

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
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| |  | | --- | | **3.2. Preparation of 1 M Hydrochloric Acid (HCl) Solution**  1 M HCl was prepared by diluting 37 % HCl with distilled water using the equations below:  (3.1)  Where;  The concentrated HCl used has density = 1.17 g/cm3, Percentage purity = 37 %, Relative molar mass = 36.45 g/mol  (3.2)  Hence, the concentration of the stock solution which the 1 M HCl was prepared from is 11.88 M. The required volume of the stock solution needed for the preparation of the 1 M HCl was computed using equation 3.4.  (3.4) | | Where;  C1 = Concentration of the stock solution = 11.88 M  C2 = The required molarity of the HCl acid  V1 = Volume of the stock solution needed to prepare the 1 M HCl  V2 = Volume of the acid required = 1000 cm3  1000 ml |   Therefore, approximately 8.42 ml of the stock solution was made up to 1000 ml using distilled water in a 1000 cm3 volumetric flask to obtain the 1 M HCl solution.  **3.3. Preparation of 1 X 10-4 M Inhibitor Stock Solution**  Stock concentration of the inhibitor = 1 x 10-4 M  Molar mass of inhibitor = 351.338 g  1 M of the inhibitor = 351.338 g,  1 x 10-4 M of the inhibitor = ? (Mass of the inhibitor required in gram)  Mass of the inhibitor needed to be dissolved in 1litre volumetric flask with distilled water was obtained to be from the calculation below:  Hence, of the inhibitor was dissolved in 1 litre of distilled water to obtain the inhibitor stock solution (). The various concentrations (M) (0.00003, 0.00006, 0.00009, 0.00012 and 0.00015) of the stock solution were prepared from inhibitor stock solution. The volume needed to obtain the various concentrations of the inhibitor stock solution were calculated using equation 3.4  Where;  C1 = Concentration of the inhibitor stock solution = 1 x 10-4 M  C2 = the required concentrations (g/L) of the inhibitor stock solution to be used  V1 = Volume of the inhibitor stock solution required to obtain the various concentrations of the inhibitor stock solution  V2 = Volume of the distilled water required = 50 ml   |  | | --- | | **3.4. Preparation of Mild Steel Coupons**  Rectangular mild steel coupons with dimensions 3.00 cm x 2.00 cm x 0.45cm were prepared by cutting commercially available mild steel sheets purchased from Ondo State, Nigeria. The mild steel coupons were abraded and polished using abrasive papers of varying grades. Afterwards, the mild steel coupons were washed thoroughly with distilled water, degreased in ethanol, dried in acetone, was weighed and stored in moisture-free desiccators prior to use for the weight loss measurement.  **3.5 Gravimetric Technique**  The gravimetric technique was carried out by employing a one factor at a time approach (OFAT), in which one factor (time) was kept constant and the other two factors (inhibitor concentration and temperature) were varied. The gravimetric (weight loss) measurements were done by immersing the prepared mild steel coupons which had been weighed into 100 ml beakers containing 100 ml of 1 M HCl in the absence of the inhibitor (blank solution) and presence of inhibitor having different concentrations (M) (0.0001, 0.00002, 0.00003, 0.0004 and 0.0005) for exposure period of Six (6) hours in the heated water bath at temperatures of 303 K, 333 K and 363 K. After the exposure time elapsed, the beakers containing the coupons were removed from the water bath and the coupons retrieved from the solution. The coupons were thoroughly washed with distilled water, followed with ethanol**,** rinsed with acetone to hasten drying after which it was reweighed and the weight loss of the mild steel coupons were computed. A triplicates measurement was carried out and the average value was computed. The corrosion rates (CR), surface coverage ()and inhibition efficiency were determined from the weight loss of the coupons using equations 3.5.  (3.5)  (3.6)  (3.7) | |  |   (3.8)  Where = Weight loss (g) of the mild steel coupons, Corrosion rates (CR) (gcm-2h-1) = Weight (g) before mild steel immersion, = Weight (g) after immersion. CRblank = Corrosion rates in the absence of inhibitor and CRinh = Corrosion rates in the presence of inhibitor, A = Area of the mild steel coupons (4.00 cm x 3.00 cm) and T = Exposure time (6 hours). 3.6. Adsorption isotherm The detailed understanding of the corrosion inhibition mechanism can be gotten from the nature of the process of adsorption of the organic inhibitor upon the surface of the mild steel surface is essential (Guol, 2017). In order to establish the nature and the strength of the adsorption process involved, data obtained from weight loss measurements was fitted to adsorption isotherms; The linearized form of Langmuir, and Freundlich isotherms are shown in equations 3.9-10 respectively.      The equilibrium constant values (Kads) was computed from the intercept of the plots 3.7. Thermodynamic Parameters The Arrhenius equation established the relationship between corrosion rate (CR) and temperature. The Arrhenius equation expressed in equation 3.11 was employed to compute value of activation energy (Ea) for the corrosion process (Verma *et al.,* 2018).    Where CR = Corrosion Rate, A = frequency factor, R = universal gas constant (8.314 JK-1Mol-1); T = temperature (K), Ea = apparent activation energy.  The value of the standard free energy (ΔGads) of the adsorption process was derived from the Kads values according to equation (3.12).  )  Where = Standard free energy of adsorption; = Equilibrium binding constant and the value of 55 is the concentration of water in solution expressed in moles per liter.  Moreso, values of enthalpy of activation, (ΔH∗corr) and entropy of activation, (ΔS∗corr) for the process of corrosion were estimated from the slope and intercept in the plot of of the Eyring transition state equation (3.13).    where h is Planck’s constant and NA is the Avogadro number  **CHAPTER FOUR**  **4.1 RESULTS AND DISCUSSION**  **4.2 Weight loss examination**  The mild steel was weighed prior to, and after 6 h immersion in uninhibited and inhibited 1 M HCl containing different concentrations of DMP1 at varying temperatures (303 K, 333 K, and 363 K) so as to examined the weight loss. The result as presented in Table 4.1 and Figure 4.2a reveals that the increase of the inhibitor’s concentration from 1 × 10−4 to 5 × 10−4 M causes a decrease in the corrosion rate CR of the mild steel from 0.0032 to 0.0008g cm2 h−1, accompanied by an increase in the inhibition efficiency WL (%) from 26 % to 74 % at 303 K (Fig. 4.2b). This outcome indicates that, increasing the inhibitor concentration leads to more adsorbed inhibitor molecules on the surface of the mild steel, which tends to cover surface active sites on the mild steel, thus, preventing corrosion and invariably retarding mass loss. However, inhibition efficiency decreased with temperature increase from 303K to 363K (Table 4.1). The decreased in the inhibition efficiency at an elevated temperature, could be attributed to decrease in the adsorption strength of the inhibitor (DMP1) as a result of increasing kinetic of the inhibitor molecules or the decomposition of the inhibitor (Lukman *et al.,* 2021). Previous report has documented similar results (Jamil *et al.,* 2018; Asegbeloyin *et al.,* 2015).    **Figure 4.2a**: A plot of corrosion rate against concentration at varying temperature  **Figure 4.2b**: A plot of inhibition efficiency against concentration at varying temperature  **4.3. Adsorption Isotherm Parameters**  The experimental data were fitted to Langmuir and Freundlich adsorption isotherm models so as to determine both the nature and strength of the inhibitor adsorption on the mild steel surface. The Langmuir adsorption isotherm plot (Fig. 4.3) entails *C/* θ *vs*. *C*, where θ are the values of surface coverage obtained via computation from weight loss evaluation corresponding to different inhibitor’s concentrations *C*. The plotted Freundlich adsorption isotherm which involves Log θ vs. Log C (Fig. 4.) best explained the adsorption process as it is best fitted by the adsorption data with regression coefficient closer to unity. The applicability of Freundlich isotherm to the DMP1 adsorption on the mild steel surface posits that the adsorbed inhibitor species interacted with each other, which infers a multilayer adsorption on the surface of the mild steel by the inhibitor species.  The values of *K*ads (0.23-0.53 L/mol) shown in Table 4.3 were obtained from the reciprocal of intercept of the Freundlich isotherm. The value of *Kads* implies that the inhibitor molecules are adsorbed on the surface of the mild steel (Verma *et al.,* 2020).  **Figure 4.3:** Langmuir adsorption plot for mild steel in 1 M HCl containing various concentrations of inhibitor DMP 1 at temperatures of 303K, 333K, and 363 K for 6 hours.  **Figure 4.4:** Freundlich adsorption plots for mild steel in 1 M HCl containing various concentrations of inhibitor at temperatures of 303K, 333K and 363 for 6 hours  **Table 4.3:** Adsorption constant and Gibb’s free energy (-ΔGads)   |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | |  | **303K** |  | **333K** |  | **363K** |  | | Kads | -ΔGads (kJmol−1) | Kads | -ΔGads (kJmol−1) | Kads | -ΔGads (kJmol−1) | |  | 0.51 | 8.4 | 0.53 | 9.4 | 0.23 | 7.6 |   **4.4. Thermodynamic Parameters of the Corrosion Process**  The Gibbs free energy of adsorption computed using equation 3.12 is presented in Table 4.3. Several studies (Naciri *et al.,* 2020; Haque *et al.,* 2018) reveals that when the value of are up to −20 kJ/mol or less negative, it indicates the presence of an electrostatic interaction between the charged adsorbed inhibitor molecules and the charged metal surface (physisorption). However, the value close to −40 kJ/mol or more entails the formation of a coordinate bond by the transfer or the sharing of electrons between the inhibitor molecules and the metal surface (chemisorption) (Chugh *et al.,* 2020). The negative values of (-7.6 to -9.4 kJ/mol) obtained in this study as shown in Table 4.3,typifies the tendency of the inhibitors to adsorbed spontaneously on the surface of the mild steel. More so, the obtained values which is less than −20 kJ/mol suggests that the adsorption of the investigated inhibitors on mild steel surface involves electrostatic interaction between charged inhibitors and charged mild steel surface (physisorption) (Verma *et al.,* 2016; Al-Amiery *et al.,* 2013).  The Arrhenius equation (3.11) was employed to have better knowledge on the kinetic process involved with respect to the impact of temperature, on the rate of corrosion of the mild steel in the acidic medium with and without the inhibitors. The activation energy (Ea) in (kJ/mol) was computed from the slope of the Arrhenius plot (Fig. 4.6). The estimated activation energies for all the inhibited acidic solutions were found to be greater in comparison to the blank solution. The highest Ea value (74kJ/mol) was obtained at the highest inhibited concentration of 5 x 10-4 M as against (62.36kJ/mol) of the uninhibited acidic solution. The higher value of activation energy, Ea corresponds to increase in the energy barrier created to protect the surface of the mild steel by the inhibitor molecules for the corrosion phenomenon (Chugh *et al.,* 2020; Yadav *et al.,* 2014).  The values of enthalpy of activation (ΔH≠) as outline in Table 4.4, and computed from the slope of the transition plot (Fig. 4.7) are all positive in both the blank solution and the inhibited concentrated solutions. This suggests an endothermic process, and that an energy barrier was created in the presence of the DMP1 inhibitor molecule. The blank solution had the least enthalpy value. Conversely, under the same conditions, the values of the entropy of activation (ΔS≠) are negative, which could be attributed to the association of the available inhibitor molecules rather than its dissociation, hence it’s disorderliness. Furthermore, the (ΔS≠) values in the presence of DMP1 inhibitor is higher than in its absence, and this suggests that the level of randomness (disorder) increased when going from reactants to the activated complex (Aouniti *et al.,* 2016). This observed rise may be due to the adsorption of the inhibitor molecules from the HCl solution which could be as a quasi-substitution process between the organic molecules present in the aqueous phase and the water molecules already adsorbed at the surface of the mild steel (Obot *et al.,* 2017). Similar trends have been documented in previous studies (Odewole *et al.,* 2021; Verma *et al.,* 2018; Jamil *et al.,* 2016).  **Table 4.4:** Thermodynamic and kinetic parameters of mild steel corrosion in the presence of DMP 1 atvarious temperatures in 1.0 M HCl.   |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | | Inhibitor | Concentration  (M) | Activation Parameter | | | | |  |  | Ea(kJ/mol) |  | ΔH≠(J/mol) | -ΔS≠ (J/mol K) | | J1 | Blank | 62.36 |  | 220.20 | 196.97 | | 1 x 10-4 | 66.21 |  | 233.37 | 196.93 | | 2 x 10-4 | 69.82 |  | 246.16 | 196.90 | | 3 x 10-4 | 67.71 |  | 241.19 | 196.92 | | 4 x 10-4 | 72.58 |  | 258.05 | 196.87 | | 5 x 10-4 | 74.00 |  | 263.49 | 196.86 |     **Figure 4.5:** Arrhenius plot **for** DMP 1  **Figure 4.6: Transition plot** DMP 1 |

