**INHIBITION EFFECT OF VALINE BASED DIPEPTIDES ON MILD STEEL CORROSION IN HCl**

**BY**

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**REG NO: 2017/242991**

**DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY**

**UNIVERSITY OF NIGERIA, NSUKKA**

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# TITLE PAGE

**INHIBITION EFFECT OF VALINE BASED DIPEPTIDES ON MILD STEEL CORROSION IN HCl**

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

**TO THE DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY,**

**FACULTY OF PHYSICAL SCIENCES,**

**UNIVERSITY OF NIGERIA, NSUKKA**

**BY**

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**CERTIFICATION**

This project is to certify that the work in this report by **Elem, Blessing Adamma** with the registration number **2017/242991** is satisfactory and was conducted under our supervision. This project has been approved for the Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, University of Nigeria, Nsukka being adequate in the scope of the award of the Degree of Bachelor of Science (B.Sc.).

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**ABSTRACT**

The study examined the inhibitive potentials of Valine based dipeptides derivatives on mild steel corrosion in hydrochloric acid (1 M HCl) for a period of six (6) hours. The outcome from gravimetric measurements, reveals that the efficiency of the inhibition process increases with inhibitor concentration increase, but a decline in the inhibition efficiency with temperature increase. The percentage inhibition efficiency of 84 % and 74 % was attained for J11 and J12 respectively at 303K at a concentration 0f 0.00015M. The adsorption of the compounds on mild steel surface was best described by the Freundlich adsorption isotherm model. The enthalpy (ΔH≠) values reveal the adsorption process is exothermic in nature. In addition, the negative and large entropy (ΔS\*) values is associated with the activated complex in the rate determining step representing an association rather than a dissociation hence its disorderliness. More so, the computation of the Gibbs free energy ( indicated the adsorption process was spontaneous.

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**CHAPTER ONE**

**1.0 INTRODUCTION**

Mild steel has found tremendous usage in industries and construction sectors which is largely attributed to its high mechanical properties and cost-effectiveness (Deghani*et al.,* 2019; Mohagheghi and Arefinia, 2018). Oil and gas sector have extensively used mild steel and other iron alloys as storage tank, production equipment’s and conveying petroleum crude and its products (Ouakki*et al.,*2020).

However, despite their outstanding properties, they are easily susceptible to corrosion which occurs via the mild steel electrochemical and/or chemical interaction with the surrounding components (Somers *et al.,* 2018).

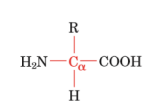
Acid solutions such as hydrochloric acid, tetraoxosulphate (VI) is widely employed in the industries for pickling, industrial acid cleaning, acid de-scaling, and oil well-acidifying processes (Ahamad and Quraishi, 2009). Because of the aggressiveness of the acid during industrial treatment, corrosion of mild steel becomes more pronounced which results in economic loss (Muralisankar*et al*., 2017).The economy of both developed and developing countries is badly affected by the damages caused by corrosion as it results into the loss of around 3.4% of the world GDP (Verma *et al.,* 2017).For instant, due to corrosion China, Japan, Australia and South Africa loss about 2127.8 billion RMB (US $ 310 billion; 3.34% GDP),2.5 trillion Yen (US $ 9.2 billion; 2.0% GDP), US $ 32 billion and R130-billion (US $ 9.6 billion), respectively (Verma *et al.,* 2017).

The use of corrosion inhibitors, amongst the various methods of preventing corrosion, is reported to be the cheapest, most effective and flexible approach of corrosion control. (Liu *et al.,* 2020; Prasanna *et al.,* 2015). An inhibitor is a substance which when added in small concentration to a corrosive solution tends to retards the rate of corrosion (Hamadi *et al.,*2018). This effect is attributed to the adsorption of inhibitor particles on to the metal surface, leading to formation of protective coherent layer (Ibrahim *et al.,* 2017). The effect of many organic and inorganic compounds on the protection of metal in different corrosive media has been investigated (Annejjar*et al.,* 2014, Verma *et al.,* 2018).

Organic compounds that possess heteroatoms (such as N, S, P, O) and multiple bonds, in addition to some functional groups are highly effective corrosion inhibitors. It’s reported also that organic compounds having –OH, –COOH, NH2, etc, are excellent corrosion inhibitors, especially in acidic media (Hamadi *et al.,* 2018).

**1.1 Amino Acids**

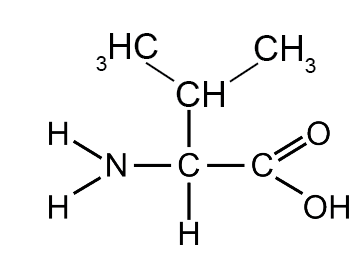
Amino acids are biological molecules which are the building blocks of proteins and many essential biomolecules like neurotransmitters, hormones and nucleic acids. (Wu, 2013). The molecules of amino acids comprise of both amino –NH2 and carboxylic acid (COOH) functional groups (Fig. 1). Amino acids are environmentally friendly compounds, completely soluble in aqueous media and produced with high purity at low cost and nontoxic. They are of uttermost importance to living organism. Moreso, these properties of amino acids justify their useas corrosion inhibitors.



