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CORROSION INHIBITION OF MILD STEEL AT ELEVATED TEMPERATURE IN

HIGHLY ACIDIC BRINES USING A GREEN CORROSION INHIBITOR

BY

MUHSEN A.M. EL HADDAD

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COMMITTEE PAGE

The members of the Committee approve the Thesis of Muhsen A.M. El Haddad
defended on 25/05/2017.

Dr. Aboubakr Abdullah
Thesis/Dissertation Supervisor

Dr. Ahmed Elzatahry
Committee Member

Dr. Khaled Youssef
Committee Member

Dr. Abdul Shakoor
Committee Member

Dr. Mohammad Hassan
Committee Member

Approved:

Rashid Al-Kuwari, Dean, College of Arts and Sciences

ABSTRACT

MUHSEN A.M. EL HADDAD., Masters : June : [2017], Material Science and Technology

Title: Corrosion Inhibition Of Mild Steel At Elevated Temperature In Highly Acidic Brines
Using A Green Corrosion Inhibitor

Supervisor of Thesis: Dr. Aboubakr Abdullah.

Corrosion Inhibition of mild steel in 5 M Hydrochloric acid solution at different temperatures was investigated using a new green corrosion inhibitor (lauramidopropylamine oxide). Various electrochemical techniques and surface characterization techniques including, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and atomic force microscopy (AFM), were utilized in this study. The kinetics of corrosion and thermodynamic parameters were calculated and discussed.

The results have shown that corrosion rate of mild steel was significantly reduced with a maximum inhibition efficiency of more than 94% at a concentration of $370 \mu\text{mol L}^{-1}$ of the inhibitor. The adsorption of lauramidopropylamine oxide corrosion inhibitor on the metallic substrate obeys Langmuir's adsorption isotherm. Examination of polarization curves indicated that the inhibitor is of a mixed type since it inhibits both anodic as well as cathodic reaction. Additionally, the adsorption of the inhibitor on the surface was found to be chemisorption.

Analyses of surface topography of the mild steel revealed an appreciable decrease in the surface roughness when the inhibitor was used compared to the uninhibited acidic solution.

The energy dispersive x-ray (EDX) and x-ray photoelectron spectroscopy (XPS) revealed the presence of nitrogen on the mild steel, which confirmed the adsorption of the corrosion inhibitor molecules on the surface.

This work provides a promising eco solution for mitigating corrosion of mild steel in an aggressive acidic environment. It will also contribute to a significant cost saving, not only in Qatar but worldwide too.

DEDICATION

The thesis is dedicated to my wife and children for their support and encouragement

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Chapter 1

1. Introduction

One of the most important mineral acids utilized widely in many industrial applications including well acidizing, water treatment, chemical cleaning, and acid pickling is hydrochloric acid (HCl). From the corrosion and material of construction stand point, HCl poses greater threat to most of engineering materials when compared to other acids [1]. This is mainly attributed to the inherent corrosivity of the acid against common metals and alloys. Selecting the most cost effective material to handle the HCl acid by itself requires extreme care and detailed engineering. The presence of certain impurities like ferric or cupric salts and chlorine in the acid would dramatically increases the corrosion rate. In addition, the increased level of aeration will amplify the oxidizing power of the solution leading to an accelerated damage of many metals and alloys [4].

In oil and gas industry, the exposure of materials to acidic environments is more common and frequent than to neutral or alkaline. This triggers the requirement for exploring alternative options and efficient techniques to mitigate and control corrosivity of these streams. Iron and its alloys constitute large fraction of the exposed metals to acidic media, which has led to increase the interest for inhibition studies and highlighted the importance for more robust inhibition practices.

Corrosion Inhibitors, utilized widely to mitigate corrosion risks, are considered the most cost effective approach for corrosion control. Fresh cooling water (Once-through or recirculation), boiler water treatment, acid gas sweetening units, refinery hydroprocessing units, well acidizing,

acid pickling are some of numerous application fields for corrosion inhibitors. It is worthy to mention that the effectiveness of corrosion inhibition is negatively impacted and diminished by the increased stream corrosivity, temperature and acidic concentration.

Unfortunately, some of the highly efficient corrosion inhibitors that were used previously to mitigate corrosion threat such as chromate and arsenic are highly toxic. The increased environmental awareness and the newly developed regulations have imposed restrictions on the use of such inhibitors. Additionally, safe disposal of corrosion inhibitors after being used is critical and usually defined as a step in any chemical treatment programs, which adds a margin to the inhibition program cost. Many of the synthetic organic corrosion inhibitors can cause distortions to the human digestive system and affect the functionality of other organs. These effects are usually unnoticed during the manufacturing or the application processes as highlighted above.

The environmental and safety concerns related to inhibition processes have encouraged researchers to explore alternatives for corrosion inhibitors that are environmental friendly and at the same time can offer acceptable inhibition efficiency, especially in any acidizing treatment process. The focus on the natural products or others that can be synthesized from natural materials has tremendously increased to produce what is called "Green Inhibitors" or "Green Chemicals". The use of green inhibitors that are biodegradable and eco-friendly has been evolutionary in the last decade [29]. However, the harsh acidic and high temperature environments always limits the full utilization of green corrosion inhibitors. A successful introduction of a highly efficient green corrosion inhibitor in highly acidic media at elevated

temperatures will definitely lead to a flourishing of the acidizing treatment industry and maximize the recovery of the energy resources.

1.1 Significance and novelty

Direct corrosion cost in Qatar has doubled in just five years to 8 Billion USD [61]. Majority of this cost is attributed to the acidic corrosion encountered in acidizing and chemical treatment applications. A development of a green corrosion inhibitor that is able to operate in an aggressive the sever acidic corrosive environment and control the corrosion of carbon steel , particularly in well acidizing, is indeed highly required in the oil and gas industry. Carbonate formation is the dominant formation found in Qatar, for which HCl offers greater advantages over other acids during drilling and stimulation processes, but unfortunately it causes significant corrosion issues for the well tubular and upstream equipment that require efficient corrosion control.

Attempts were made within the past decades to test and qualify green corrosion inhibitors in a highly acidic environment. However, these attempts were limited by the exposure to high temperature.

This thesis, to the best of our knowledge, presents a new green inhibitor that was able to overcome these challenges and suppress the corrosion of mild steel in 16% HCl solution at 80°C with an inhibition efficiency of more than 94%. This achieved through introducing lauramidopropylamine oxide.

Hence, this work does not only guide other future research possibilities on other inhibitors development and testing , but it is also considered a keystone in the direction of reducing the corrosion costs that are related to acidic corrosion and supporting the acidizing treatment , which

in turn will lead to increase the wells' productivity as well as maximize the recovery of oil/gas energy resources.

1.2 Objective & Hypothesis

The objective of this thesis is to introduce and test a new green corrosion inhibitor that is capable of inhibiting the corrosion rate of mild steel in highly acidic brine (16% HCl) at different temperatures. The inhibition efficiency will be assessed using electrochemical and non-electrochemical characterization techniques.

