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Investigation of Hybrid Inhibitors: Impact of DNA of Two Varieties of *Musa* on Mild Steel

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ABSTRACT **Original Research Article**

The ever present threat to the integrity of a metals' structure called corrosion has led to the heavy use of preventive measures in order to slow down its' progression. One of such preventive measures is the use of corrosion inhibitors. The use of corrosion inhibitors has proven to be very successful making their application one of the most used measures against corrosion. However, despite the successful use of corrosion inhibitors, having high corrosion inhibition efficiencies; some corrosion inhibitors have been found to be moderately to highly toxic to man and the environment. A call for alternative inhibitors to the toxic inorganic corrosion inhibitors was made and the answers arrived at by researchers, were the use of "Green Inhibitors". This research focused on the use of DNA extracted from two varieties of plants from the *Musa* species and a hybrid of the two as corrosion inhibitors of mild steel with the corrosive medium being HCl. Experiments were undertaken at varying temperatures of the corrosive medium and at varying concentrations of DNA in order to determine the optimal temperatures and concentrations that give the highest corrosion inhibition efficiencies of the two Musa varieties and the hybrid. The highest corrosion inhibition for *Musa acuminate* DNA was 58.1818% at the conditions, 55˚C and 5 **mg/L** while for *Musa paradisiaca* DNA, the highest corrosion inhibition was 55.0720% at the conditions, 10˚C and 20 **mg/L** and for the hybrid, the highest corrosion inhibition efficiency was 60.8697% at the conditions, 10˚C and 20 mg/L.

Keywords: Corrosions, Metal, *Musa*, HCI, Hybrid, Inhibitors.

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Introduction

Metals play a large role in modern society, they can be found in almost everything from the simple things like spoons and pens to more complicated things like heavy machinery and airplanes. Corrosion is the inevitable degeneration of the properties possessed by a material due to interactions with their surrounding (Shaw et al., 2006). Corrosion eats away at metals causing them to be weakened. Unfortunately, corrosion cannot be stopped but its progression can be slowed down. Several techniques can be adopted in order to decelerate or hinder corrosion of structures made of metal. The most popular treatments are protective coatings on metals by organic molecules, plastics, polymers; cathodic and/or anodic protection by organic or inorganic inhibitors (Devarayan, 2012). Materials that decrease the rate of corrosion in a corrosive environment, even in trace amounts, are called "inhibitors". The modes of operation of inhibitors are as follows:

- the inhibitor is chemically adsorbed (chemisorption) on the metal surface and a protective thin film with inhibitor effect is generated.
- the inhibitor supports creation of oxides of the base metal on the surface of the base metal. The oxide layer serves as a shield against further corrosion.
- the inhibitor interacts with a potential corrosive component existing in aqueous media and creates a complicated product (Camila, 2013).

The classification of inhibitors varies. Inhibitors have been grouped by their chemical functionality resulting in there being

three inhibitors: Inorganic inhibitors, organic anionic inhibitors and organic cationic inhibitors (Jones, 1988), inhibitors are also classified as adsorption inhibitors and film forming inhibitors (McCafferty, 2010). Furthermore, inhibitors are classified by their inhibition mode of operation as follows: anodic (or passivating) inhibitors, cathodic inhibitors, mixed inhibitors and volatile corrosion inhibitors (Montemor, 2016).

Passivating inhibitors are oxidizing substances, which, under certain conditions, provide corrosion protection by one (or more) of the following mechanisms: (i) Enhancement of the passive ability by incorporation of species into the passive layer; (ii) stabilization of passive oxide layers; (iii) reduction of the probability of absorption of aggressive ions, such as chloride ions; (iv) ability to shift the corrosion potential towards more positive values, forcing the metallic surface into the passive range. Passivating inhibitors are well recognized. Examples are chromates and nitrites. The inhibitors are stable in several pH ranges and are particularly efficient in near neutral solutions. They create sparingly soluble corrosion products such as oxides, hydroxides or salts which are protective in different surfaces (Montomer, 2016).

Cathodic inhibitors will precipitate at cathodic sites or slow down the cathodic process, as the pH rises owing to hydroxyl release, thus raising the local impedance and preventing the diffusion of reducible species to these sites. These inhibitors work by multiple ways including: (i) selective precipitation on the cathodic areas (cathodic precipitators); (ii) decrease of the reduction reaction rates (cathodic poisons). Montomer (2016) usually adds oxygen scavengers in the family of cathodic inhibitors. Rare earths are popular examples, notably the cerium cation able to generate stable oxides or hydroxides on the cathodic regions (Mishra, 2007).

Mixed corrosion inhibitors are among the most commonly used inhibitors and are mainly compounds that are organic and can be neither classified as cathodic nor as anodic inhibitors (Montomer, 2016). Mixed inhibitors form a thin protecting layer by suppressing the cathodic and anodic corrosion reactions, generally by adsorption on the metal surface (Richardson, 2008). Due to this, these inhibitors are also called ‘film-forming inhibitors’ (Elsener, 2002), or ‘adsorption inhibitors’ (Kondratova, 2003). This process depends strongly on the metallic surface morphology, roughness and composition, structure of the inhibitor and chemical composition. Organic substances with polar groups containing sulphur (S), nitrogen (N) and hydroxyl (OH) are usually effective mixed inhibitors (Soeda, 2003). Volatile corrosion inhibitors (VCIs) are material molecules that are adsorbed on the surface of the metal after vaporizing at a significant pressure and form a thin corrosion protection layer (Saini, 2013). Aminocarboxylates (products of reaction between amine or amine derivatives and organic acids) are usually volatile corrosion inhibitors. VCIs can protect metals in enclosed spaces by condensing on the metal surface without being directly in contact with the metal because their vapor pressure is sufficient (Gangopadhyay, 2018). Compounds that are nonvolatile but release volatile components on hydrolysis can also be called

VCI. VCIs can be used in the form of porous emitters (VCI desiccants), inhibited air and packaging materials (VCI films and VCI papers) to provide temporary protection (Valdez, 2006).

Many of the synthesized corrosion inhibitors are mostly from cheap raw materials or their natural derivatives include heteroatoms in aromatic rings and long-chain carbon structures. Although these inhibitors are effective in minimizing the corrosion process, most of them have a toxic nature making them environmental hazard and ecological risk (Kumar, 2016). As a result, there has been an increasing demand for developing sustainable and eco-friendly corrosion protective alternatives. A potential solution makes use of hybrid organic–inorganic sol-gel coatings, which are widely regarded as effective surface protection materials. Sol-gel coatings exhibited lots of advantages properties such as flexibility, hydrophobic property, corrosion resistance ability, transparency and adhesion strength with the substrate surface. The addition of polysiloxane, siloxane and polymeric substances leads to the formation of hybrid coatings and improved corrosion protection. These materials work mainly by building a barrier layer, which protects the metal surface to prevent the diffusion of oxygen and other corrosive species. Hybrid coatings made by sol-gel offer a telecomposite properties due to the incorporation of both organic and inorganic components within a dual network polymer where Inorganic portions have strong chemical linkages with polymer chains. In addition, the integration of active corrosion inhibitors within the coating matrix leads to a higher effect on corrosion resistance, particularly when localized defects or discontinuities arise in a protective layer enhancing durability and aging-related events in a more effective manner (Khoshkhou et al., 2018).

Mild steel, also known as plain-carbon steel and low-carbon steel, is the most prevalent embodiment of steel due to its cost being comparatively low and its material characteristics being tolerable for many applications. 0.05–0.21% carbon is contained by mild steel, giving it properties of malleability and ductility (Baker, 2018). Mild steel is inexpensive and easy to shape, but has low tensile strength. The elemental composition of mild steel is seen in table 1.1.

Table 1.1: Elemental Composition of Mild Steel

Element	Composition (%)
Iron	99.2
Carbon	0.15
Silicon	0.17
Manganese	0.43
Aluminum	0.006
Chromium	0.001
Phosphorus	0.02
Sulfur	0.033
Nickel	0.007

The environmental and health effects of numerous synthetic corrosion inhibitors have pushed researchers towards searching for safe and sustainable alternatives from natural resources. Thus, considerable research efforts have been paid for developing green inhibitors which are eco-friendly compounds derived from their natural resources like plant extracts. The current study examines Musa for the first time as an organic corrosion inhibiting agent of two varieties. Musa is the scientific name of a genus of plants in Musaceae that includes bananas and plantains but not Ensete. Since the first scientific description made by Carl Linnaeus in 1753, about 70 species belonging to the genus have been recognized with considerable economic, nutritional and industrial potential (Hai, 2015). The Banana and the 'Green Banana'· in my part of South Florida ranked as one of the quickly. growing, most basic food crops on earth ·and is so important that botanists claim it to be a 4th staple (to Rice, Wheat and Maise) world-wide. Musa spp. grow in a variety of environmental conditions and have many uses, including an edible fruit growing in tropical regions to fiber and ornamental purposes elsewhere; These plants have been integral part of human diet and survival since the dawn of civilization. Musa species are a cornerstone of many Pacific cultures, being sources of foods, beverages, fermentable sugars, medicines and agents for flavouring and cooking as well as providing materials for numerous ceremonial and religious practices (Nelson et al., 2006). Musa species have shown great potential for development as sustainable green corrosion inhibitors owing to their abundance, biodegradability, and rich composition in phytochemicals.

Statement of Problem

Corrosion is the detrimental attack of a material by electro/chemical contact with its environment. The severe consequences of the corrosion process are now clear internationally. The overall annual evaluations in the U.S. were expected to exceed $1 trillion in 2013. But the cost of rusting isn't merely economic. Corrosion causes plant shutdowns, loss of precious resources, product loss or contamination, reduced inefficiency, maintenance expense and expensive overdesign (Dikici et al., 2014).

The toxicity levels of inorganic inhibitors such as chromates and chromium compounds caused them to be deemed unsuitable for use. The term 'green inhibitors' refers to the materials that are compatibility with the natural world. The inhibitors like plant extracts doubtlessly possess biocompatibility because of their natural origins (Devarayan et al., 2012).

Aim and Objectives of the Study

Aim

The aim of this study is to research the impact of hybrid DNA of two varieties of *Musa* inhibitors on mild steel.