**Fig. 1.1:** Structure of Amino acids

**1.1.2 Valine**

Valine (chemical formula is C5H11NO2) is an alpha-aminocarboxylic acid. Valine amino acid structure includes a central alpha carbon atom that is adjacent to a carboxylic acid moiety (−COOH) and carries three other components: an amino group (−NH2), a hydrogen atom (−H) and an isopropyl −R side chain. The central alpha carbon and the carboxylic acid moiety act as the amino acid backbone, which is similar to all amino acids. The carboxylic acid moiety and the amino group can bind to other amino acids or chemicals to form macromolecules or donate its hydrogen.Due to its hydrophobicity, the R-side chain of valine is non-reactive and repels water. It is, thus, usually located in the interior domain of proteins in the body and is important for the correct folding of protein three-dimensional structure. Valine also plays a role in protein recognition as it is one of the main components of binding/recognition domain of hydrophobic ligands.Valine also belongs to the branched-chain amino acid groups consisting of leucine, isoleucine and valine. They are characteristic of having an aliphatic side-chain. (Ho, 2022)



**Figure 1.2: Structure of Valine**

**1.1.3 Peptides**

A peptide bond is a chemical bond formed between two molecules when the carboxyl group of one molecule reacts with the amino group of the other molecule, releasing a molecule of water (H2O). Peptides can be classified into polypeptides (> 10 amino acids) and oligopeptides (2–9 amino acids) based on the number of amino acids in their composition (Liao *et al.,* 2018). As a class of oligopeptides, small peptides have attracted more attention by researchers in recent yearsdue to its biological properties and they are attributed to have good solubility, permeability and bioavailability (Thompson *et al.,* 2012). Moreso, peptides have been reported to be resourceful pharmacophores ([Day and Greenfield, 2004)](https://www.frontiersin.org/articles/10.3389/fchem.2020.583926/full#B3), antimalarial, antioxidant, and antimicrobial properties (Ezugwu *et al.,* 2020);antiplasmodial ([Amit *et al.,* 2015](https://www.frontiersin.org/articles/10.3389/fchem.2020.583926/full#B2)), antihypertensive agent ([Kitts and Weiler, 2003](https://www.frontiersin.org/articles/10.3389/fchem.2020.583926/full#B13)).

**1.2. CORROSION**

Corrosion is defined as deterioration of metallic materials (metals and their alloys) through reaction with the constituents of the environment. Corrosion is a spontaneous process of metallic materials dissolution that results into huge economic and safety losses. Corrosion can initiate by natural or manmade activities (Verma *et al.,* 2018).

**1.2.1. Forms of corrosion**

The classification of electrochemical corrosion into various forms is somewhat arbitrary. The commonest classification is that, according to Fontana and Green, into eight forms of corrosion:

1. Uniform or general corrosion

2. Galvanic or bimetallic corrosion

3. Crevice corrosion

4. Pitting corrosion

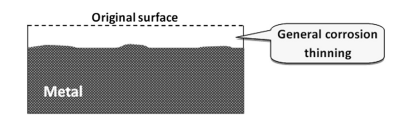
5. Intergranular corrosion

6. Selective leaching or dealloying

7. Impact corrosion (erosion corrosion, impingement corrosion, cavitation corrosion, and fretting corrosion)

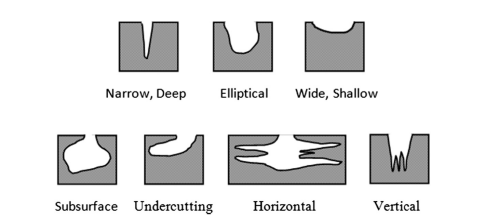
8. Stress corrosion cracking (including corrosion fatigue).

i. **Uniform Corrosion:** This type of corrosion is also called general corrosion. This definition is based on a visual assessment and it is assumed that corrosion damage is characterized by a relatively regular loss of metal from the surface. Even in the presence of shallow open pits, corrosion in many cases may still be called general (Figure 1.3). The general attack takes place when great number of corrosion elements acts simultaneously, the anodic and cathodic areas are constantly changing places and moving along the metal surface. If the anodic and cathodic areas are fixed in permanent places it leads to nonuniform (localized) corrosion. Uniform corrosion can be relatively easily measured as mass loss or an average surface thinning (penetration). Uniform attack is a very widespread form of corrosion.



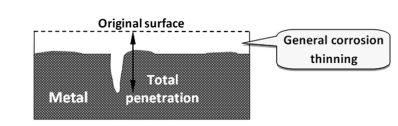
**Fig 1.3: Schematic view of Uniform corrosion**

**ii. Localized Corrosion:** As the name implies, the corrosion attack that occurs at discrete sites of the metal surface may be called localized corrosion.



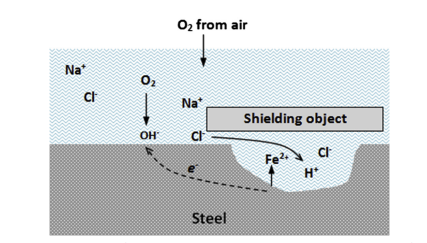
**Fig. 1.4: Pits with variation of cross-sectional shape**

**iii. Pitting:** Pitting corrosion is characterized by the formation of small cavities (pits) in the metal. The pits can vary greatly by depth and shape and be scattered on the surface with a different frequency. Pitting is often difficult to detect and monitor. The resulting cavities may be very small and be covered by corrosion products. Sometimes pitting develops very quickly. On the surface, there can be only one, but a through pit, and this will lead to equipment failure. The main cause of pitting phenomena is the formation of a stable corrosion cell, usually on the surface of a passive metal, as a result of a breakdown or perforation of the protective oxide layer. In this cell, the passive area plays the role of a cathode when the metal bottom in the pit actively dissolves as an anode. Chlorides are the most widespread factor that initiates pitting corrosion and maintain pits in the active state.



**Fig 1.5: Combination of pitting with general corrosion**

**iv. Crevice Attack:** Crevice corrosion is a type of localized corrosion, resulting from functioning of a differential aeration cell. This occurs at narrow spaces (gaps/crevices) formed between metals or between a metal and not-metal material. Usually, the electrolyte in the gap is in a stagnant state and the oxygen concentration here is much lower than its concentration outside the gap. As a result, the metal surface in the gap acts as an anode, and the adjacent outer metal surface plays the role of a cathode. If the crevice attack begins, it progresses very quickly. The typical elements are gaskets of different kinds, lap joints, flanges, bolt holes, rolled pipe ends, threaded joints, rivet heads, seams, etc. The tendency to crevice attack depends on metallurgical factors (alloys composition and metallographic structure). Environmental conditions (pH, oxygen concentration, chloride concentration, temperature) also play a major role in initiation and propagation of crevice corrosion.