Chapter 2

2. Literature Survey

2.1 Background

Since carbon steel (CS) is usually the first and most cost effective material choice used widely for upstream and downstream facilities, protecting it from the internal aqueous aggressive environment e.g. acidic brines is significantly important. Exposure of CS to these acidic brines in industry is encountered very often, particularly during gas/oil well completion. Qualification and testing of corrosion inhibitors in such environments have received a great attention as CS and low-alloy steel constitute the main metallic materials exposed to such harsh and corrosive streams. HCl (acidic brine) solutions cause uniform and localized thinning of CS and low-alloy steel and affects several units including crude unit, hydro processing units, catalytic reforming units, well acidizing, and chemical treatment. The aggressiveness of HCl solutions tends to increase as the temperature and acid concentration increase [8]. Selection of a robust corrosion inhibitor that prevents the reaction of metal with HCl has a substantial economic value. This survey outlines the importance of corrosion inhibition in acidic environment, particularly for well acidizing and secondary for other related applications. It also reviews benefits and the different formulations of various corrosion inhibitors used with HCl.

Exposure of CS to HCl is widely taking place in industry either directly through chemical treatment, acid pickling, and well stimulation or indirectly where HCl-enriched water vapors condenses from overhead loops of fractionation or distillation towers leading to dew point corrosion. Local electrolytic cells are formed due to the presence of oxidizing species like

oxygen and ferric and cupric ions, which will aggravate the corrosion rate leading to an accelerated metal loss and probable unexpected failures [9].

Candidate materials used for handling HCl should demonstrate an aqueous corrosion rate of less than 0.5 mm/yr (20 mils/yr). However, CS (at $\text{pH} < 4$) cannot maintain this low corrosion rate because the stability of its oxide film decreases at such low pH values leading to corrosion rates that exceed 100 mm/yr [8, 11]. In such cases, different protection approaches must be implemented to control corrosion.

Corrosion is usually controlled by utilizing four techniques:

2.1.1 Corrosion prevention through proper material selection and design

Material selection and design play a vital role in designing equipment and piping that achieve the required performance and corrosion protection as well as meet the life expectancy. For a specific corrosive environment the most common method to prevent corrosion is the correct selection and design of construction material. The material designer should ensure compliance of the candidate material to the properties required for the required application as the most effective time for proper selection is during determination of relevant specification. Critical operation parameters that affect the corrosion resistance of a material should be properly identified so that the selected material will not be subject to premature failure due to design deficiencies.

The type and severity of corrosion is related to the environment conditions in which the component is exposed. The component should sustain throughout the lifetime stages includes manufacturing, procurement, installation, a commissioning, and operation. Corrosion control

starts from the design phase and awareness about corrosion impact should be raised during all project stages.

The first stage for proper material selection is the definition and review of the operation conditions in which the designed component is going to operate. The defined operating envelop should take into consideration the occasions for process upset and operation excursion where normal operating envelop is usually breached. By accurate designation of all possible scenarios the confidence in selecting a reliable component is highly increased.

When all corrosive species are accurately defined and operation conditions are well described, credible damage mechanisms that affect the integrity of the component can be confidently listed. Trace amounts of impurities may have a detrimental impact on the corrosivity of the stream, which will lead to accelerated corrosion. Nickel alloys for example are highly resistant to Hydrochloric acid (HCl) environment. However, the presence of ferric ions (Fe^{3+}) in negligible quantities would lead to accelerated corrosion and probable premature failure.

Equipment size and design is also an important aspect to mitigate corrosion in early stages. Criticality, complexity and size of equipment are taken in consideration while designing. Greater attention is paid towards designing of critical and unique components like turbines or boilers than when designing simple utility small storage tanks. Welding and jointing of components require more attention than the construction component themselves. This is attributed to the inherent susceptibility of weld to pick up impurities and generate defects that could jeopardize the overall integrity of the joined component. Selection of filler wires and welding electrodes may affect the metal- weld dilution which in turn affects the corrosion resistance of weldment and may promote galvanic corrosion.

Once operating conditions and all physical and design consideration have been fully understood, candidate materials are considered passed on their properties and resistance to corrosion. Numerical values using computer software are usually employed where property index and performance indicator of individual material is weight against others. The list of materials to select from is frequently narrowed based on field experience and engineering judgment. Next stage of selection may involve laboratory testing for more in depth understanding of the candidate material under the proposed conditions. This is may be considered as the only reliable means for final assessment and determination. Testing coupons machined from the candidate material are exposed to the corrosive while controlling several variable including testing temperature, static conditions, velocity, and others.

Not always the exotic material and more expensive offers high corrosion resistance. Stainless Steel for example is generally weak against pitting in chloride rich environment at temperature more than 60°C. Where as Carbon steel has higher corrosion and pitting resistance in similar environment. So the material selection a process for short-listing of applicable materials in a proposed environment and then choosing the most cost effective taking into account the required design life. To ease the process of selection combination lists of material and corrosive media are employed to ensure optimum resistance against corrosion. Examples of these combinations include Stainless steels in nitric acid, Monel as K500 in hydrofluoric acid, and others that yield the utmost degree of corrosion resistance for the minimum amount of money spending.

In addition to metallic materials nonmetallic are widely used in oil and gas industry. They can be used as a substitute for metallic materials under specific condition where metallic components do

not perform well. Rubber offers great resistance to acidic environment through wide range and that is why it is used for lining of tanks and piping systems for handling Hydrochloric acid.

Proper design before construction is very important and a key stage to highlight corrosion concerns that could be avoided earlier before execution of the project. Numerous references and books are used to provide guidance on the material selection strategy. However, an equipment or structure designer is seldom has full understanding of the corrosion engineering concepts in the design phase. And that is why it is always important to engage a competent corrosion engineer in the design phase since corrosion control starts from the design. Design deficiencies as per literature review constitute more than 58% of the failure causes in oil and gas facility [28]. The rate of failure of a facility is increased after commissioning due to design faults as shown in figure 2.1.

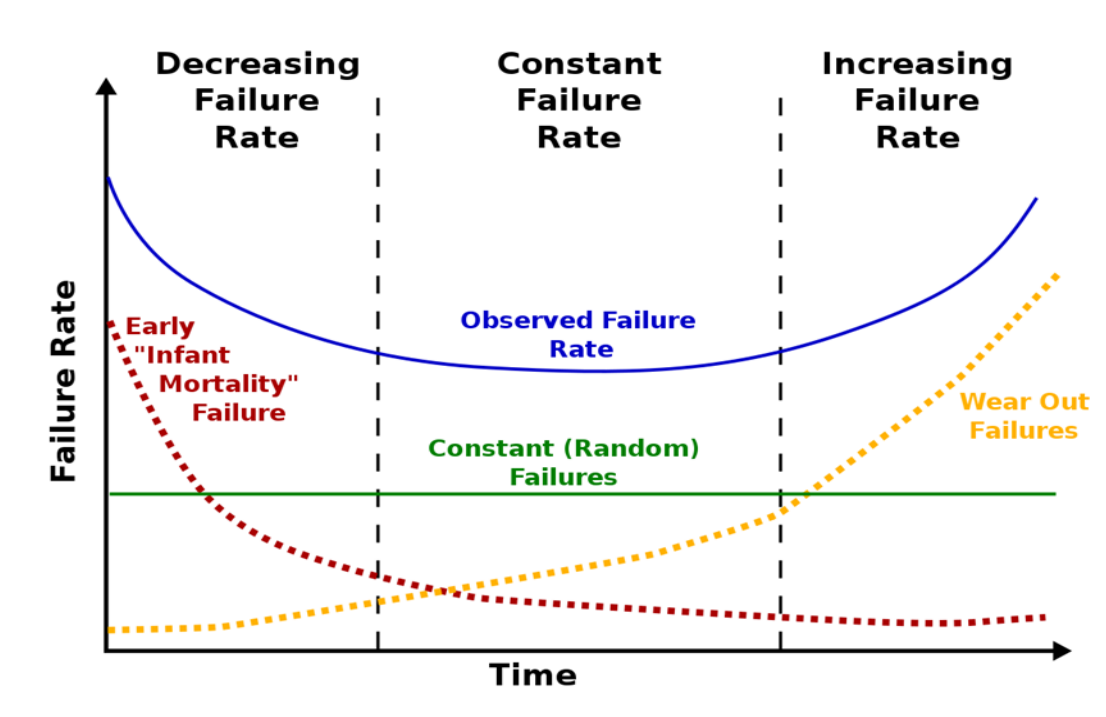


Figure 2.1: Hypothetical failure rate versus time represented as a bathtub curve

2.1.2. Corrosion prevention by alteration of environment and introduction of Corrosion inhibitors

One of the versatile means of controlling corrosion is by controlling the corrosivity of the environment. Decreasing corrosion can be done by controlling the hydrodynamic of the medium, lowering temperature, scavenging of oxygen or other oxidizing agent. The control of these parameters shall be done with care as different systems may require different corrosion control philosophy.