Objectives

The objective of this study is:

- To synthesize a new hybrid inhibitor to produce an effective barrier against metal corrosion.
- To show the impact of DNA of *Musa paradisiaca* and *Musa acuminata* on mild steel.
- To identify which variety of *Musa* out of the ones focused on has the highest corrosion inhibition efficiency.

Literature Review

Concept of Corrosion

The main reasons corrosion is studied are because it affects the safety of humans and the cost it inquires. Corrosion is a phenomenon that garners a lot of attention because of its destructive nature and the fact that it cannot be stopped. All metals will eventually corrode, because of this the integrity of structures imbued with metals as supports comes into question and the safety of humans with it. Corrosion of water pipes such as in plate 2.1 and the subsequent contamination of water supplies is also hazardous to human health.

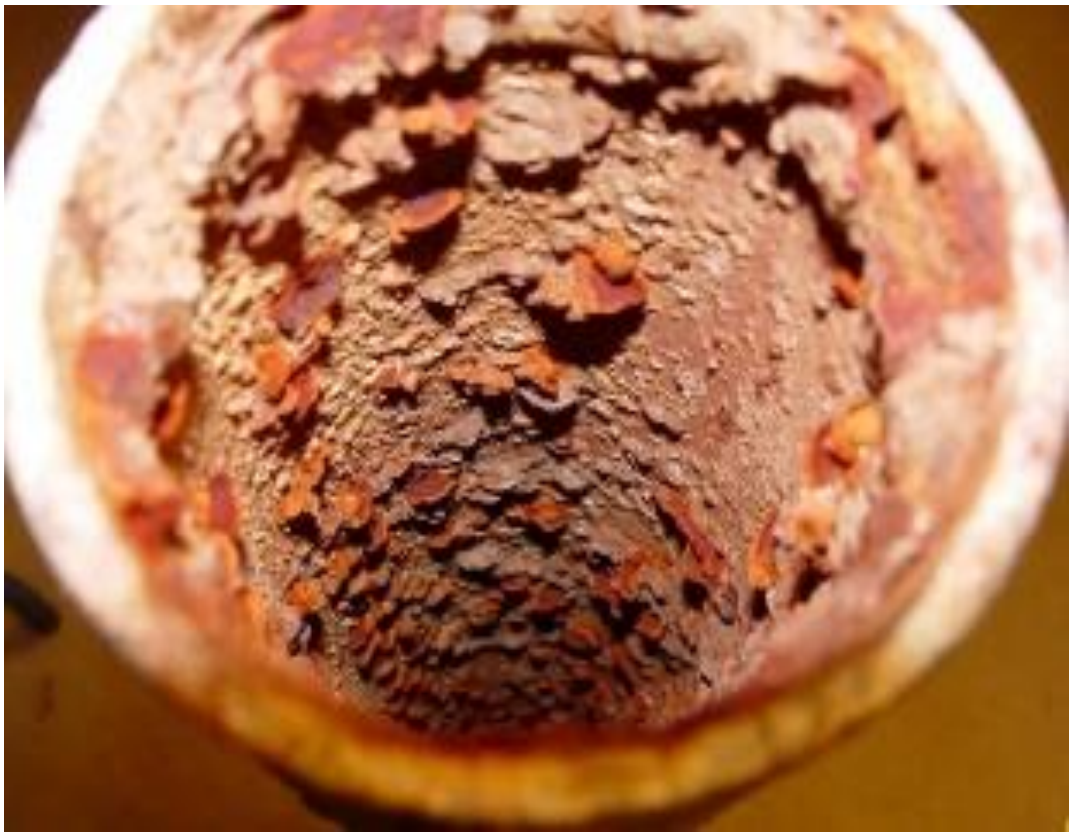

Plate 2.1: Corroded Metal Pipe (Adapted from Jerner, 2016)

In order to ensure the safety of man, corroded parts of structures and machines are repaired or replaced and measures are corrosion-resistant alloys, corrosion inhibitors and coatings are put in place. Corrosion can also lead to the shutting down of plants, loss of products or even the contamination of products. This leads to high costs inquired by individuals and industries.

The System of Corrosion

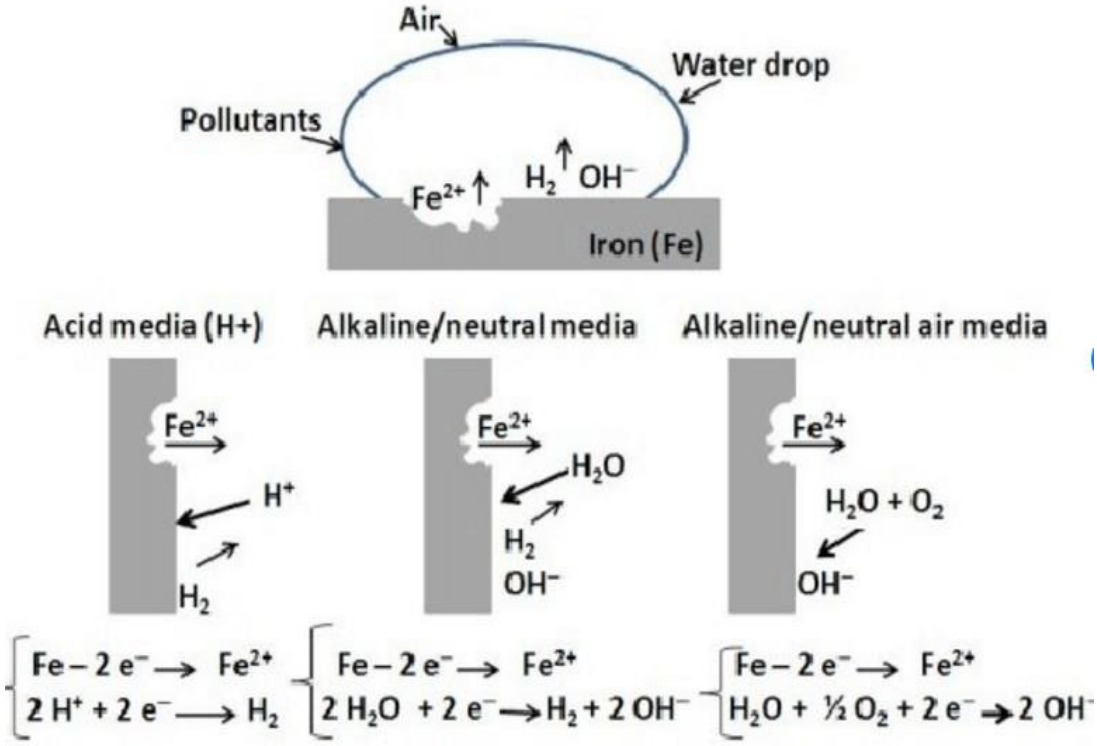

Figure 2.1: System of Corrosion (Adapted from Mainier, 2013)

Metals are usually obtained in nature in their stable states or other naturally occurring compounds. The metals are usually in an unsteady state and will therefore lose energy in order to return to more stable forms as seen in figure 2.1 above. Corrosion reactions are usually electrochemical.

Corrosion Inhibition

Corrosion inhibition is the act of altering the composition of a corrosive medium to impede the progression of corrosion. Since corrosion is an electrochemical reaction or a combination of electrochemical reactions that occur at the electrodes, it is logical to assume that if the velocities of all or some of the reactions at the electrodes are stopped or hindered then the rate of corrosion will also be hindered (Parkins, 1981). Corrosion inhibitors are substances that cause a reduction in the rate of corrosion when they are introduced in a corrosive medium in small quantities.

The grouping of corrosion inhibitors varies between authors. Some classify inhibitors by their chemical functionality while others prefer to just classify them by their functionality.

Methodology

Gravimetric Method

This method of analysis uses the weight loss of a metal in a corrosive medium in order to compute the rate of corrosion and corrosion inhibition efficiency of any inhibitor added. The rate of corrosion and corrosion inhibition efficiency are calculated using the formulas:

$$CR = (87.6 * W)/ (D*A*T) \qquad \text{Equation 3.1}$$

Where,

CR = Corrosion Rate (mm/yr)
W = Weight loss (Initial Weight – Final Weight) (mg) D = Density of Mild Steel (7.86 /cm^2)
A = Total Surface Area (cm^2)
T = Time of Exposure to corrosive medium (hrs)

$$IE = ((R_0-R_i) / R_0)*100 \qquad \text{Equation 3.2}$$

Where,

IE = Inhibition Efficiency (%)
R_i = Corrosion rate of metal with inhibitor (mm/yr)
R_0 = Corrosion rate of metal without inhibitor (mm/yr)

Preparation of Solutions

Preparation of CTAB Buffer

Table 3.1: Materials and their quantities' needed to make 100ml CTAB Buffer

Materials	Quantity
CTAB (Hexadecyl trimethyl-ammonium bromide)	2.0 g
1 M Tris pH 8.0	10.0 ml
0.5 M EDTA pH 8.0 (Ethylenediaminetera Acetic acid Di-sodium salt)	4.0 ml
5 M NaCl	28.0 ml
H_2O	40.0 ml
PVP 40 (polyvinyl pyrrolidone)	1 g

Adjust all to pH 5.0 with HCl and make up to 100 ml with H_2O

The metal samples with dimensions 10 mm by 10 mm by 2 mm were cleaned with three (3) grades of sand paper (P60 D, P220 D and P320 D) in order to remove any preexisting impurities such as rust and smoothen the surface of the metal.

The cleaned metal samples were then washed with ethanol and then with distilled water and left to dry. If an inhibitor is to be added it is added at this point to the 1 M HCl, preparation of which will be discussed in detail later in this chapter, after the HCl has been raised or lowered to the appropriate temperature needed.

The metal sample to be used was then tied up with twine and suspended in the 1 M HCl for a duration of either 8 hours or 3 days.

Extraction of Plant Genomic DNA Using CTAB (Hexadecyl trimethyl-ammonium bromide)

4.8 g of plant extract was put into a clean centrifuge tube and approximately 12 ml of CTAB Buffer, preparation of which is detailed in Table 3.1, was added to it. The CTAB/Plant material mixture was then shaken vigorously to ensure proper mixture. The CTAB/plant extract mixture was then left for 15 minutes at 55˚C in a CO_2 incubator (Plate 3.2) to incubate.