**Fig. 1.6: Schematic mechanism of crevice corrosion development.**

**v. Erosion corrosion:** This refers to the repetitive formation (a corrosion process) and destruction (a mechanical process) of the metal's protective surface film, which typically occurs in a moving fluid. Erosion corrosion is used to describe the degradation process of a metallic material, where mechanical wear by solid particles, liquid or the combination of both processes interacts with corrosion caused by dissolution or surface oxidation (Stack *et al.,* 2011). An example is the erosion corrosion of copper water tubes in a hot, high velocity, soft water environment. Also, cavitation is a special form of erosion corrosion. Plastics inserts are used to prevent erosion –corrosion at the inlet to heat-exchanger tubes.

**vi. Galvanic Corrosion**

Galvanic corrosion can also be called bimetallic corrosion. It is a type of corrosion that can occur when two dissimilar metals are in contact in electrolyte. In this case, corrosion is the result of functioning of a dissimilar electrode (galvanic) cell. The main condition for galvanic corrosion occurrence is the potential difference between the coupled metals in a given environment. The geometrical ratio of the metal components involved in the cell can strongly affect the resulting corrosion. The greater the potential difference between the coupled metals and the larger the cathode surface with respect to the anode surface, the more intense the anode corrosion will be. Initially, the evaluation of the tendency (electromotive force) to galvanic corrosion was based on a comparison of thermodynamically calculated standard potentials of anodic reactions for contacting metals. The lower the metal potential, the greater its propensity to anodic reaction. By these criteria, in a metal pair, a metal with a higher potential is a cathode and with a lower potentialan anode. The difference between these standard potentials is the electromotive force of the corrosion process.

#### vii. Intergranular Corrosion

Intergranular corrosion is a form of localized attack in which a thin path is corroded out favorably along the grain boundaries of a metal. It regularly initiates on the surface and proceeds by local cell action in the immediate vicinity of a grain boundary. Although the detailed mechanism of intergranular corrosion varies with each metal system, its physical appearance at the microscopic level is relatively comparable for most systems. The effects of this form of attack on mechanical equipment may be enormously destructive (NACE, 2002).

**viii. Stress corrosion cracking:** Stress corrosion cracking is defined as the growth of cracks due to the simultaneous action of a stress and a reactive environment (Shoji *et al.,* 2011). Stresses may be due to applied loads, residual stresses from the manufacturing process, or a combination of both. Stress corrosion cracking can be prevented by using protective coatings, selecting the proper alloy for a given environment, putting the equipment in service in a stress-free condition, or using appropriate heat treatment.

**1.3. Corrosion Mechanism**

(i) HCl solutions (overall chemical reaction):

(ii) Aqueous solutions (oxidative dissolution):

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

The Equations revealed that upon exposure of iron to the above solutions, it tends to dissolute and loseFe2+ to the electrolyte, which simultaneously produces free electrons that cantravel through the metal. [FeOH]ads and [FeClOH]ads are the adsorbed intermediates, each of which is involved in the rate determining step of Fe dissolution according tomechanisms (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).

On the other hand, 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 1.5



**Figure 1.7: Mechanism of corrosion process**

**1.4. Corrosion inhibitors**

The corrosion inhibitor is a substance that drastically reduces the rate of corrosion of metals when added in small amounts to the respective corrosive medium. The added inhibitor compound controls the rate of corrosion either by decreasing the rate of attack or by decreasing the probability of its occurrence or by doing both. Inhibitors can be broadly grouped into two types namely, interface inhibitors and scavengers. Scavengers reduce the corrosion rate by removing the corrosive agents from the medium. Interface inhibitors reduce the corrosion rate due to film formation on adsorption at the metal/solution interface. They are further grouped as liquid phase and vapor phase inhibitors. Liquid phase inhibitor may be anodic, cathodic or mixed inhibitor depending on their control over anodic, cathodic or both the reactions. The substances that reduce the anodic area by acting on the anodic sites and polarize the anodic reaction are called anodic inhibitors. They displace the corrosion potential towards positive direction and retard anodic reaction, thereby reducing the rate of corrosion. Chromates, molybdates, tungstates, and nitrites are used as anodic inhibitors. The substances that reduce the cathodic area by acting on the cathode sites and polarize the cathodic reaction are called cathodic inhibitors. They displace the corrosion potential towards negative direction and retard cathodic corrosion reaction, thereby reduce corrosion current and suppress the corrosion rate. Most of the organic compounds containing heteroatoms (N, O, S, and P), in an acidic environment function as effective cathodic inhibitors. The substances which retard cathodic, as well as anodic reactions, are called mixed inhibitors. The extent of the possible control over the corrosion of any metal using a suitable inhibitor mainly depends on the nature of metal, corrosive medium (i.e. its concentration, temperature and flow velocity), inhibitor compound (i.e., its chemical structure, physicochemical properties, cost, solubility and stability) and the dissolved impurities present in the medium (Bardal, 2004). Generally, an organic compound as a corrosion inhibitor can control the deterioration of metal in the respective corrosive media by forming a protective film on the metal surface due to its adsorption. An efficient corrosion inhibitor is one which is soluble and stable in the medium, easy and economical for usage, and provides better inhibition activity at a lower additive concentration.

**1.4.1 Classification of Inhibitors**

Inhibitors can be classified in several ways, as follows

1. Passivation inhibitors

2. Organic inhibitors

3. Precipitation inhibitors

4. Vapor phase inhibitors

**1.5. Corrosion Inhibition Mechanism**

Organic inhibitors usually control corrosion in the aggressive acid medium by covering the metal. The inhibitor can adsorb at the metal/solution interphase due to the replacement of water/solvent molecules at the metal surface with its molecules (Equation (11)), the electrostatic attraction between the charged metal surface and its charged species, interaction of unshared electron pairs in its molecule with the metal, interaction of pi-electrons in its molecules with the metal or combination of these

Org(sol) + xH2O(ads) Org(ads) + xH2O(sol) (11)

where Org(sol) and Org(ads) are inhibitor molecules dissolved in solution and inhibitor molecules adsorbed on the metal surface, respectively, and H2O(sol) and H2O(ads) are water molecules and adsorbed water molecules on the surface of the metal respectively. x, the size

ratio, depicts the number of water molecules displaced by one molecule of organic inhibitor (Zadeh *et al.,* 2013). It is very important to know which substance is getting adsorbed on the metal surface and at what potential range the adsorption will occur. It is noteworthy that the size ratio depends on the geometry of the organic inhibitor. In general, an organic inhibitor with planar geometry provides higher surface coverage and thereby behaves better as a corrosion inhibitor (Verma *et al.,* 2015).