Chemical reactions are almost increased with increase in the exposure temperature [1]. The oxidizing power for some acids is usually amplified in consequent to the rise in temperature, which will cause exponential increase in corrosion rate. A famous example in the exponential increase in corrosion rate of stainless steel once exposed to hot nitric acid.

Therefore, lowering the temperature of the system will induce significant suppression of deterioration rate for most of reaction. Increase in temperature could lead to decrease in corrosion rate is specific conditions where the diffusion of the corrodent i.e. oxygen is decreased as the system is brought to higher temperature. This case is evident in fresh water brought to near boiling point.

A second contributor to corrosion is the dynamic properties of the system. Control of the flow velocity is usually a critical factor to control corrosion. In general high flow velocity will result in higher corrosion rate. Presence of suspended solids of second phase could increase the erosional effect of the fluid and induce more damage to the piping system, particularly at areas of flow turbulence and sharp change in direction. However, reducing the velocity significantly may create stagnant condition that will promote fouling and activate damage mechanisms like

microbiological and under deposit corrosion to the system. Erosional threshold velocity is established for many metallic materials to mitigate the risk of accelerated metal loss due to erosion corrosion.

Control of oxygen content and ingress to the medium is another approach of controlling corrosion by altering the environment corrosivity. Reduction reactions will be controlled by controlling oxygen ingress which will in turn affect oxidation reaction and as a result slow down the overall corrosion reaction. This is considered one of the oldest techniques to minimize corrosion. Boiler water systems are usually equipped with deaerators to mechanically scavenge oxygen and other dissolved gases like carbon dioxide. Oxygen scavengers chemicals like disodium Sulphite are injected downstream of the deaerators to further decrease oxygen to 5 -25 ppm. Utilization of oxygen scavengers and reduction of oxygen to less than 5ppm may be avoided depending on the cycle of chemistry of the boiler to avoid sever reduction tendency of boiler internals and activation of flow accelerated corrosion (FAC). Deaeration is not recommended for metals that have active passive transition, which rely on the protective passive film for corrosion control like Stainless steel. Oxidizing environment are recommended for these metals to ensure presence and formation of passive film to protect them against corrosion .Similar to oxygen other oxidizers contaminants are usually controlled which tend to accelerated corrosion aggressiveness of hydrochloric acid against materials that are normally resistance in absence of these oxidizing agents. During production of hydrochloric acid or storage contamination with ferric chloride is frequently encountered that will render hydrochloric acid corrosive to even nickel based alloys like Hastelloy.

Another important field for mitigating corrosion damage is the application of corrosion inhibitors. These are widely used in chemical and petrochemical industries as well as in other applications like protective coatings and shipping and storage preservation. Different forms of inhibitors are added depending of the system to be protected. Corrosion inhibitors reduce the corrosion rate appreciably when added in small concentration and this affect was adopted as a widely used definition for corrosion inhibitors in general. Corrosion protection through utilization of corrosion inhibitors can be traced back to mid of nineteenth century. The first patent for corrosion inhibitors was about reducing corrosion rate of carbon steel in pickling acid using vegetable oils [24]. Since then tremendous research has been done related to corrosion reduction using corrosion inhibitors. The action or the function of the corrosion inhibitor can be considered as a catalyst that retards corrosion. The number of corrosion inhibitors tested and being used is extravagant. And the search for new products, that are environmentally friendly and can be classified as green inhibitors in endless. Since most of inhibitors are developed using empirical experimentations and their formulations and ingredients are proprietary in nature, their detailed composition and inhibition affects cannot be fully understood for these reasons [1]. However, it is still possible to classify inhibitors based on their general composition and mechanism for corrosion control. Corrosion inhibitors form a barrier film on situ on the corroding substrate which will decrease the reaction rate and minimize corrosion. Inhibitors can also be added as a conditioning chemical to control pH and reduce acidic corrosion. Since inhibitors are reversible in nature it is important to maintain minimum residual of corrosion inhibitor in the system so good circulation of the system is required.

Corrosion inhibitors influence the corrosivity of environment in a number of ways. Attachment of the corrosion inhibitor to the corroding metallic substrate in a form of thin barrier film is one mechanism for protection. The second mechanism includes formation of a thick protective corrosion product. Altering the corrosivity of the medium by eliminating corrosive species or formation of precipitates is another function of corrosion inhibitors [5]. Frequently, the effect of these mechanisms combine in a synergic fashion to reduce corrosion. Thus, Corrosion Inhibitors can be broadly classified as film forming or barrier, environmental conditioners (Scavengers), and few other miscellaneous inhibitors.

Figure 2.2 illustrates a qualitative classification of corrosion inhibitors in which interface inhibitors are subdivided into liquid phase and vapor phase. The Liquid (Aqueous)-Phase inhibitors are further classified to cathodic, anodic or mixed. This classification is based on the resultant blocking of the anodic sites, cathodic sites or both imposed by injection of a corrosion inhibitor. Inhibitors that suppress the reduction reactions in addition to the oxidation reactions are usually considered more effective [5].

Anodic type inhibitors are usually added to aqueous solutions with pH near neutral where chances of getting corrosion products and presence of salts, oxides, or hydroxides are few and far between. Anodic inhibitors impose a thin layer that passivate the metal, and hence called passivating inhibitors. Risk of accelerated corrosion and pitting may arise in case of under dosage (Below the recommended critical value for oxidation). Cathodic inhibitors control corrosion by decelerating of cathodic reduction reaction, which is known as cathodic poisoning or by masking out of cathodic sites with precipitates. Cathodic poisoning can introduce a severe damage mechanism to steel known as Hydrogen Embrittlement. Nascent hydrogen atoms are

prevented from recombination to form Hydrogen molecules in gaseous form and instead are absorbed into the metal that causes blistering and cracking. This problem is more prevalent in acidic environment where Hydrogen gas evolution dominates the reduction reaction.

Mixed inhibitors are those which can neither be classified as anodic or cathodic. They constitute more than 80% of organic inhibitors in market. The effectiveness of corrosion control offered by mixed inhibitors is directly related to the degree they adsorb to the substrate and cover the corroding areas. Adsorption is affected primarily by three factors: The inherent structure of the corrosion inhibitor, Interface charge of the substrate, and the chemistry of the aqueous electrolyte. Chromate is one example that affects both polarization curves of the anodic and cathodic reactions.