After incubation had concluded, the CTAB/plant extract mixture was spun in a centrifuge (Plate 3.1) at 12000 rpm for 5 minutes to push down the cell debris. The supernatant was then transferred to clean centrifuge tubes using a micropipette (Plate 3.3).

3 ml of Chloroform: Iso Amyl Alcohol (24:1) was then inserted to each centrifuge tube and the solution mixed by inverting the tubes. The tubes were then spun again at 13000 rpm for 1 minute. After spinning, the supernatant of the solution was transferred to clean tubes and 0.6 ml of 7.5 M Ammonium Acetate was inserted to each tube followed by 12 ml of ice cold absolute ethanol. The tubes were inverted slowly and kept in a freezer for a few hours in order to precipitate the DNA (appears white and stringy). After the DNA has precipitated, the Ammonium Acetate/Absolute ethanol mixture was decanted out and 70% ice cold ethanol was added to the DNA to clean it.

Preparation of 1M HCL

In order to determine how much of 12 M HCL is required to produce 1 L of 1 M HCL, the formula below was used:

$C_1V_1 = C_2V_2$ *Equation 3.3*

Where,

C_1 = Original Concentration (12 M)

V_1 = Volume needed (unknown)

C_2 = Final Concentration (1 M)

V_2 = Final Volume (1 L) 12x = 1

X = 83 ml

83 ml of 12 M HCL was added to 1000 ml of water to yield 1 L of 1 M HCL

Results

Results of Gravimetric Analysis

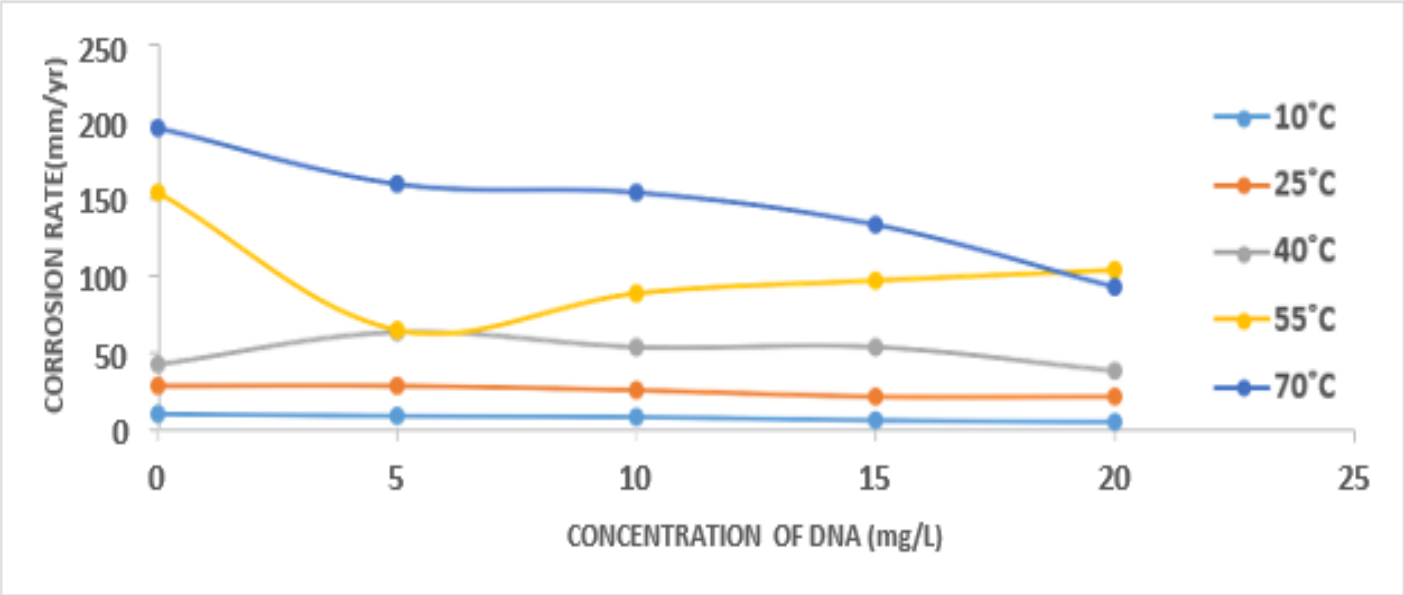

Figure 4.1: Corrosion Rate vs. Concentration of Musa acuminate DNA inhibitor at intervals of 15˚C for a temperature range of 10˚C-70˚C

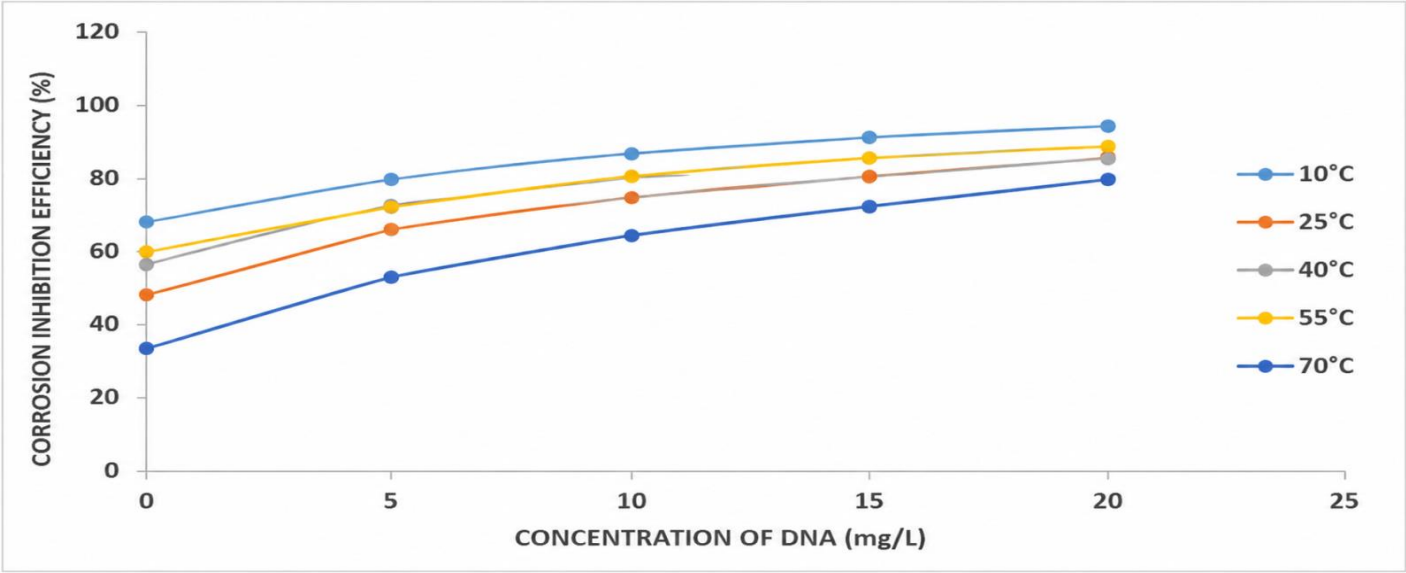

Figure 4.2: Corrosion Inhibition Efficiency vs. Concentration of Musa acuminate intervals of 15˚C for a temperature range of 10˚C-70˚C

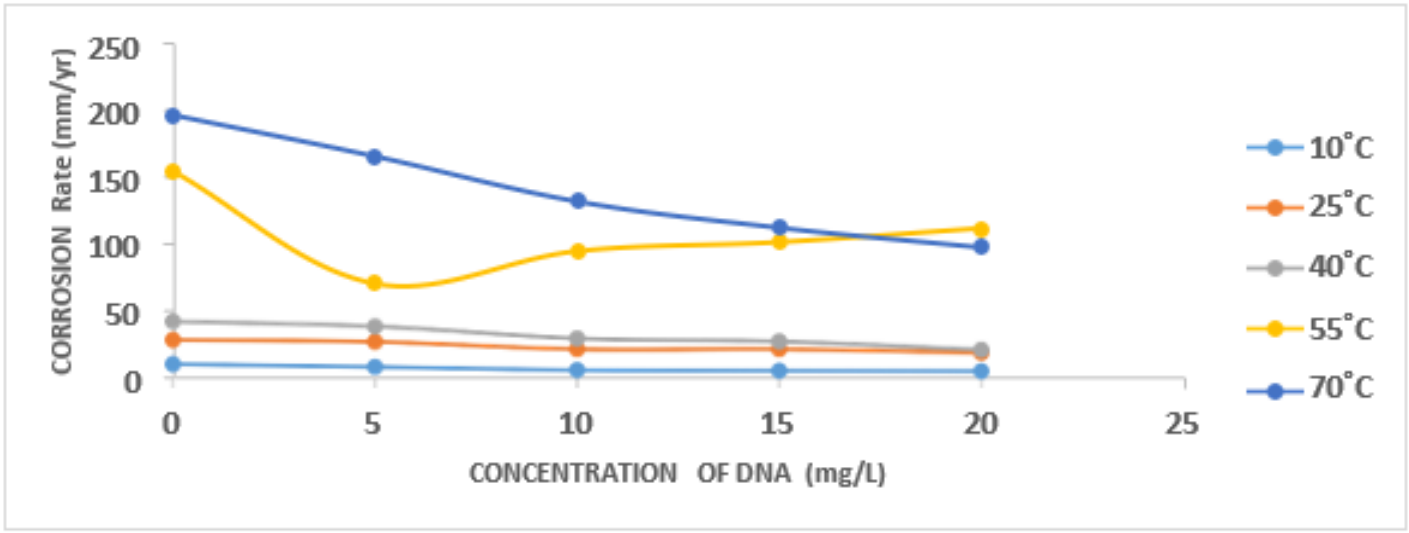

Figure 4.3: Corrosion Rate vs. Concentration of Musa paradisiaca DNA inhibitor at intervals of 15˚C for a temperature range of 10˚C-70˚C