The physicochemical properties of the metal, inhibitor and the medium decide the extent of

adsorption possible. Two different types of interactions can be possible during the adsorption process, namely physisorption and chemisorption.

Physisorption usually takes place by the electrostatic forces of attraction between the charged

metal surface and inhibitor species. The metal surface in contact with hydrochloric acid or sulfuric acid solution can acquire negative charges as a result of adsorption of chloride ions or sulfate ions respectively. Organic compounds can get protonated in acid media which resulted in the formation of positively charged protonated inhibitor molecules, [Inh–Hx]xþ. The positively charged protonated inhibitor molecules can be easily attracted towards the negatively charged metal surface leading to its physisorption.

Generally, physisorption is a weaker type of adsorption. The extent of such adsorption decreases with the increase in temperature and physisorption is characterized by low activation energy (Verma *et al.,* 2018).

Chemisorption usually occurs through transfer or sharing of electron pairs between molecules of inhibitor and metal resulting in the formation of the coordinate bond. The lone pair electrons of heteroatoms (such as N, O, S), pi-electrons of double or triple bonds or aromatic rings present in the inhibitor molecule are responsible for the formation of a coordinate bond with the metal. This process is favoured when the metal contains an empty orbital with lower energy. Inhibitor molecule acts as a donor, while metal as an acceptor of electrons. The extent of chemisorption increases with temperature and associated with a higher activation energy (Landolt, 2007).

Organic inhibitors containing heteroatoms (N, S, O, and P), electron releasing groups, multiple bonds, and aromatic rings usually undergo chemisorption. The inhibitor molecules containing heteroatoms can form complexes with the metal ions at the anodic region. These complexes can get adsorbed over the metal forming a film. Thus, inhibitor forms a physical barrier between the metal surface and corrosive environment. This physical barrier prevents the metal from undergoing dissolution and hence controls the corrosion (Shetty, 2019).

**1.6. Corrosion Control**

For control of the corrosion, a selection may be made from among the following measures:

**1. Choice of a different material:**

Application of another more corrosion-resistant material. However, the choice of material is determined not only by the corrosion resistance but also by the mechanical properties and economic considerations.

**2. Design modifications:** By adapting the design, treatment, and construction, the part of the system can be rendered less vulnerable to corrosion.

**3. Application of coatings:** In this way, material can be separated from the environment (metallic, inorganic nonmetallic, or organic coatings to be applied after appropriate pretreatment).

**4. Change of environment:** For example, removal of oxygen and/or raising the pH, dosing of inhibitors in combination with appropriate checks, change/control of temperature, flow velocity, stray currents.

**5.Intervention in the reactions:** The intervention in the reactions most especially with electrochemical methods such as cathodic protection (with sacrificial anodes or with inert anodes with impressed current) and anodic protection (e.g., to stainless steel).

**6. Changing the procedures:** Introduction or modification of procedures for start-up, shutdown, operation, and stoppage; recommendation concerning inspection, corrosion monitoring, maintenance.

**1.7. Adsorption Isotherm**

Adsorption Isotherm is a curve that expresses the variation in the amount of adsorbate (molecules) adsorbed by the given amount of adsorbent (steel surface) with pressure at constant temperature. Different adsorption isotherms have been derived to illustrate the relationship between the surface coverage (θ) and the pressure of the adsorbed molecules (Atkins and Depaula, 2010). In this study two distinct isotherms namely, Langmuir, and Freundlich isotherms shall be apply in the study of corrosion inhibition.

### 1.7.1. Langmuir Adsorption Isotherm

The Langmuir isotherm is one of the simplest and most important isotherms, for both physical and chemical adsorption. This model assumes that adsorption of an adsorbate on the surface of an adsorbent is limited to a monolayer coverage (Hassan *et al.,* 2018). Once a site is occupied, no further adsorption can take place in that site; the intermolecular attractive forces rapidly decrease as distance rises (Saadi *et al*., 2015).

Langmuir isotherm can be represented by the equation 1 (Anadebe *et al*., 2018)

()

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 should be linear with a positive intercept on C/θ axes and of unity slope.

### 1.7.2. Freundlich Adsorption Isotherm

This isotherm is one of the first isotherm introduced to describe the adsorption phenomenon (Watcharenwong and Kaeokan, 2018). This isotherm premised on adsorption characteristics of the heterogeneous surface of an adsorbent, which results to multilayer adsorption (Vadi and Tolou, 2014). The adsorbate occupies the stronger binding sites first, until adsorption energy is exponentially decreased upon the completion of adsorption process (Saadi *et al*., 2015). This isotherm can be used to find the amount of adsorbate adsorbed, which is a function of temperature and pressure. It is also 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)

**1.8. Statement of the problem**

Corrosion process has been of serious concern over the years due to its negative economic and environmental impacts on individuals, industries and nations. It has remained a far-reaching global scientific problem with devastating effects on metallurgical, chemical, food processing, oil industries and even human lives and properties. Although, most inhibitors used to mitigate corrosion have been toxic, and expensive. Thus, the quest for a less toxic, more effective and environmentally noble corrosion inhibitors has been on the increase in recent time. Although, amino acids have found wide usage as corrosion inhibitor, the presence of the acidic carboxylic group in the compound could also induce the corrosion process, therefore, it is necessary to perform the protection of carboxylic functional group. The protection of carboxylic functional group via making a peptide bond could increase the corrosion inhibition activity of amino acid. dipeptide derived from amino acids seems to be more promising towards achieving an eco-friendly and effective prevention of mild steel corrosion.