Mixed Inhibitors offers protection of metals from corrosion in number of ways, either by physical (Electrostatic) adsorption, chemisorption, or by buildup of barrier film. The first possible way is resulted from the electrostatic charge that exists between the metallic substrate and the injected inhibitor molecules. If the metal to be protected carries a net positive charge, then the physical adsorption will be facilitated by anionic inhibitor. Cationic inhibitor can also protect positively charges substrate in presence of anionic intermediates in the electrolyte. The anionic colloids will first attract to the metal enabling bridging assistance for the cationic molecules to adsorb to the dipole. This synergic affect is best demonstrated while protecting carbon steel against the attack of Sulphuric acid in presence of halide ions like chlorides using cationic quaternary ammonium [7].

The time taken for physical adsorption of corrosion inhibitors is less when compared to chemisorption. This makes them rather vulnerable to ease detachment from the surface. Because there is no charge transfer or charge sharing involved in the physisorption process amongst metal surface and inhibitor molecules, physically adsorbed inhibitor reverses back and detaches as temperature increases. On the contrary to the chemisorption process adsorption nature where both the degree of inhibition and the surface adsorption increase as function of temperature. The surface formed inhibitor film quality is very crucial for optimum inhibition. Corrosion of substrate will be greatly reduced as the protective adsorbed film grows from merely a single layer to three dimensional layers. The film should be impermeable, strongly adheres to the substrate, and shall not be soluble under operating conditions.

In contrast to the old misconception that corrosion inhibitors can only be used for aqueous environment application of copper magnesium oxide or ammonium ions to reduce corrosivity of combustion product Vanadium pentoxide is one example for non-aqueous application. As far as the scope of the thesis is concerned the primary focus will be on testing and qualifying of corrosion inhibitors in aqueous acidic environment encountered in oil and gas industries.

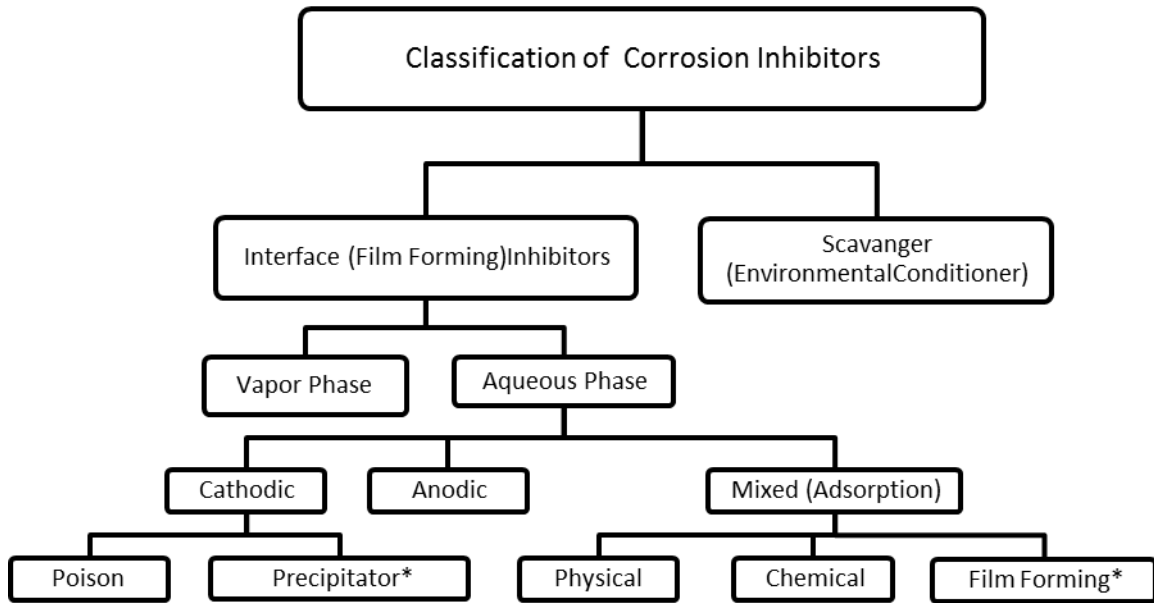


Figure 2.2: Typical representation of different types of corrosion inhibitors

*Tend to form three dimensional multi layers at boundary, hence called interface inhibitors

2.1.3 Corrosion prevention by application of Cathodic Protection (CP)

The first theory of cathodic protection (CP) was offered 1938 by Mears and Brown that where corrosion is electrochemical in nature it is necessary to polarize the cathodic sites in a corrosion cell to the potential of the anodic sites in order to achieve a complete cathodic protection. Cathodic protection is vastly used to protect metallic piping, structures, concrete rebars, and tank bottom from the effect of corrosion and minimize the corrosion rate to a minimal value. The cathodic protection can be explained by considering the dissolution of a metal in acidic environment.



Corrosion protection using cathodic protection is achieved when stream of electrons is supplied to the metallic item under protection. Reviewing equation one and two indicates that supplying of electrons will suppress the dissolution of metal and increase hydrogen evolution. There are two ways of applying cathodic protection either by introducing an external supply of by using a more active metal to create a galvanic coupling. The first technique is called impressed current cathodic protection (ICCP), whereas the second is called sacrificial system. Figure 2.3 illustrates the concept of impressed current cathodic protection system. Direct current is impressed to all surface of pipeline line to be protected. The applied current will shift the potential of the pipeline in the negative direction resulting in corrosion rate reduction.

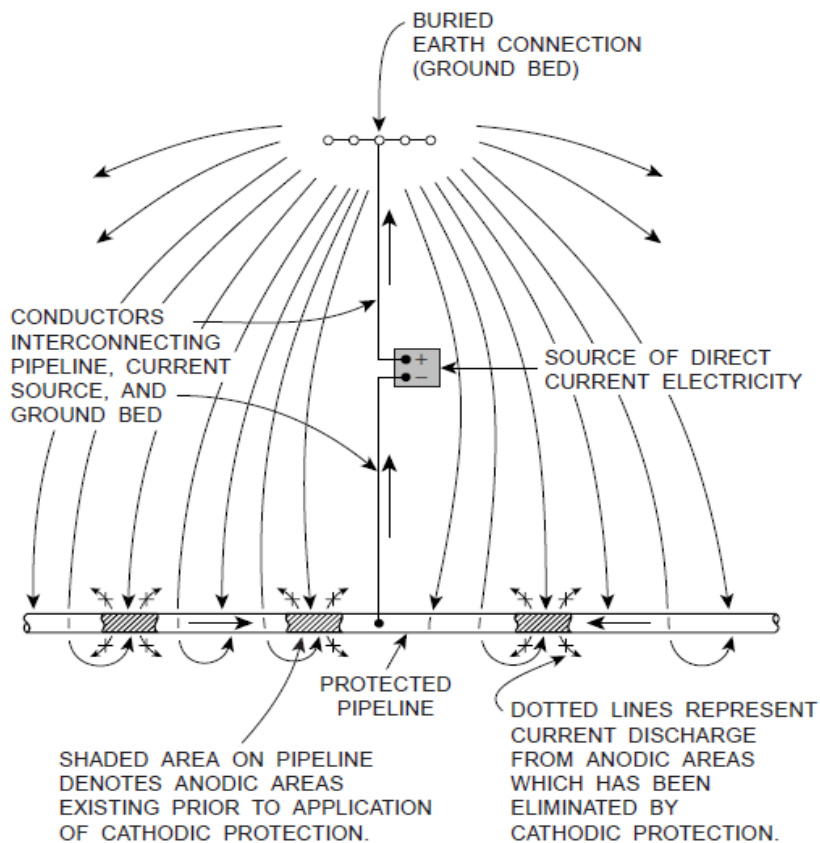


Figure 2.3: Basic impressed current cathodic protection system installation [33]