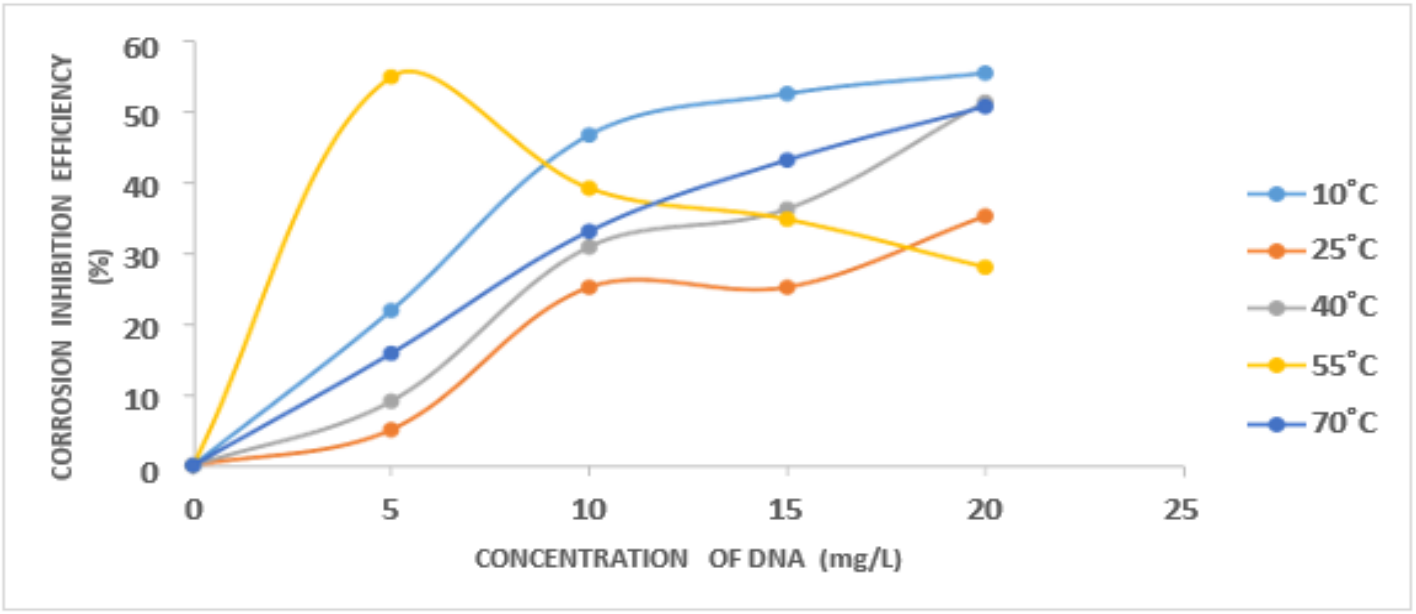

Figure 4.4: Corrosion Inhibition Efficiency vs. Concentration of Musa paradisiaca intervals of 15˚C for a temperature range of 10˚C-70˚C

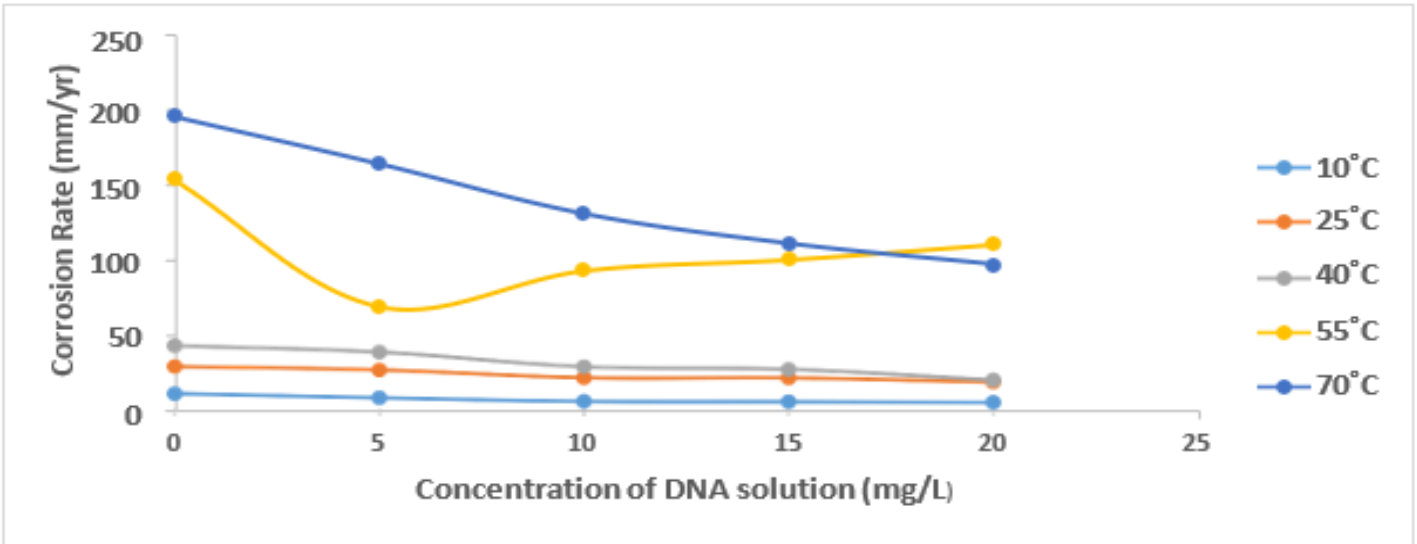

Figure 4.5: Corrosion Rate as a Function of Hybrid (*Musa acuminata* and *Musa paradisiaca*) DNA Inhibitor Concentration at 15℃ Temperature Intervals over the Range of 10℃–70℃

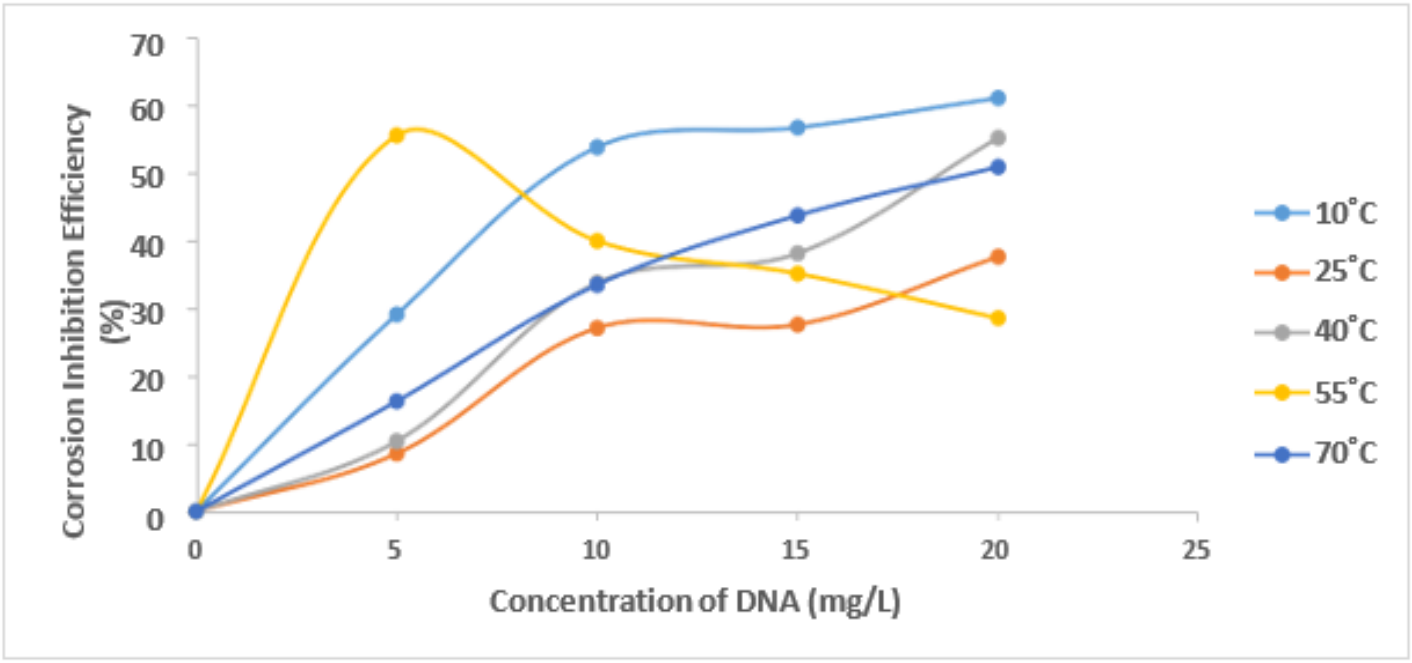

Figure 4.6: Corrosion Inhibition Efficiency as a Function of Hybrid (*Musa acuminata* and *Musa paradisiaca*) DNA Inhibitor Concentration at 15℃ Temperature Intervals over the Range of 10℃–70℃