**1.9. Aim of the Study**

The aim of this study is to investigate the corrosion inhibitive properties of dipeptide derivatives on mild steel in 1 M hydrochloric acid solution through gravimetric method (weight loss).

**1.10. Objectives of Study**

**The objectives of study are:**

**i.** To investigate the corrosion inhibitive properties of the derivatives of dipeptides using different concentrations of the inhibitor solution (ranging from 0.00003 to 0.00015M) on mild steel in 1 M HCl solution at different temperatures of 303 K and 333K for 6 hours through gravimetric analysis (weight loss method).

**ii.** To evaluate the corrosion rate, surface coverage and inhibition efficiency of the Valine derived dipeptide inhibitors base using weight loss method.

**iii.** Evaluate the nature of adsorption using empirical models of Langmuir and Freundlich isotherm.

**iv.** To determine the effect of temperature and thermodynamic properties of the inhibitors on the mild surface.

**1.11 Scope of Study**:

**i.** Weight loss study of mild steel in 1M hydrochloric acid media in t at temperatures of 303 K, and 333K.

**CHAPTER TWO**

**2.0. LITERATURE REVIEW**

**2.1. Review of related literatures**

Liu *et al.,* (2020) reported the corrosion inhibition and adsorption behavior of glutamic acid (Glu), glutamine (Gln), and their cerium complexes: cerium glutamate (Ce(Glu)) and cerium glutamine (Ce(Gln)) on mild steel in 0.5 M HCl solutions at 25 and 55 oC at a concentration range of 25–200 ppm using potentiodynamic polarization (PDP) and electrochemical impedance spectroscopic (EIS) techniques. Their findings shows that inhibition efficiency was dependent on the concentration and temperature of the system. The outcome of their potentiodynamic polarization results suggest that the compounds act as mixed-type inhibitors with dominant cathodic inhibition. The authors reported the mechanism of adsorption to be significantly physisorption. They further documented the adsorption obeyed the Langmuir and El-Awady kinetic adsorption models. The researchers found the extent of inhibition to be Ce-Gln > Gln and Ce-Glu > Glu and showed that the complexation of amino acid to rare-earth metal (Ce) improves the corrosion inhibition ability of the amino acids. The computation simulation of the adsorption process they carried out, shows that the carbonyl-oxygen atoms of the inhibitors are the main adsorption site on Glu, Gln and the complexes for bonding with the Fe surface and the preferable orientation of the molecules is the parallel/flat (bi-coordinated) adsorption configuration.

Zhu *et al.,* (2020) documented the inhibitive effect and inhibition mechanism of L-lysine derivatives, namely α-*N*benzyloxycarbonyl- l-lysine (α-NL) and ε-*N*-benzyloxycarbonyl-l-lysine (ε-NL), on the corrosion of carbon steel in 0.5 M H2SO4 solution. They investigated by employing the methods of electrochemical, weight loss, scanning electron microscope, atomic force microscope, infrared attenuated reflectance spectroscopy and quantum chemical calculation. Their results showed that α-NL and ε-NL as moderate cathodic inhibitors mainly inhibited the cathodic reaction of carbon steel in 0.5 M H2SO4 solution, and that the terminal substituted ε-NL showed better corrosion inhibition than the α-*N*-benzyloxycarbonyl protected α-NL. Their outcome revealed inhibition efficiencies increased with the increase in inhibitor concentration, and the inhibition efficiency of α-NL and ε-NL with concentration of 10 mmol reached 53.4% and 61.5%, respectively, but decreased with rising temperature. They further revealed adsorption of investigated inhibitors on the surface of carbon steel obeyed the modified Langmuir isotherm and El-Awady thermodynamic-kinetic model, Moreover, Quantum chemical calculation they carried out gave further insight into the inhibition mechanism of α-NL and ε-NL.

Goni*et al.,* (2019) study the corrosion inhibition of synthesize biogenic amino acid methionine-based corrosion inhibitors of mild steel in acidic media. They evaluated the inhibitive behaviour using gravimetric mass loss, potentiodynamic polarization, and electrochemical impedance spectroscopy techniques and their study revealed all the techniques agreed well with each other. Their results shows that corrosion efficiencies increase with increasing concentration of the polymers. Also, they reported an optimum concentration of 175 μM yielded the maximum inhibition efficiency of the synthesized copolymer compounds at 92%, 97%, and 95%, respectively. The synthesized polymer compounds acted as mixed-type inhibitors. The adsorption was reported to be chemisorption and physisorption which obeyed Langmuir, Temkin, and Freundlich adsorptionisotherms. Their morphological studies indicatedthat the adsorbed polymers formed a thin film on the metal surface and prevented further corrosive attack.

Phenylalanine (P1) and Aspartic acid (P2) have been studied by Oubaaqa*et al.,* (2019) for inhibiting mild steel (MS) corrosion in molar hydrochloric acid solution. They evaluated the anti-corrosion activity using electrochemical impedance spectroscopy (EIS), potentio-dynamic polarization (PDP), Density Functional Theory (DFT), Monte-Carlo Simulation (MCS) and Molecular Dynamic Simulation (MDS). Their outcome shows that the inhibition efficiency of the two amino acids (P1 and P2) increased by the increase in their concentration and reached an optimal value of 87% and 89% for P1 and P2 respectively. Their adsorption mechanism was consistent with the isotherm Langmuir. The result they obtained from polarization measurements indicated that the two compounds acted as mixed inhibitors. Also, the result from the UV–visible they carried out shows that the addition of the two compounds decreases the dissolution of ferric ions in the corrosive solutions. Moreso, the morphology studies they investigated using Scanning Electron Microscopy (SEM) shows that both inhibitors were well adsorbed on the MS surface. They employed computational approaches of the metal-inhibitor interaction type using DFT, MCS and MDS which were all in agreement.