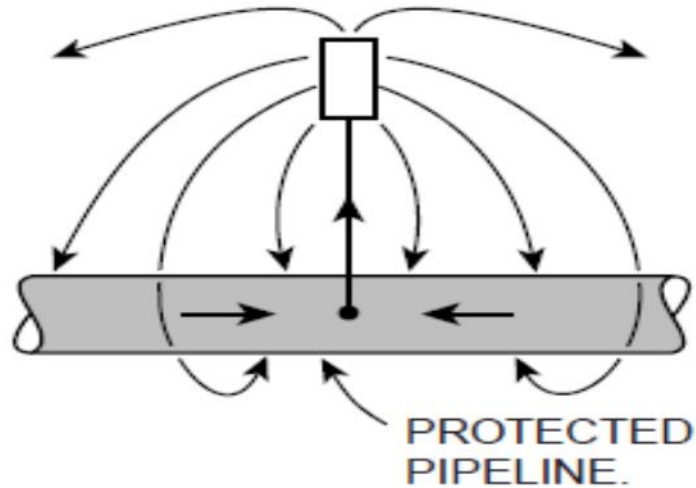


Figure 2.4: Basic sacrificial (Galvanic) anode cathodic protection system installation [33]

For sacrificial systems different anodes exist like magnesium, aluminium or zinc depending on where the structure to be protected is installed. The off-potential is required versus a reference electrode to evaluate degree of polarization and protection. Several criteria have been specified to measure the effectiveness of installed CP system. Virtually all pipelines are coated with organic coating to provide barrier against corrosion. This coating is supplemented by cathodic protection to account for holidays in the coating.

2.1.4. Corrosion prevention by application of protective coating and linings

Application of protective coating and lining to cover metallic surface and prevent corrosion is the most applied technique amongst other protection approaches. The metallic surfaces covered by protective coating and lining are more than the other methods combined. In addition to offering corrosion protection, coatings are also applied for cosmetic purposes and process identification requirement. The principle behind coating and lining is the isolation of the metallic surface from

the corrosive medium. Coatings come in variety of forms include liquid and powder to suit application techniques and ensure proper bonding to the surface. Different binders are used to carry and bind formulation ingredients of the coating together. The exposure condition and the type of substrate are key elements in selecting proper coating system for the intended application. Organic coating use polymeric binders like epoxies, polyurethane, silicone, Acrylic, polyamide epoxies etc. as resins that affect their properties. These are usually thin films provide barrier between the environment and the metal to be protected. The rule for utilizing coating for corrosion control is where the environment would attach the metallic substrate otherwise. There are important stages while applying protective coating to protect steel. Surface preparation, selection of primer for primer coat, and of top coat are some of these factors. Typical coating systems for atmospheric exposure consist of three coats, a first coat (primer), a thickness build up second coat, and a final top coat. The first coat is usually equipped with zinc particles to act as a sacrificial anode to protect the metallic substrate underneath. Therefore, it would corrode in preference to the metallic substrate. The second or mid coat generally ensures low permeability of water molecules to the substrate by introducing leafing effect that increase the passage distance of water to the substrate as shown in figure 2.5.

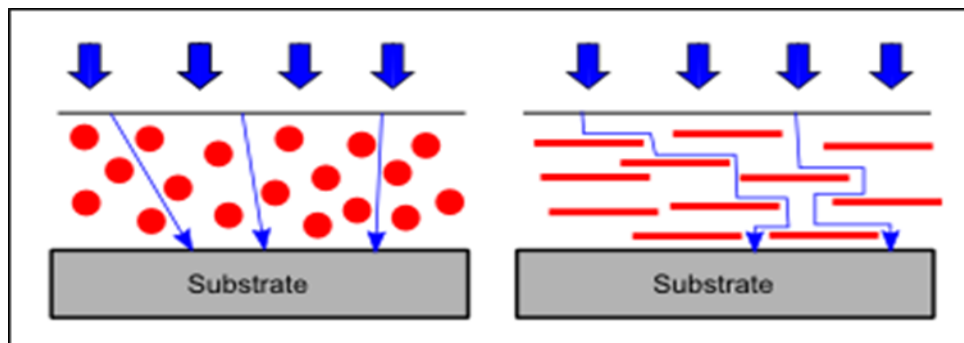
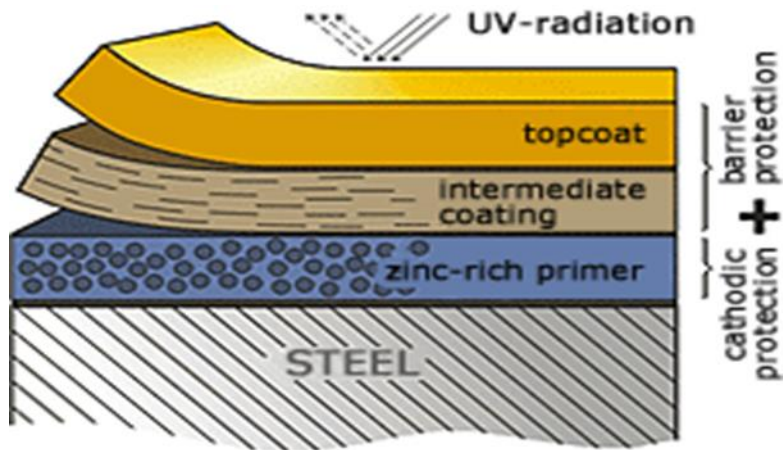


Figure 2.5: Representation of the leafing affect offered by the Micaceous iron oxide coat (MIO)

to hinder passage of water and moisture to the substrate.

The final coat, which is usually manufactured from chemical curing polyurethane provides ultraviolet (UV) protection for the coating system and also ensure high gloss degrees and less chances for direct build up. The overall dry film thickness of the total number of coats will be in the range of 250-275 μ m depending on the manufacturer paint data sheets. Figure 2.6 shows typical coating system for atmospheric exposure [34].



Top Coat (Polyurethane) to enhance ultraviolet degradation resistance
Intermediate Coat (Micaceous Iron Oxide)
Primer (Zinc Silicate or zinc rich coat)
Metallic Substrate after proper surface preparation

Figure 2.6: Typical representation of atmospheric coating system used for atmospheric corrosion control

Metallic and inorganic coatings are also used for protection against corrosion. These coatings have proven providing a strong barrier coat isolates the metal from the environment. Several techniques are used to apply this type of coating include flame spraying, electrodeposition, cladding, and hot dipping. Thermal spraying metals are increasing in popularity due to their short application time and high durability, which provide a solution for corrosion protection during shutdown of plants where time does not permit for complete replacement of intensive welding jobs.

The search for smart coating which can bridge the gap of conventional coating's limitations and provide sustainable and cost effective solution is ongoing. Several products have been tested including hydrophobic coating; self-healing coating and they showed promising results and potential candidates for future deployment.

Since common corrosion problems in industry are primarily attributed to acidic corrosion and because hydrochloric acid is used to a large extent in GCC countries and other parts of the world, it becomes very important to search for an environmental friendly solution to counterattack corrosion threat. Well acidizing and acid pickling conditions put limitations on the application of conventional coatings to mitigate severe corrosion of carbon steel. It is also not economically viable to upgrade all tubing and piping from carbon steel to exotic materials which will add extravagant cost to the operating cost of the asset. Corrosion inhibitors have been one option to mitigate corrosion in these severe acidic environment. However, some of the earlier corrosion inhibitors used were discontinued due to their toxicity and environmental negative impact. Arsenic for example was previously used as inhibitor for well acidizing with hydrochloric acid, but due to high toxicity of arsenic and production of arsine gas upon reaction

of acid with metal, the use of arsenic was therefore banned [5].