Thermodynamic Functions of Activation

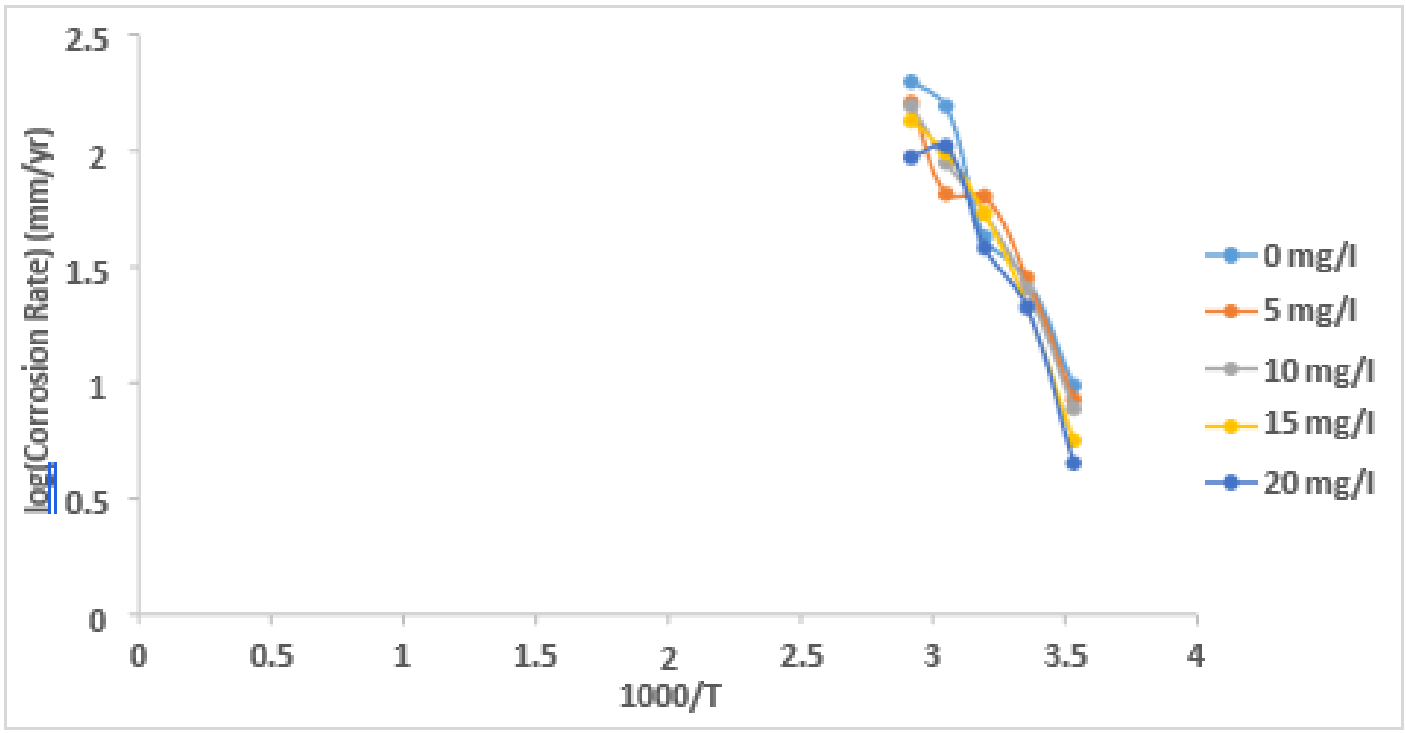

Figure 4.7: log (Corrosion Rate) versus (1000/T) for Musa acuminata DNA Inhibitor at Varying Concentrations (0–20 mg/L)

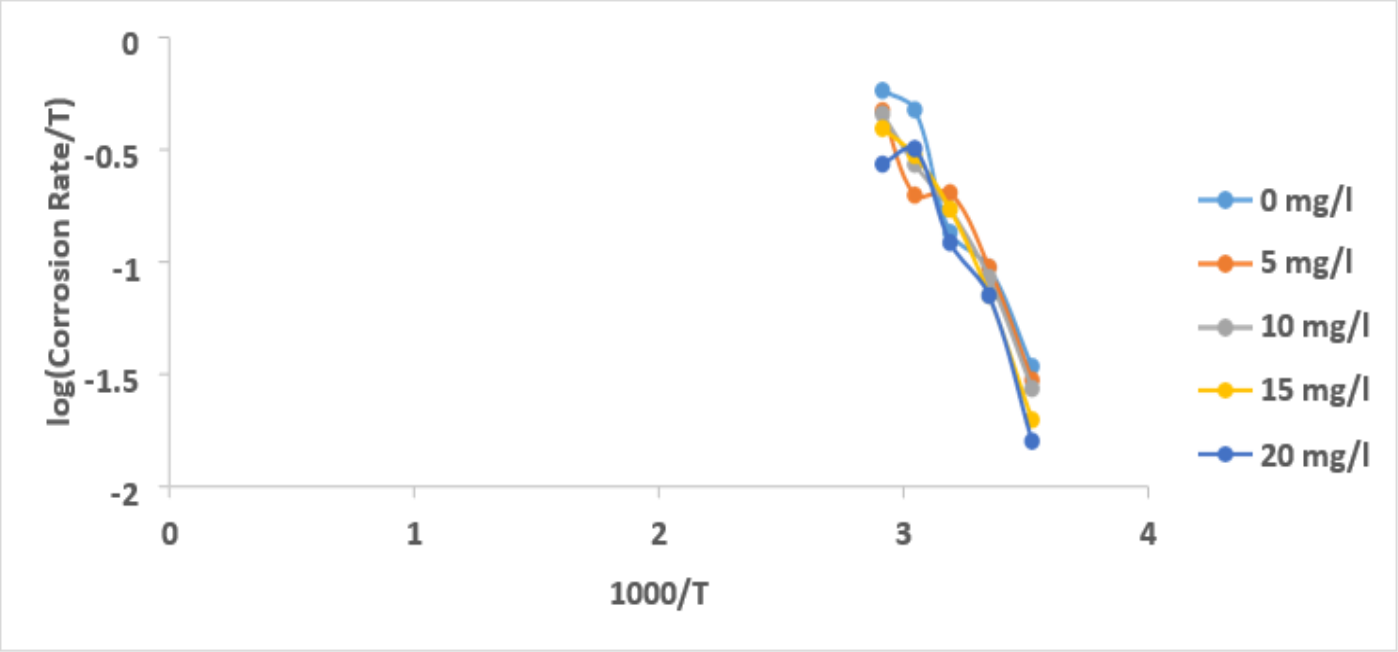

Figure 4.8: log (Corrosion Rate/T) vs. (1000/T) of Musa acuminate DNA inhibitor at varying concentration (0-20 mg/L)

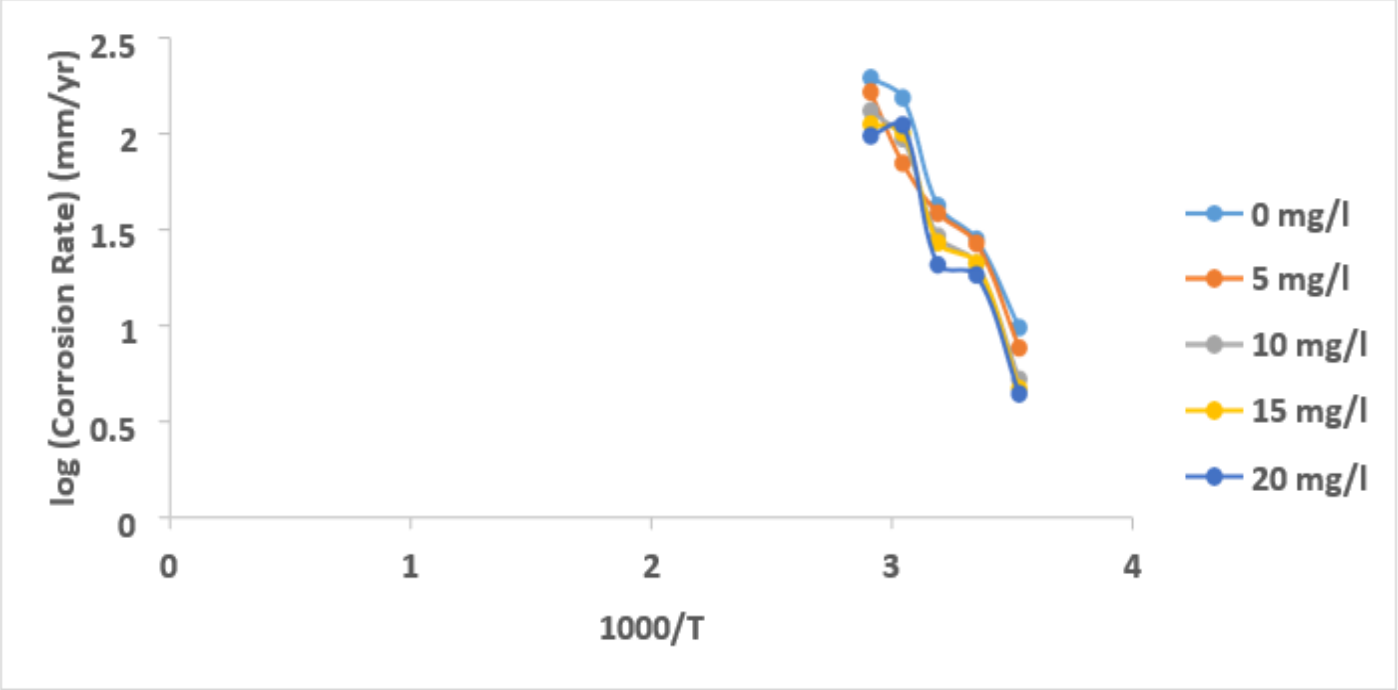

Figure 4.9: log (Corrosion Rate) vs. (1000/T) of Musa Paradisiaca DNA inhibitor at varying concentration (0-20 mg/L)

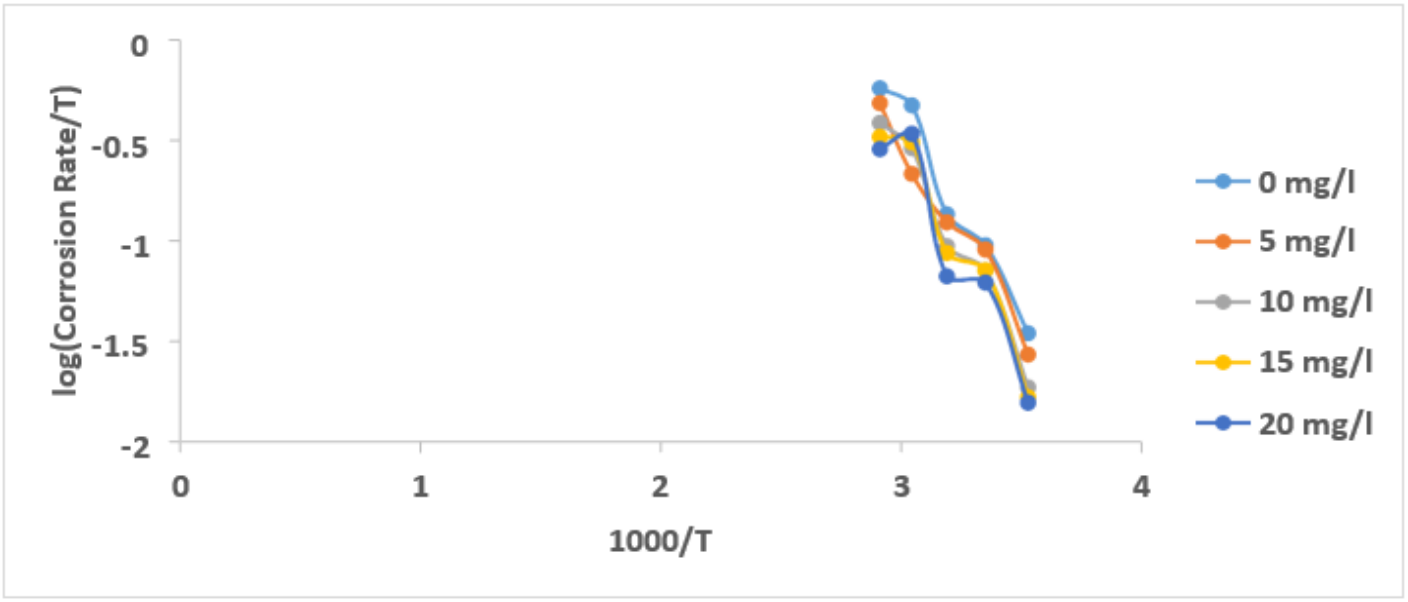

Figure 4.10: log (Corrosion Rate/T) vs. (1000/T) of Musa Paradisiaca DNA inhibitor at varying concentration (0-20 mg/L)