**CHAPTER FIVE**

**5.0 CONCLUSION**

This study investigated the anti-corrosive potential of derivatives of naphthalene‐2‐carbohydrazide against the mild steel in aggressive acidic medium of 1 M HCl for six (6) hours. The study employed the techniques of gravimetric and surface morphology. The outcome as obtained from the gravimetric study indicates an enhancement in the inhibition efficiency with inhibitor concentration increase, attaining a maximum efficiency of 74% at 303K. However, the inhibition efficiency decreases with temperature increase, attaining inhibition efficiency of 44.21% at 363K. The study revealed a decrease in corrosion rate with inhibitor concentration increase. The anti-corrosive performance of the compound under study could be attributed to pie bonds in the structure and heteroatoms.

Moreso, for the thermodynamic studies, the computed values for the enthalpy (ΔH≠) which were all positive indicates endothermic nature of the enthalpy of the adsorption process. Conversely, the entropy (ΔS\*) values were all negatives and large which signifies an association rather than a dissociation, hence, its disorderliness. Also, the negative values of (-7.6 to -9.4 kJ/mol) obtained in this study posits the adsorption of the inhibitors on the surface of the mild steel adsorbed spontaneously via physisorption. Hence, the derivative of naphthalene‐2‐carbohydrazide compound could serve as a good potential corrosion inhibitor in acidic medium in low temperature environment but fairly usable in an elevated temperature of 363 K.

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