This is the first time to the best of our knowledge that lauramidopropylamine oxide is introduced and tested as a candidate corrosion inhibitor to mitigate acidic corrosion in this harsh corrosive medium. Lauramidopropylamine oxide has many advantages when compared to other conventional inhibitors: (1) it is considered safe with no reported toxicity concerns. (2) It is eco-friendly and being used in human cosmetics, hair conditioning products, and baby products (3) High compatibility with various types of surfactants (4) considered cheap (5) it has neutral pH range 6-8 (4) No pre-immersion is required for effective protection.

This work to test and qualify lauramidopropylamine oxide will markedly reduce corrosion of carbon and low alloy steels in hot acidic brines. This research field has a major industry impact in Qatar and other parts of the world. Tremendous costs saving will be made in drilling and stimulation processes through successful implementation of this project.

2.2. Mechanism of Inhibitors in acid systems

Different definitions exist in the literature for defining corrosion inhibitors. The famous one, which is adopted by National Association of Corrosion Engineers (NACE) describes a corrosion inhibitor as a substance when added to a corrosive environment in small amounts markedly reduces corrosion. The definition implies the cost feasibility of inhibitors when using in small concentrations. The testing of an inhibitor to reduce corrosion in an acidic environment is challenging, particularly well is acidizing due to the high concentration of acids , temperature , agitation and other factors. The emphasis for using inhibitors in acidic media is related to the

vulnerability of carbon steel or mild steel to corrosion in these conditions and the extravagant costs related to the search for more exotic material to withstand acidic corrosion.

When designing corrosion inhibitors for specific environment it is very important to understand the pertinent factors to an optimum design. It is commonly agreed that the theoretical explanation of inhibitor's adsorption phenomena involve the following:

1. Proton acceptors;
 2. Accepting electrons; and
 3. "Mixed " type molecules
1. For the first one which is electron acceptors the generic organic molecule can be thought of a cathodic site absorber. Materials classified under this category accept hydrogen ion then migrate to the cathodic sites. This category involves organic inhibitors used in various acidic environments like quinoline, anilines, urea, and aliphatic amines.
 2. Materials for the second type can be considered effective at anodic sites. They inhibit corrosion through their ability to accept electron and suppress the anodic sites. These materials are very effective for reactions under anodic dissolution control. Examples of passivating inhibitors found in this group are organic peroxides, and inorganic chromates.
 3. Mixed molecules comprise more than one orienting groups attached to them like $-NH_2$ and $-SH$. Because of this inherent structure, mixed molecules can influence and reduce both anodic as well as cathodic reaction. Thus called ambiodic inhibitors. It is apparently obvious that the molecule which controls both reactions is more effective than affecting only anodic or cathodic reaction. 2-aminobenzenethiol is an example of ambiodic designed corrosion inhibitor [5].

Corrosion inhibitors that are used processing oil and gas plants are polar in nature. Hydrophobic and hydrophilic moieties are present within the same molecular structure to enhance surface activity of the inhibitor. Figure 2.7 illustrates typical adsorption of a corrosion inhibitor to the metallic substrate and displacement of aqueous molecules off the surface to isolate the substrate and provide a barrier isolating film.

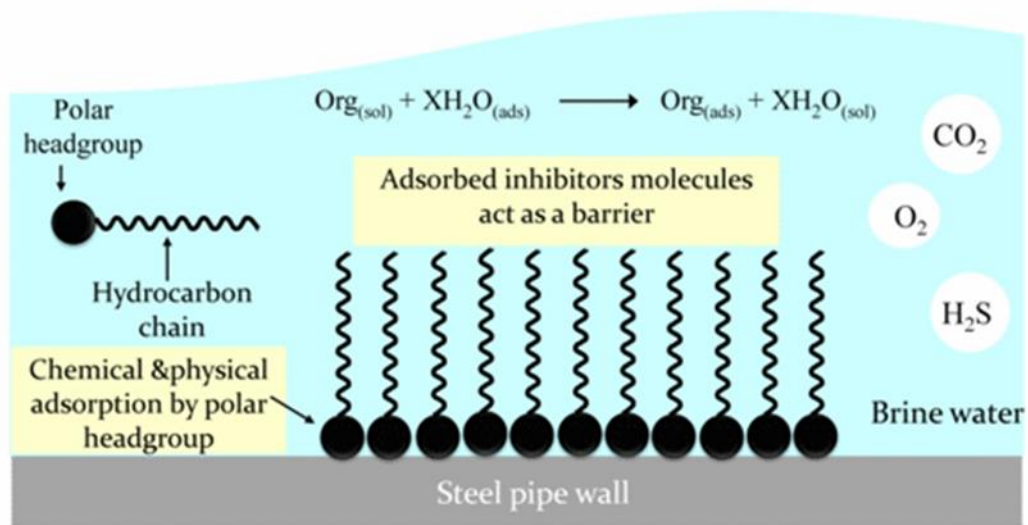


Figure 2.7: Representation of inhibitor action to mitigate corrosion in brine water [43].

There is increased interest in corrosion and corrosion inhibition research and developed represented in below table. This is a direct indication of increased corrosion activities and increased efforts in order to mitigate it.

Table 2.1: Number of submitted abstracts versus the number of years related to corrosion and corrosion inhibition studies.

Year	Passivity	Corrosion	Corrosion inhibitors
1910	4	26	2
1911	2	75	12
1912	5	61	10
1957	38	>800	280
1994	100	>2000	400

Not all acidic environments are the same. Therefore, inhibitor testing should be conducted in the environment of interest. Due to the widespread of using hydrochloric acid in various applications, qualification of an inhibitor under this harsh environment will serve many sectors in the industry.

2.2.1. Inhibitors in well acidizing

Hydrocarbons are retrieved through reservoirs predominantly made of carbonate formation or carbonate – bearing sandstones. Carbonatite is a hard rock, which is tight with fractures and pores. During well completion activities acidic solution are used widely to ease drilling and stimulate wells for enhanced productivity. Well acidizing practice has been used for major oil and gas operators for almost 120 years. Acids are pumped at high pressure through the bore hole, which will chemically react with the reservoir rocks to dissolve them and enlarge the opening in the rock for better productivity and utilization of energy resources. The rocks are primarily made of limestone and dolomite. Acidizing procedure is usually done with hydraulic fracturing techniques. The acid seeps through the fracture to enlarge the opening and allow for more

passage of the desired fluid. Acidizing is also employed to detach and remove scales build up from the well tubing and also for cleansing of mud residuals before putting the well into production. Large quantities of acid are pumped at high flow rates through the tubing to the production formation. Well acidizing is considered a rough test for inhibitors to perform satisfactorily. The acidic concentration used is quite high usually 15% HCl by weight with a high temperature profile downhole reaching up to 177°C. The process of acidizing is frequently repeated couple of times until removal of scales is found satisfactory. Chances of getting contaminants in the acidic solution due to corrosion are also available, which will accelerate corrosion of tubing and other equipment.

Acidizing treatment processes can therefore be classified into three main categories: Acid washing; fracture acidizing; matrix acidizing. In acid washing HCl is used only for cleaning of tubular and wellbore from scales and debris obstructing flow of the well. Formation treatment is not intended. For fracture acidizing treatment of the formation is required to restore or improve oil or gas well productivity where as in matrix acidizing the treatment acid is injected below the fracturing pressure for the formation.