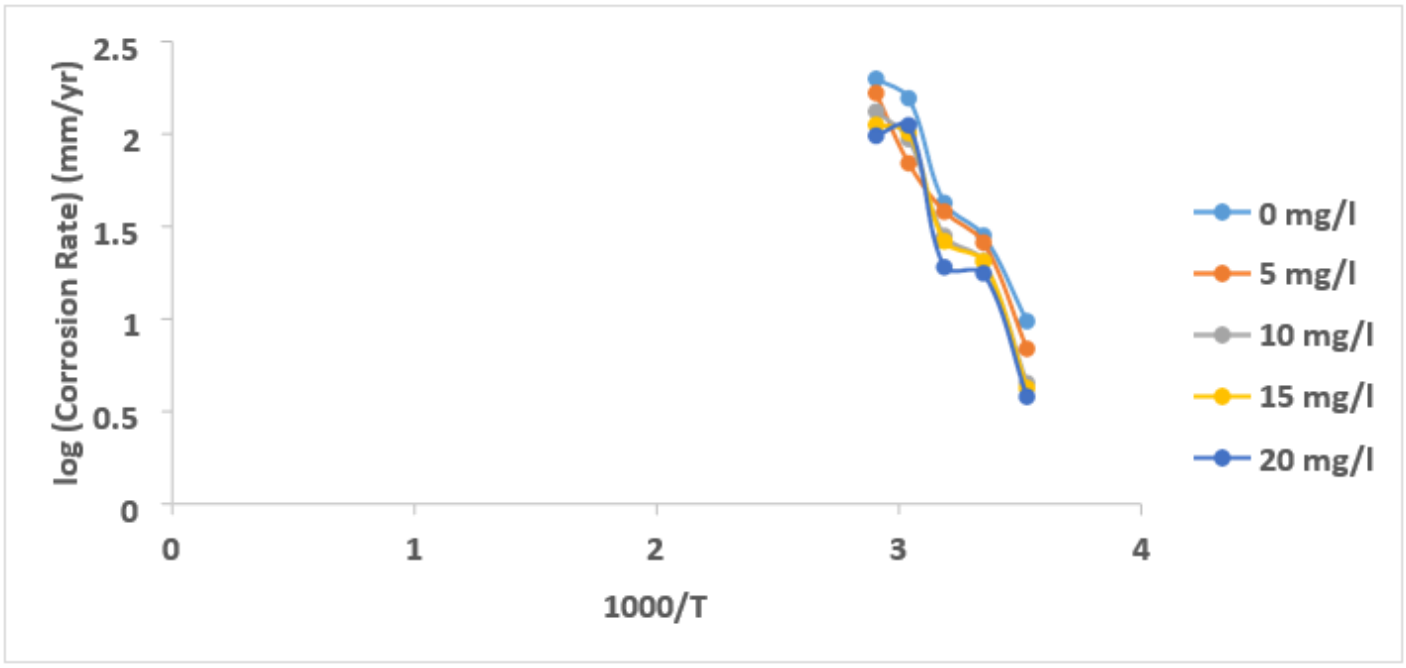

Figure 4.11: log (Corrosion Rate) vs. (1000/T) of Hybrid of Musa acuminate and Musa paradisiaca DNA inhibitor at varying concentration (0-20 mg/L)

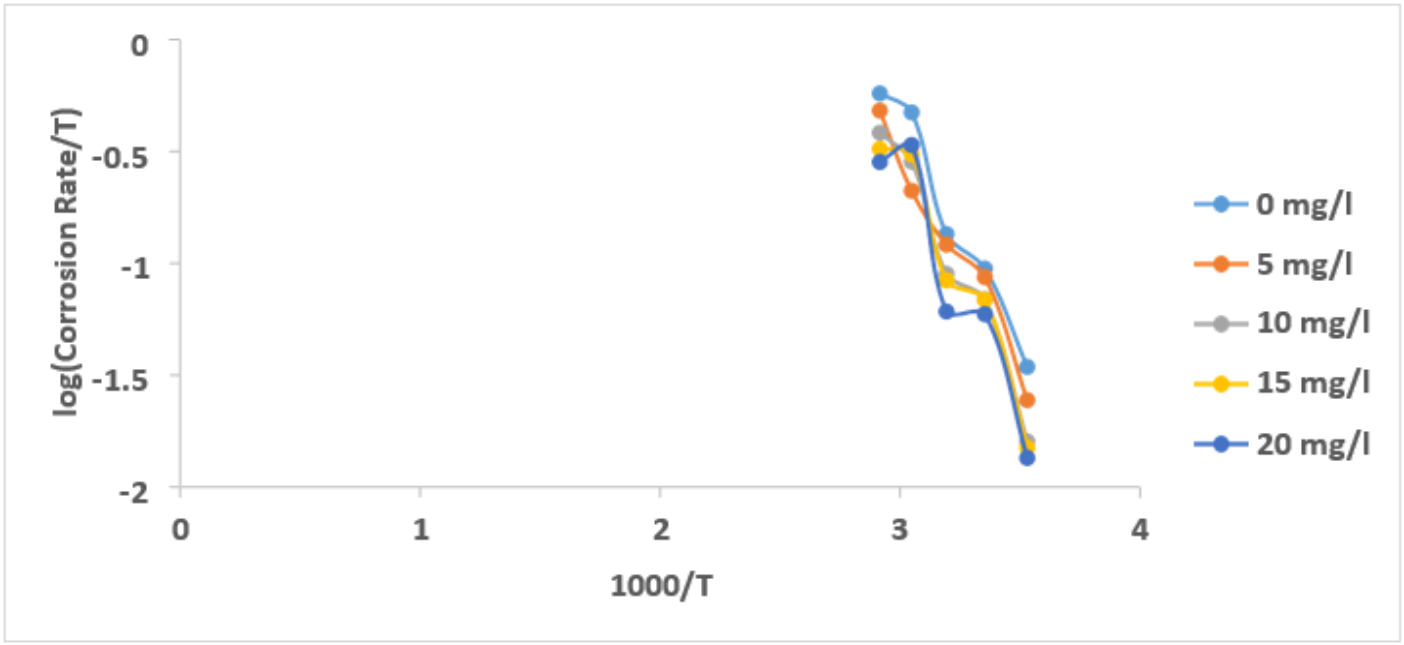

Figure 4.12: log (Corrosion Rate/T) vs. (1000/T) of Hybrid of Musa acuminate and Musa paradisiaca DNA inhibitor at varying concentration (0-20 mg/L)

Adsorption Isotherms

Musa Acuminate

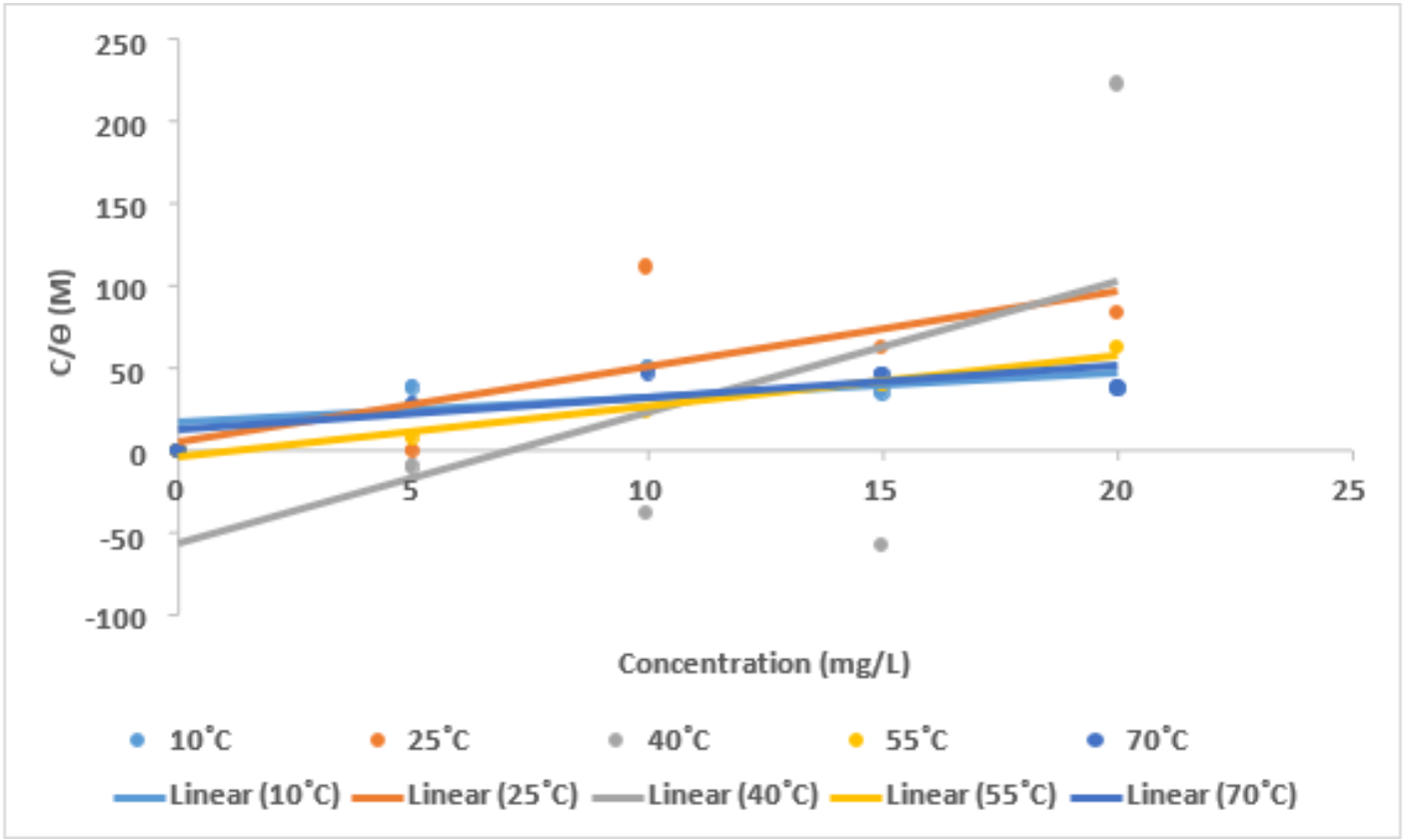

Figure 4.13: $^{c/o}$ vs. Concentration of Musa Acuminate DNA inhibitor at intervals of 15℃ for a temperature range of 10℃-70℃