Srivastava *et al.,* (2017) synthesized three novel amino acids based corrosion inhibitors namely 2-(3-(carboxymethyl)-1H-imidazol-3-ium-1-yl)acetate (AIZ-1), 2-(3-(1-carboxyethyl)-1H-imidazol-3-ium-1-yl)propanoate (AIZ-2) and 2-(3-(1-carboxy-2-phenylethyl)-1H-imidazol-3-ium-1-yl)-3-phenylpropanoate (AIZ-3) and investigated the corrosion inhibition performance by electrochemical impedance (EIS) and potentiodynamic polarization (PDP) methods. They revealed that AIZ-3 showed the maximum inhibition efficiency (IE) of 96.08% at a concentration as low as 0.55 mM (200 ppm) among the studied inhibitors. The results from their potentiodynamic study revealed that AIZ-1 acted as cathodic inhibitor while AIZ-2 and AIZ-3 acted as mixed type inhibitors. They reported that adsorption of AIZs on the mild steel surface followed the Langmuir adsorption isotherm and that the result of scanningelectron microscope (SEM), atomic force microscope (AFM) and energy-dispersive X-ray spectroscopy (EDX)supported the formation of inhibitors film on the metal surface. They documented that the results of the theoretical investigation and experimental studies well complimented each other.

Migahed*et al.,* (2016) synthesized polyaspartic acid (PASP) and evaluated the performance as corrosion inhibitor employing potentiodynamic polarization and EIS techniques. Their outcome shows increase in inhibition efficiency with concentration increase. Also, their studies using SEM and EDX revealed the inhibitor formed a good protective layer that isolated the surface from the aggressive environment. the surface morphology of carbon steel alloy in the absence and presence of the inhibitor molecules. They reported the compound exhibited maximum corrosion inhibition efficiency for GLYPASP adduct was 83.8 % at 250 ppm, while its scale inhibition efficiency reaches 90.2% at 125 ppm dosage.

Hu *et al.,* (2016) investigated the anti-corrosive potential of a novel amino acid corrosion inhibitor derived from cytosine-L-alanine (CLAD) against X80 steel surface in HCl solution. They employed the techniques of weight loss measurement, polarization curves, electrochemical impedance spectroscopy (EIS) and SEM measurement to evaluate its inhibition performance of CLAD. Their results showed that the corrosion inhibition efficiency of CLAD reached 91%, which was 78% higher than that of L-alanine. They further revealed that the impeded electron transfer, reduced metal dissolution and inhibited corrosion progress of metal surface were derived from the compact and uniform protective film. Their study revealed adsorption of CLAD obeyed the Langmuir adsorption isotherm, and adsorption behaviours was both physical adsorption and chemical adsorption. Moreso, the outcome of their computational study reveals that the high corrosion inhibition efficiency of CLAD was associated with its strong adsorption as a barrier film on the steel surface. Their results further demonstrated that the KI mixed CLAD was an alternative strategy to enhance the inhibition efficiency and reduce the cost.

Amin and Ibrahim (2011) synthesized glycine derivative (GlyD1), 2-(4-(dimethylamino)benzylamino)acetic acid hydrochloride and employed it to control mild steel corrosion in 4.0 M H2SO4 solutions at different temperatures(278–338 K). They evaluated the efficiency of the inhibitor using Tafel extrapolation, linear polarization resistance (LPR) and impedance methods. Their findings were compared with an available glycine derivative (GlyD2) and glycine (Gly). They revealed that the Tafel polarization measurements suggests the inhibitors function as mixed-type compounds. Also, they reported the inhibition efficiency increased with increase in inhibitor concentration and decreased with temperature, suggesting the occurrence of physical adsorption.

Furthermore, their results proved the adsorptive behaviour of the three inhibitors followed Temkin-type isotherm. Their comparative analysis shows the inhibition performance of GlyD1 was much better than those of GlyD2 and Gly itself. All their findings from varying methods employed were in good agreement.

**CHAPTER THREE**

**EXPERIMENTALS**

### 3.1. Materials and methods

### 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, bowl, masking tape.

**3.1.2. Reagents**

37 % HCl (Hydrochloric acid), acetone, dichloromethane, 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.