Depending on the nature of the reservoir different acids are employed for acidizing procedure. Hydrochloric acid is the most famous one for the well acidizing due to the high solubility of metal chlorides that are formed during acidizing. HCl concentrations in the range of 15-28% were used in the acidizing treatments [35]. The use of other acids like sulfuric acid, phosphoric acid, nitric acid was discouraged due to the resultant insoluble Sulphate, nitrate, and phosphate salts. HF is sometimes mixed with HCl to form what is called mud acid. Three stages are involved in this procedure namely preflushing, main flushing, and after flushing. In the first

stage highly concentrated HCl (15%) is used whereas the second stage uses 12% HCl with the addition of 1.5% HF. Methanol is used in the after flushing to ensure rapid cleaning of the formation [36]. Another advantage of HCl over other acids is that it is the most economical choice for fast dissolving of CaCO₃. However, and depending on factors like concentration of the acid used metal loss in a form of pitting is usually encountered.

The severe corrosion of steel piping and equipment exposed to uninhibited acidizing solution is a challenge and contributes to additional added operating costs. Successful introduction of a reliable green corrosion inhibitor to suppress the aggressiveness of the acidic solution at high temperatures is indeed a key crucial objective and industrial requirement.

Inhibitor performance in a specific environment is sensitive towards changes in the operation conditions beyond the qualified ranges. Inhibitors qualified in a concentrated acid solution may not perform as good in less acidic environment and vice versa [35]. During acidizing process corrosion inhibitor is added to the holding tank in a batch treatment before injection of the solution for stimulation process. Poisonous compounds like arsenic were used before as corrosion inhibitors with hydrochloric acid. But soon were banned due to their toxicity, pitting tendency, and poisoning of refinery catalyst. Arsenic was also used as inhibitor during transportation of acidic solutions in mild steel containers [37].

Tin has been used previously as corrosion inhibitor in acidic pickling baths. It was also used for preserving of containers used to store acidic slats from corrosion [38]. Similar to Tin ferrous salts were reported to be used as inhibitors for protecting steels exposed to acidic media. It was suggested that ferrous salts inhibit corrosion of carbon steel satisfactorily in hydrochloric acid [39], where as in Sulphuric acid the corrosion rate tends to increase in presence of ferrous salts.

Previous work done by few researchers suggested that ferric ion has the capability to retard corrosion on stainless steel exposed to oxalic acid. But most researchers have found that corrosion rate increases in acidic environment inhibited using organic inhibitors in the presence of ferric ions. Ferric ions are classified as contaminants of acidic solution that act as promoters of more corrosion [5]. Earlier attempts to inhibit corrosion of steel in acid environment used copper as an inhibitor. An example is the utilization of copper to reduce corrosion susceptibility of stainless steel in sulfuric acid. It is also used to introduce a synergistic inhibition effect and support to the performance of the injected organic inhibitor in acidic environment. With the presence of copper, the performance of amines, aldehydes, and thiocompounds is improved [40].

Halides were also used previously as corrosion inhibitors in acidic conditions. During shipping of phosphoric acid Iodides were mixed with sulfuric (76%) acid to protect transportation drums from corrosion. Studies were conducted to evaluate performance of iodides as corrosion inhibitors for sulfuric acid and perchloric acid [41]. Based on corrosion inhibition testing and decrease in corrosion rate, the degree of adsorption of the halide anions to the surface were affected by the type of the halide anion. The largest adsorption tendency was reported for Iodide. The real impact of halide ions on corrosion inhibition is still debatable. They have been thought of being corrosion accelerators and their presence in many services were kept to the minimum. Chloride ions strongly adsorb to the surface, which makes passivation of metallic substrate using corrosion inhibitor is rather difficult. More quantities of corrosion inhibitor will be required as chloride content increases [42].

Differences exist in the type of corrosion inhibitors used depending on the kind of the acidic media. In addition to above inorganic inhibitors previously used in acidic conditions, organic

inhibitors have been used in various acids. For hydrochloric acid nitrogen containing compounds have been effective in inhibition of carbon steel in acid environment. These compounds contain aryl or alkyl amines that are primarily saturated with nitrogen ring compounds. Mannich bases are amongst these compounds synthesized from amines and also from condensation of amines using ethylene oxide. The performance of nitrogen containing compounds is enhanced through addition of various additives. Acetylenic alcohols are some of these useful compounds to support performance of nitrogen containing elements. In particular, propargyl alcohol offers outstanding performance. Acetylenic alcohols can be used independently and yet offer satisfactory degree of inhibition.

To ensure effective inhibition of the selected inhibitor in well acidizing process the lab testing procedure shall mimic the actual conditions as much as possible. In this work 5 M HCl was used as a testing medium heated up to 80 °C to simulate the static conditions for well acidizing. Lauramidopropylamine oxide green corrosion inhibitor was used to inhibit corrosion of mild steel in this environment. To the best of our knowledge, this inhibitor has not been previously tested to mitigate corrosion of mild steel in acidic brines

Since the minimum HCl concentration is 5 % in well acidizing , the review will be confined to 5% and higher[35]. McDougall has tested inhibition of N-80 carbon steel oil tubing in 5% HCl solution using four corrosion inhibitors. A dramatic increase in corrosion rate was noted between 66°C - 93°C [4]

Twenty three compounds were studied as corrosion inhibitors for carbon steel in 15% HCl solution at around 60 °C. In order to minimize hydrogen permeation and embrittlement of steel, formaldehyde compound was added to the inhibitor during testing. Aniline, diphenylamine, n-

octylamine, tributylamine, and 1,3-dibutyl-2-thiourea were found most effective in reducing corrosion compared to other compounds [45].

The inhibition of Polypropylene glycol (PPG) was examined to inhibit corrosion of API X60 pipeline material in 15% hydrochloric acid. Several electrochemical techniques were employed in addition to weight loss analysis. Inhibition efficiency of PPG was found to increase in line with the increased inhibitor's concentration up to 55 °C. The inhibition efficiency declined as the immersion time prolonged and the temperature increased to 60°C. The highest inhibition efficiency of 99.5 % was obtained at 55 °C with the addition of 1000ppm of PPG. PPG acted as a mixed-type inhibitor, which reduced anodic as well as cathodic reaction [46].

The corrosion inhibition performance of two new Chromenopyridine derivatives was tested in 15% HCl as potential environment friendly candidate inhibitors for N80 steel. The inhibition efficiency of both inhibitors after addition of 200 mg L⁻¹ is 82% and 92 % respectively. Both inhibitors reduced the corrosion rate by blocking the cathodic sites and therefore classified as cathodic inhibitors [47].

Furfuryl alcohol was reported by Vishwanatham to act as efficient mixed corrosion inhibitor predominantly affecting the cathodic reaction in 15 % HCl. N80 carbon steel was used as the testing electrode. The inhibition efficiency was reported to increase corresponding to the corrosion inhibitor dosage increase, whereas efficiency decreased as the temperature reached 110°C [48].

A triazole compound (SAHMT) was tested in 15% HCl to inhibit the corrosion of tubular steel N80. Various electrochemical techniques were utilized to quantify the effect of the inhibitor electrochemically at 28°C. Investigation indicated that the inhibitor can be classified as a mixed-

type inhibitor and adsorption of the inhibitor obeyed Temkin isotherm [49].