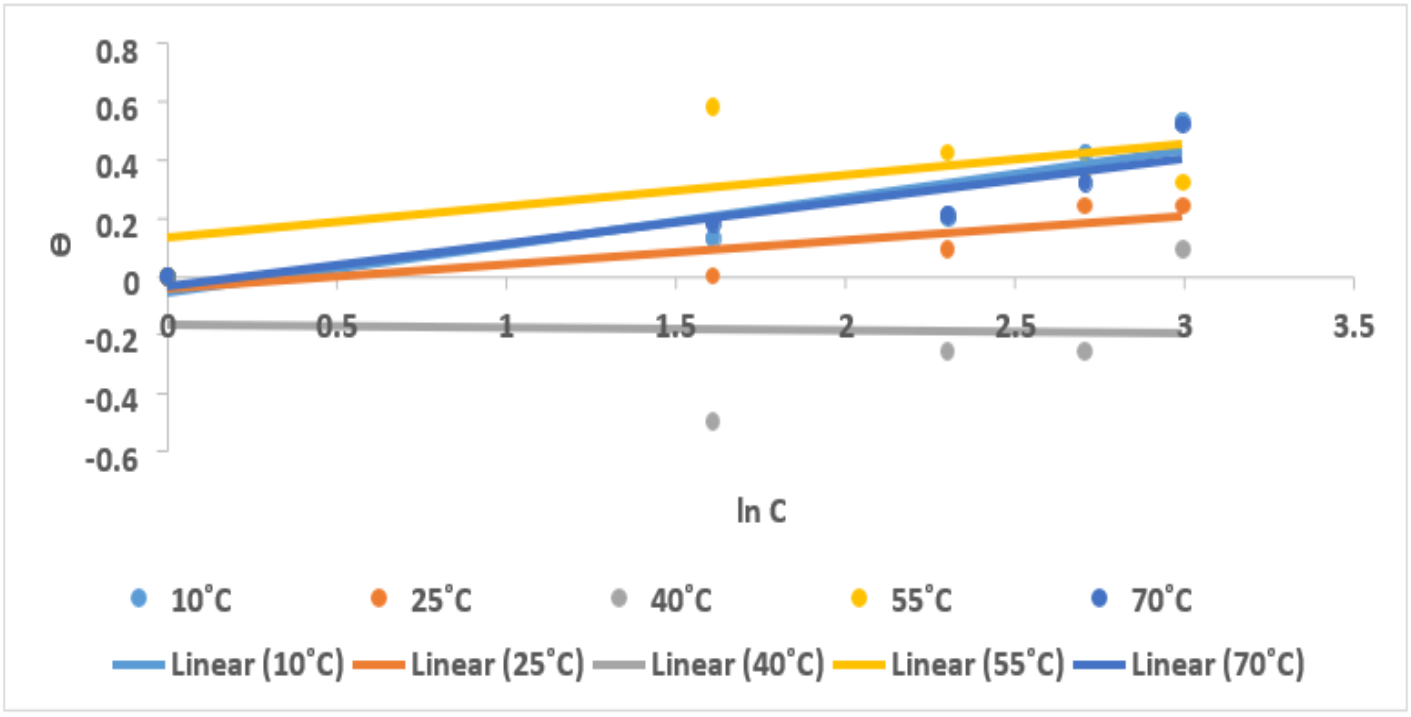

Figure 4.14: Θ vs. ln (Concentration) of Musa Acuminate DNA inhibitor at intervals of 15˚C for a temperature range of 10˚C-70˚C

Hybrid of *Musa Acuminate* and *Musa Paradisiaca*

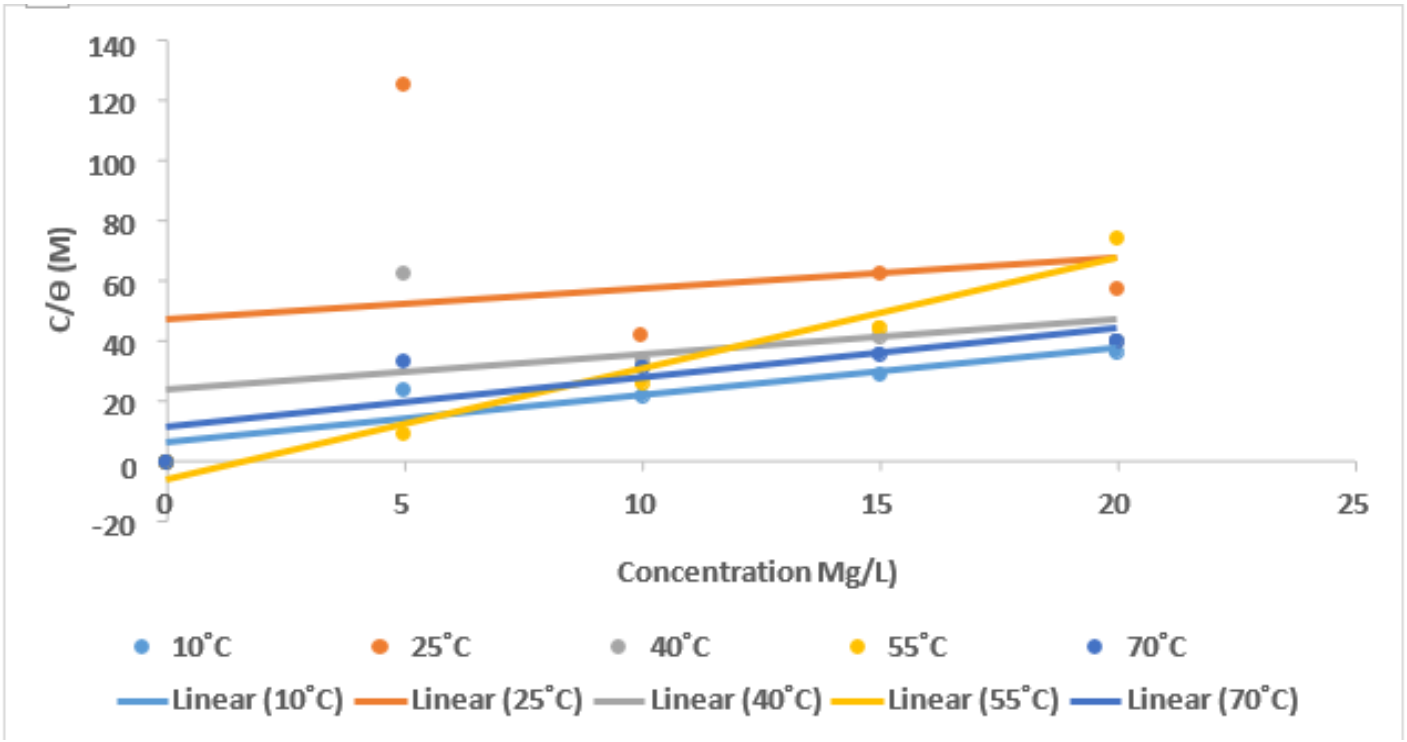

Figure 4.17: $\boldsymbol{C}$ vs. Concentration of hybrid of Musa Acuminate and Musa Paradisiaca DNA inhibitor at intervals of 15˚C for a temperature range of 10˚C-70˚C

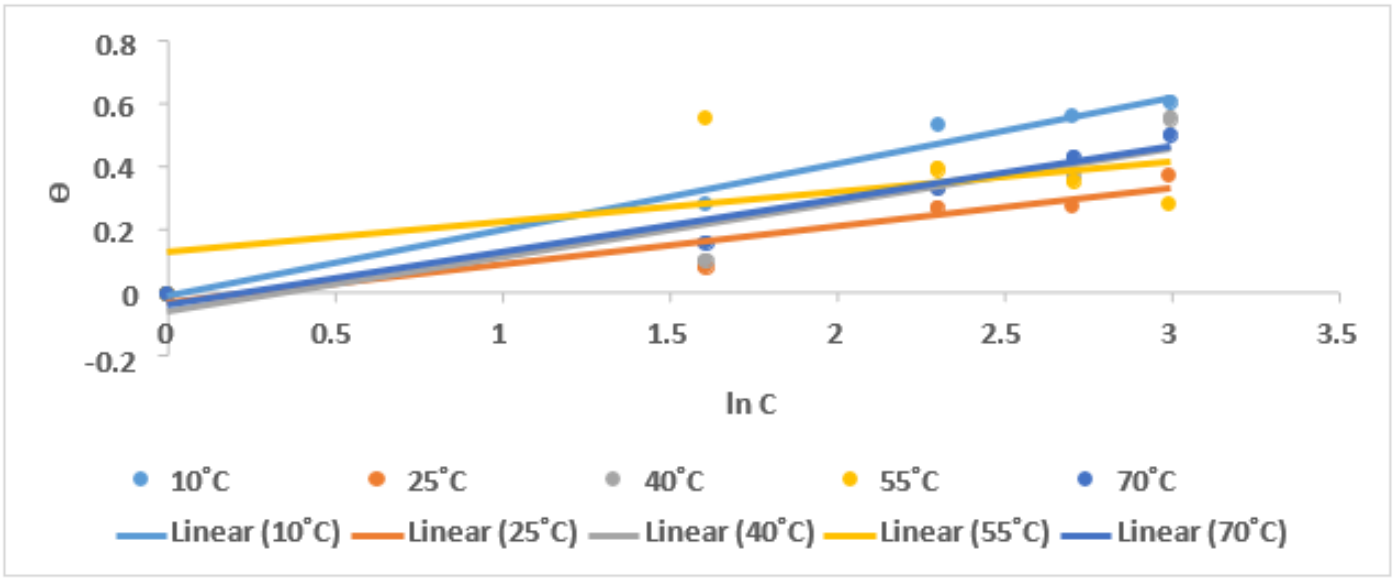

Figure 4.18: Θ vs. ln (Concentration) of hybrid of Musa Acuminate and Musa Paradisiaca DNA inhibitor at intervals of 15˚C for a temperature range of 10˚C-70˚C