**Structure of the……. Dipeptide(James *et al.,* 2020)**

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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/cm3Percentage purity = 37 %  Relative molar mass = 36.45 g/mol  (3.2)  Thus, the concentration of the stock solution which the 1 M HCl was prepared from is 11.88M. The volume of the stock solution needed to prepare the 1 M HCl was then obtained 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 usingdistilled water in a 1 litre volumetric flask using distilled water to obtain the 1 M HCl solution.  **3.2.1. Preparation of 1.0 X 10-4 M Inhibitor Stock Solution**  Stock concentration of the inhibitor = 1.0 x 10-4 M  Molar mass of J11 inhibitor = 601 g  1M of the J11 inhibitor = 601 g  1.0 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 0.0601 g from the calculation below:  Hence, 0.0601 g of the inhibitor was dissolved in 1litre of distilled water to obtain the inhibitor stock solution.  Molar mass of J12 inhibitor = 557 g  1M of the J12 inhibitor = 557 g  1.0 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 0.0601 g from the calculation below:  Hence, 0.0557 g of the inhibitor was dissolved in 1litre 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 (0.23 g/L). So, the volumes needed to obtain the various concentrations of the inhibitor stock solution were calculated using equation 6b.  Where; C1 = Concentration of the inhibitor stock solution = 1.0 x 10-4 M  C2 = the required concentrations (g/L) of the inhibitor stock solution to be used (0.0002, 0.0004, 0.0006, 0.0008 and 0.0001)  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  After the calculations, the volume of the inhibitor stock solution needed to obtain the various concentrations (M) of the stock solution (0.00003, 0.00006, 0.0000, 0.00012 and 0.00015) were 10 ml, 20 ml, 30 ml, 40 ml and 50 ml respectively.   |  | | --- | | **3.3. 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 and the elemental composition of the mild steel which was carried out at the African University of Science and Technology, Abuja. 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.  **3.4. 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 1M HCl in the absence of the inhibitor (blank solution) and presence of inhibitor having different concentrations (M) (0.00003, 0.00006, 0.0000, 0.00012 and 0.00015) for exposure period of Six (6) hours in the heated water bath at temperatures of 303 K, and 333 K. After the exposure time was attained, 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 and afterwards reweighed to determine the weight loss of the mild steel coupons. The measurement was repeated in triplicates and the average value was documented. 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). 3.5. Adsorption isotherm The nature of adsorption of the Schiff base inhibitors on the mild steel surface is important in understanding the mechanism of corrosion inhibition. As the corrosion rate is sufficiently reduced, the adsorption of an inhibitor on the mild steel surface tends to reach a quasi-equilibrium state (Ghosal and Guptal, 2017). In order to define the nature and the strength of adsorption, the extracted data by 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) were computed from the intercept of the plots 3.6 Thermodynamic and Activation Parameters Thermodynamics of corrosion process was investigated. Corrosion rate (CR) varies with temperature in conformity with the Arrhenius equation (Lukman *et al.,* 2021).  The value of activation energy (Ea) for the corrosion process was calculated using the Arrhenius equation expressed in equation 3.11 (Lukman *et al.,* 2021).  Where CR = Corrosion Rate, A = frequency factor, R = universal gas constant (8.314 JK-1mol-1); T = temperature (K), Ea = apparent activation energy. The values of the standard free energy (ΔGads) of the adsorption process will be 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.  Furthermore, values of enthalpy of activation, (ΔH∗corr) and entropy of activation, (ΔS∗corr) for the process of corrosion was computed 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**  **Table 4.1:** Weight loss result of corrosion of mild steel in 1 M HCl solution without and with varying concentrations of the inhibitors at varying temperatures of 303 K and 323 K   |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | | Inhibitor | 303 K | | | | |  | 323 K | | | | | C (M) | ∆w (g) | CR | (θ) | (%) |  | ∆w (g) | CR | (θ) | (%) | | J 11 | Blank | 0.110 | 0.0031 | **--** |  |  | 0.026 | 0.00070 |  |  | | 3×10-5 | 0.100 | 0.0028 | 0.091 | 9.1 |  | 0.023 | 0.00063 | 0.1154 | 11.5 | | 6×10-5 | 0.090 | 0.0025 | 0.182 | 18.2 |  | 0.022 | 0.00061 | 0.154 | 15.4 | | 9×10-5 | 0.065 | 0.0018 | 0.409 | 40.9 |  | 0.022 | 0.00061 | 0.1538 | 15.4 | | 12×10-5 | 0.060 | 0.0017 | 0.455 | 45.5 |  | 0.016 | 0.00044 | 0.3846 | 38.5 | | 15×10-5 | 0.010 | 0.0003 | 0.909 | 90.9 |  | 0.015 | 0.00042 | 0.4230 | 42.3 | |  |  |  |  |  |  |  |  |  |  |  | | J12 | Blank | 0.122 | 0.0034 | -- |  |  | 0.026 | 0.00072 |  |  | | 3×10-5 | 0.110 | 0.0031 | 0.098 | 9.8 |  | 0.023 | 0.00064 | 0.1154 | 11.5 | | 6×10-5 | 0.061 | 0.0017 | 0.500 | 50.0 |  | 0.019 | 0.00053 | 0.2692 | 26.9 | | 9×10-5 | 0.060 | 0.0017 | 0.508 | 50.8 |  | 0.017 | 0.00047 | 0.3461 | 34.6 | | 12×10-5 | 0.041 | 0.0011 | 0.664 | 66.4 |  | 0.017 | 0.00047 | 0.3461 | 34.6 | | 15×10-5 | 0.010 | 0.0003 | 0.918 | 91.8 |  | 0.014 | 0.00039 | 0.4615 | 46.2 |   **Figure 4.1a**: A plot of inhibition efficiency against concentration at 303K and 333K for J11  **Figure 4.1b**: A plot of inhibition efficiency against concentration at 303K and 333K for J12  **4.1.2 Weight Loss Examination**  The evaluation of inhibition by weight loss technique was carried out for mild steel samples prior and after 6 h immersion in 1 M HCl having varying concentrations of the Valine based derived inhibitors (J11 and J12) at different temperatures (303 K, and 333 K). The data obtained via computation as presented in Table 4.1 and Figures 4.1a-b indicates the increase in the inhibitor’s concentration from 3×10-5 to 15 ×10-5 M resulted to decrease in the weight loss of the mild steel with a corresponding decrease in rate of corrosion from 0.0031 to 0.0003 g cm2 h−1. Also, the Table 4.1 and Figures4.1a-b shows an increment in the inhibition efficiency up to 90.9 % and 91.8 % for J11 and J12 respectively at 303 K (Fig. 4.3). This could be due to strong adherence of the inhibitor molecules on the surface of the mild steel (Naciri *et al.,* 2020). More so, there exist a decline in the inhibition efficiency with increasing temperature from 303K to 333K which could be due to decrease in the adsorption bond of the inhibitors as a result of increasing kinetic of the inhibitor molecules which leads to its desorption from the surface of the mild steel (Chaouiki *et al.,* 2021).Moreover, rapid etching, molecular decomposition and molecular rearrangements may also decrease the inhibition efficiency of inhibitor molecules at elevated temperature (Verma *et al.,* 2018).  **4.1.3 ADSORPTION ISOTHERM**  The experimental results were fitted to Langmuir and Freundlich adsorption isotherm models to determine the nature of adsorption strength of the inhibitor on the mild steel surface. An isotherm plot of Langmuir adsorption model (Fig. 4.2aand b) involves *C/* θ *vs*. *C*, The Freundlich adsorption isotherm plotted involves Log θ vs. Log C (Fig. 4.3aand b). In this study, the adsorption process obeyed the Freundlich adsorption isotherm due to the closeness of the regression coefficient to 1. The implication of this outcome typified that the adsorbed inhibitor molecules on the surface occurs via multilayer coverage, hence, species interacted with each other.The computed *K*adsvalues shown in Table 4.2 were obtained from the reciprocal of intercept of the Langmuir isotherm. The estimated Gibbs free energy of adsorption are presented in Table 4.2. The negative value of stipulates the spontaneous nature of the adsorption process. Furthermore, literature survey reveals that value of are frequentlyused to describe the nature of adsorption. In general, adsorptionof an inhibitor with large negative value of (-40 kJmol-1or more negative) is related with transfer of charge between inhibitor and metal (chemisorption), while one with lower negative value of (-20 kJmol-1 or less negative) could involve electrostatic interaction (physisorption) between charged inhibitor molecules and metallic surface (Pandey *et al.,* 2017). However, in this work, the values of which falls within -20 to -40 kJ/mol (Table 4.2) clearly posits that the mechanisms involved in the adsorption of the inhibitor molecules on the surface of the mild steel could be both physisorption and chemisorption.  **4.2a Langmuir Adsorption Isotherm**  **Figure 4.2a:** Langmuir adsorption plot for mild steel in 1 M HCl containing various concentrations of inhibitor J11 at temperatures of 303K, and 333K for 6 hours  **Figure 4.2b:** Langmuir adsorption plot for mild steel in 1 M HCl containing various concentrations of inhibitor J12 at temperatures of 303K, and 333K for 6 hours.  **4.3a. Freundlich Adsorption Isotherm**  **Figure 4.3a:** Freundlich adsorption plots for mild steel in 1 M HCl containing varying concentrations of J11inhibitor at temperatures of 303K, and 333K for 6 hours  **Figure 4.3b:** Freundlich adsorption plots for mild steel in 1 M HCl containing various concentrations of J12 inhibitor at temperatures of 303K, and 333K for 6 hours  **4.4. THERMODYNAMIC PARAMETERS**  In order to better understand the kinetics involved as a result of the influence of temperature on the rate of corrosion of the mild steel in the acidic medium during the corrosion process, the Arrhenius equation was employed. The activation energy (Ea) in (kJ/mol) was estimated from the slopes of the Arrhenius plots (Fig. 4.4a and b). The estimated activation energies for all the inhibited acidic solutions were found to be greater in comparison to the blank solution (Table 4.3). The highest Ea value was obtained at the highest inhibited concentration of 15 x 10-5M for both inhibitors with J12 (94.09 kJ/mol) higher when compared to J11 (11.34 kJ/mol). 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 (Damej *et al.,* 2021).  The values of enthalpy of activation (ΔH≠) computed from the slope of the transition plot (Fig. 4.5a and b) as presented in Table 4.3 reveals the values are all negative in both the blank solution and the inhibited concentrated solutions with exception to the highest concentration which was positive. This suggests an exothermic process occurs for the uninhibited and other inhibited concentration with exception to the maximum concentration of 15 x 10-5 M which was endothermic. Similar trend occurs for the two inhibitors. Furthermore, under the same conditions, the entropy of activation (ΔS≠) values computed are all negative, this posit a degree of disorderliness in the corrosion process which might be due to the association of the available inhibitor molecules rather than its dissociation. Literature have documented similar trend in previous studies (Gupta *et al.,* 2016; Haque *et al.,* 2020).  **Table 4.2:** Values of the Freundlich adsorption constants and the adsorption energies corresponding to the J11 and J12 compounds   |  |  |  |  |  | | --- | --- | --- | --- | --- | | Inhibitor | 303K | | 333K | | | Kads(103) | -ΔGads(kJmol−1) | Kads | -ΔGads(kJmol−1) | | J11 | 2.50 | 29.83 | 3.33 | 30.55 | |  |  |  |  |  | | J12 | 3.33 | 30.55 | 5.00 | 34.70 |      |  |  |  |  |  | | --- | --- | --- | --- | --- | |  |  |  |  |  | | Inhibitor | Concentration  (M) | Ea(kJ/mol) | -ΔH≠(J/mol) | -ΔS≠ (J/mol K) | | J11 | Blank | -40.33 | -72.97 | 197.94 | | 3 ×10-5 | -41.10 | -74.47 | 197.95 | | 6 ×10-5 | -39.39 | -68.48 | 197.93 | | 9 ×10-5 | -30.29 | -38.45 | 197.84 | | 12×10-5 | -36.96 | -57.81 | 197.91 | | 15×10-5 | 11.34 | 102.13 | 197.43 | |  |  |  |  |  | |  | Blank | 43.23 | 82.53 | 197.97 | |  | 3 ×10-5 | 43.76 | 83.27 | 197.97 | | J12 | 6 ×10-5 | 32.62 | 44.90 | 197.86 | |  | 9 ×10-5 | 35.26 | 52.71 | 197.89 | |  | 12×10-5 | 24.62 | 17.57 | 197.78 | |  | 15×10-5 | 94.09 | 96.33 | 197.45 |   **Table 4.3:** Apparent activation energy (Ea),ΔH≠, ΔS\* of J 11 and J12 at different concentration obtained from Arrhenius and Transition State Equations  **Figure 4.4a: Arrhenius plot for J11**  **Figure 4.4b: Arrhenius plot for J12**  **Figure 4.5a: Transition plot of J11**  **Figure 4.5b: Transition plot of J12** |
| **CHAPTER FIVE**  **5.0 CONCLUSION**  Valine based dipeptide-sulphonamide conjugates were employed in this study to ascertain their inhibitive performance against the degradation of mild steel in aggressive solution of 1 M HCl for a period of six (6) hours. The results obtained from gravimetric measurements, reveals that the efficiency of the inhibition process increases with inhibitor concentration increase, whereas, there exist a decline in the inhibition efficiency with temperature increase. The percentage inhibition efficiency of 84 % and 74 % was attained for J4 and J26 respectively at 303 K. However, a percentage inhibition of 64 % and 61 % was obtained for J11 and J12 at 333K The inhibition performance of the inhibitor compounds is largely attributed to the heteroatoms present in the compound. The adsorption of the compounds on mild steel surface was found to agree with Freundlich adsorption isotherm model. The enthalpy (ΔH≠) values reveal the adsorption process is exothermic in nature. In addition, the negative and large entropy (ΔS\*) values is associated with the activated complex in the rate determining step representing an association rather than a dissociation hence its disorderliness. More so, the computation of the Gibbs free energy ( indicated the adsorption process was spontaneous.  **References** |
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