Discussion of Results

Gravimetric Analysis

The weight loss technique, also referred to as gravimetric analysis (Section 3.4.1), was employed in this study to evaluate the corrosion behavior of the metal samples. The experimental results presented in Appendices A-1 to A-3, B-1 to B-3, and C-1 to C-3 were analyzed and used to generate the corresponding graphs with the aid of Microsoft Excel 2013. Examination of the corrosion rate plots (Figures 4.1, 4.3, and 4.5) revealed that the corrosion rate increased as temperature increased, whereas it decreased with increasing inhibitor concentration. These findings indicate that the concentration of the inhibitor within the corrosive medium is inversely related to the corrosion rate and directly related to the corrosion inhibition efficiency. The observed trend demonstrates the effectiveness of the hybrid extract of *Musa acuminata* and *Musa paradisiaca* as a corrosion inhibitor for DNA steel, with the highest inhibition efficiency of 60.8697% achieved at a temperature of 10℃ and an inhibitor concentration of 20 mg/L. The results further confirm the significant influence of temperature and concentration on reaction kinetics and corrosion processes, highlighting their importance as key factors in determining the effectiveness of corrosion inhibition systems.

Although most of the samples follow the expected trend, samples using *Musa acuminate* DNA corrosion inhibitor at 40˚C and all samples at 55˚C exhibited anomalous behaviour. At 40˚C, corrosion was being aided with decreasing aid up until the concentration of 20 **mg/L** where corrosion inhibition began. At 55˚C for both samples of DNA and the hybrid, it was observed that the rate of corrosion decreased after 5 **mg/L** before gradually rising up slowly.

Linear Polarization Resistance

Data acquired from the linear polarization experiments (Appendix H-1 and H-2) were used to plot the Tafel polarization graphs (Figure 4.23 – 4.35). From the plots, the inhibitor is shown to be efficient because of the displacements present in the curves. Corrosion inhibition efficiency can be calculated from data extracted from the software NOVA 2.1 that was used to perform the polarization experiments by using the equation below:

$$\textit{Corrosion inhibition efficiency (\%)} = \frac{R_p - R_p^*}{R_p} X\ 100 \qquad \textit{Equation 4.1}$$

Where,

$\boldsymbol{R_p}$ = Polarization resistance with inhibitor

$\boldsymbol{R_p^*}$ = Polarization resistance without inhibitor

From the Tafel polarization plots of Figure 4.29 – 4.43, anodic and cathodic curves indicating that the inhibitors act as a mixed type inhibitor that affects both anodic and cathodic reactions.

Thermodynamic Assessment

Temperature plays a vital role in aiding the understanding of the mechanism of the inhibition in corrosion and as such temperature was varied in this study. In order for thermodynamic parameters of activation such as Enthalpy (ΔH_a^*) Entropy (ΔS_a^*) and Activation Energy (E_a^*) to be calculated, the Arrhenius equation and an alternate form of it, the transition state equation, were used:

$$CR = \frac{k_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \qquad (4.2)$$

$$CR = \frac{k_B T}{h} \exp\left(\frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}\right) \qquad (4.3)$$

C_R = Corrosion Rate
K = A constant that depends on the type of metal and the electrolyte used
E_a^* = Activation energy
h = Planck's constant (6.626176×10^{-34} J s) N = Avogadro's number (6.02252×10^{23})
R = Universal gas constant T = Absolute Temperature
ΔH_a^*= Activation Enthalpy
ΔS_a^* = Activation Entropy

The Arrhenius plot for mild steel corrosion in 1 M HCl for 0-5 mg/L concentrations of *Musa Acuminate*, *Musa Paradisiaca* and Hybrid of *Musa Acuminate* and *Musa Paradisiaca* are presented in Figure 4.7, 4.9 and 4.11

From Appendix E-1, the apparent activation energy (E_a^*) of the uninhibited acid solution is initially greater than that of the inhibited acid solution but is surpassed at 15 mg/l. This trend continues with appendix E-2 and E-3 with difference being that the apparent activation energy of the uninhibited acid solution is surpassed at 10 mg/l. An increase in the thickness of the double layer can be lead to an increase in activation energy (Solomon, 2010). This also indicates a strong inhibitive action of *Musa Acuminate*, *Musa Paradisiaca* and Hybrid of *Musa Acuminate* and *Musa Paradisiaca DNA* inhibitor.

Data from Appendix A-1 to A-3, B-1 to B-3 and C-1 to C-3 was used to obtain Enthalpy (ΔH_a^*) and Entropy (ΔS_a^*) using Equation 4.3 and graphs plotted. From Figures 4.8, 4.10 and 4.12, the slope $\frac{-(\Delta H_a^*)}{R}$ and intercept $\frac{Ln^R}{Nh}$ - $\frac{\Delta S_a^*}{R}$ were obtained and used to calculate (ΔH_a^*) and (ΔS_a^*).

Appendix E-1, E-2 and E-3 show that (ΔH_a^*) has positive values while (ΔS_a^*) values are negative. The positive values of (ΔH_a^*) indicate the reaction is endothermic in nature (i.e. heat/energy is absorbed) while the negative values of (ΔS_a^*) show that the activated complex is not the dissociation step but rather it is the rate determining step.

Adsorption Isotherms

Corrosion inhibition of organic compounds stems from their innate ability to create a protective film by adsorption on the metal surface. Isotherm establishment is important to understand the adsorption mechanism of a corrosion inhibitor. Data from appendix F-1, F-2 and F-3 gotten from the equations below were used to plot Figures 4.13 to 4.18:

Langmuir: $\frac{C}{\theta} = 1 + \frac{C}{K_{ads}}$ *Equation 4.4*

Temkin: exp ($f\Theta$) = KC *Equation 4.5*

Θ = Surface coverage
K = Adsorption-desorption equilibrium constant C = Concentration of the inhibitor
f = Factor of energetic inhomogeneity
The values of surface coverage were gotten using the equation below: = $\frac{C_R - C_{R\,(inh)}}{C_R}$ *Equation 4.6*

Where,

C_R = Corrosion Rate without inhibitor

$C_{R(inh)}$ = Corrosion Rate with inhibitor

From appendix G-1, G-2 and G-3, I is seen that the Temkin adsorption isotherm is closer to unity than the Langmuir adsorption isotherm. The value of K_{ads} can be calculated from the intercept of the Temkin adsorption plot. Standard free energy of adsorption ΔG^*_{ads} is related to K_{ads} by the equation:

$\Delta G^* ads = -RT\ In\ (55.5 K_{ads})$ *Equation 4.7*

Where,

R = Universal Gas Constant ($Jmol^{-1}K^{-1}$)

The value 55.5 is the concentration of water in acid solution (mol/L) T = Absolute temperature (K)

Appendix G-1, G-2 and G-3 show that the adsorption interaction between the surface of the metal and the molecules of the inhibitor is very weak because of the small values of K_{ads}; this can be improved by increasing the concentration of the inhibitor. These results also confirm that physisorption rather than chemisorption is taking place.

The values of $\Delta G°_{ads}$ from the same appendix range from –8501.4724 to –11551.3545 kJ/mol. Usually, adsorption of organic compounds on a metal surface is classified as physisorption when the absolute value of $\Delta G°ads$ is ≤ 20 kJ/mol and chemisorption when the absolute value of $\Delta G°_{ads}$ is ≥ 40 kJ/mol.

Going by the usual classifications, the DNA inhibitor's nature of adsorption is chemisorption. The contradiction between the implications of the values of K_{ads} and those of $\Delta G°_{ads}$ indicates that the adsorption nature of the inhibitors may be mixed.

Where:

R = Universal Gas Constant (J mol^{-1} K^{-1})
The value 55.5 is the concentration of water in acid solution (mol/L)
T = Absolute temperature (K)

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Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) Analysis

The photos in figure 4.19 – 4.28 (a) clearly depict the mild steel samples subjected to 1 M HCl with and without Musa Acuminate and Musa Paradisiaca DNA inhibitors of different doses. After exposure to the corrosive media, some cracks and deformations on the surface of the samples produced by acid corrosion appeared. From the figures it is seen that the surface of the samples are protected by the protective layer generated by adsorption of the inhibitors on the surface of the metal and corrosion does not happen uniformly on the surfaces of the metals (Ojha et al, 2017).

The energy dispersive x-ray spectrometer is an x-ray detectors that collects, measures and analyses the signal in a specific way that identifies elements and their concentrations in a sample as seen in figure 4.20 (b) – 4.28 (b).

Conclusion and Recommendation

Conclusion

From this research I conclude that,

- *Musa paradisiaca* DNA is a better corrosion inhibitor than *Musa acuminate* and the hybrid of *Musa acuminate and Musa paradisiaca* is a better corrosion inhibitor than both of them individually.
- The highest corrosion inhibition efficiency for *Musa acuminate* DNA was 58.1818% at the conditions, 55˚C and 5 **mg/L** while for *Musa paradisiaca* DNA, the highest corrosion inhibition efficiency was 55.0720% at the conditions, 10˚C and 20 **mg/L** and for the hybrid, the highest corrosion inhibition efficiency was 60.8697% at the conditions, 10˚C and 20 **mg/L**.
- The concentration of DNA present in the corrosive medium is inversely proportional to the corrosion rate and directly proportional to the corrosion inhibition efficiency.

Recommendation

I recommend that,

- The metal samples be immersed in the corrosive medium for a longer period of time. This will provide a better understanding of the corrosion rate because the metal sample would have acclimatized to the corrosive medium.
- The concentration of DNA used in the corrosive medium be increased in order to achieve very high corrosion inhibition efficiencies.

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