Plant extract (*Zenthoxylum alatum*) was tested to inhibit the corrosion of mild steel immersed in 5% hydrochloric acid solution. Weight loss techniques and electrochemical methods were used to evaluate the impact of this inhibitor and its efficiency. The inhibition efficiency improved in line with inhibitor concentration increase up to 2400ppm. The highest efficiency obtained at 30 °C was 95% [50].

Mahendra studied inhibition of N80 steel using amino acid (BIFP and BIFM) in 15% HCl (Table 2.2). Potentiodynamic and electrochemical impedance techniques were employed in the study. Investigation showed that the two compounds are considered as mixed type inhibitors with inhibition efficiency directly proportional to the increase of the inhibitor's concentration. Maximum efficiencies obtained for the two compounds from potentiodynamic calculation at 30°C were 97.5% and 97.7% respectively [51].

Pyranopyrazile derivatives (AMPC and ACPC) was tested in another research to inhibit Corrosion mild steel in 15% HCl. Different electrochemical techniques and weight loss analysis were employed in the study. Inhibition efficiency increased with increasing inhibitor dosage, whereas with increasing testing temperature a decline in inhibition performance was noted. The charge transfer resistance in EIS testing increased upon addition of corrosion inhibitors. The highest efficiencies obtained from potentiodynamic testing were 95.5% and 95.3% for AMPC and ACPC respectively at 300ppm of inhibitors concentration and 30°C [52].

Naphthyridine derivatives (ANC1, ANC2, and ANC3) were tested as a candidate inhibitor to control corrosion of N80 steel in 15% Hydrochloric acid. Various electrochemical techniques, surface characterization, and quantum calculations were employed to evaluate the overall

performance of the inhibitors. Inhibitors were noted to affect oxidation and reduction reactions and therefore classified as mixed type inhibitors predominantly affecting the cathodic reaction. The calculated inhibition efficiencies from potentiodynamic polarization obtained for the three ANC, ANC2, and ANC3 inhibitors were 90.2, 87.0, and 80.7% respectively in presence of 200ppm of inhibitor concentration at 30°C [53]

Corrosion inhibition of N80 steel using Isatin compounds (MMTOI, and PATMTOI) was studied in 15% Hydrochloric acid solution by polarization techniques, EIS, and weight loss measurements. Both inhibitors were found effective with increasing efficiency in line with concentration increase. Interpretation of polarization curves revealed that both inhibitors affect anodic and cathodic reactions. Maximum inhibition efficiency recorded for PAMTOI was 91.23% , where as for MMTOI was 84.33% at 200ppm of concentration and 25°C [54].

1-(2-oleylamidoethyl)-2-oleylimidazoline (OAEIOI) and 1-(2-aminoethyl)-2-oleylimidazoline (AEIOI) were investigated as nontoxic inhibitor to provide corrosion protection for N80 steel in 15% Hydrochloric acid. Potentiodynamic polarization, EIS, weight loss, and AC impedance measurements were employed to evaluate the inhibition performance of candidate inhibitors. Surface analysis using SEM and FTIR were also used in the study. The maximum inhibition efficiencies obtained for the two inhibitors were 90.26 % and 96.23% respectively with concentration of 150ppm and at 25°C. Both compounds were classified as mixed-type inhibitors [55]

Corrosion inhibition of Pyridine derivatives (ADP and AMP) was investigated in 15% Hydrochloric acid solution for protection of N80 steel. Electrochemical and surface characterization techniques were employed in the study. ADP showed inhibition efficiency

calculated from polarization curves of 90.31 % at inhibitor concentration of 200ppm. Similarly, AMP showed inhibition efficiency of 87.06% at 35°C. Both derivatives affected anodic and cathodic reaction. Thus they were classified as mixed-type inhibitors [56].

A mixture of organic compounds containing formaldehyde in addition to cresol (TVE3A, TVE3B, TVE3C, Table 2.2) were tested to inhibit corrosion of N80 steel in 15% Hydrochloric acid using different electrochemical and weight loss measurements. TVE3B showed maximum efficiency 68.6%, where inhibition efficiencies for TVE3A and TVE3C were 62.2% and 65.7% respectively at ambient temperature. The inhibitor mixtures acted as mixed type inhibitors with predominant effect of the anodic reaction. At higher temperatures (at 115°C) TVE3B and TVE3C showed increase of corrosion inhibition whereas for TVE3A efficiency gradually increased up to 60 °C then decreased at temperatures higher than 60 °C.

Three Carbonyl unsaturated compounds were tested as corrosion inhibitors for N80 steel in 20% HCl at 90°C. Results showed that both benzalacetone and cinnamaldehyde are effective in terms of corrosion inhibition due to the inherent structure of the compound and the synergistic effect of inhibitors [59].

Xanthan gum (XG) in addition to its graft copolymer (XG-g-PAM) were investigate to inhibit corrosion of mild steel in 15 % HCl. Various electrochemical polarization, EIS methods, and gravimetric analysis were employed in the study to evaluate effectiveness of candidate material as a corrosion inhibitor. Maximum inhibition efficiencies calculated from the polarization curves with the concentration of 0.4 g/l at 25 °C for XG, and XG-g-PAM were 86.82 % and 92.94% respectively. Adsorption of the inhibitor molecules obeyed Langmuir isotherm.

Table 2.2: Summary of corrosion rate (CR) and inhibition efficiencies (IE%) of various corrosion inhibitors for protecting steel materials in HCl at different temperatures.

Inhibitor	Medium	Testing Temp. °C	Efficiency% or CR	Material	References
Aniline, diphenylamine, <i>n</i> -octylamine, tributylamine, and 1,3-dibutyl-2-thiourea	15% HCl	55	99.5%	API X60	45
Polypropylene glycol (PPG)	15% HCl	55	99.5%	API X60	46
Chromenopyridine derivatives, namely 2-4-diamino-5-phenoxy-5H-chromenochromeno[2,3-b]pyridine-3-carbonitrile (PPC-2) and 2,4-diamino-5-(phenylthio)-5H-chromenochromeno[2,3-b]pyridine-3-carbonitrile (PPC-1)	15% HCl	35	82% and 92%	N80	47
Furfuryl alcohol	15% HCl	110	75%	N80	48
Triazole compound (SAHMT)	15% HCl	25	98.29%	N80	49
Plant extract (<i>Zenthoxylum alatum</i>)	5% HCl	30	95%	Mild Steel	50
Amino acid compounds 1-(1 <i>H</i> benzo[<i>d</i>]imidazole-2-yl)-N-((furan-2-yl)methylene)methanamine (BIFP) and 1-(1 <i>H</i> -benzo[<i>d</i>]imidazole-2-yl)-N-((furan-2-yl)methylene)-2-phenylethana- mine (BIFM)	15% HCl	30	97.5% and 97.7%	N80	51
Pyranopyrazole derivatives namely, 6-amino-4-(4-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3- <i>c</i>]pyrazole-5-carbonitrile (AMPC) and 6-amino-4-(4-chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3- <i>c</i>]pyrazole-5-carbonitrile (ACPC)	15% HCl	30	95.5% and 95.3%	Mild Steel	52
Naphthyridine derivatives, namely 2-amino-4-(4-methoxyphenyl)-1,8-naphthyridine-3-carbonitrile (ANC-1), 2-amino-4-(4-methylphenyl)-1,8-naphthyridine-3-carbonitrile (ANC-2) and 2-amino-4-(3-nitrophenyl)-1,8-naphthyridine-3-carbonitrile (ANC-3)	15% HCl	30	90.2%, 87.0%, and 80.7%	N80	53
Isatin compounds, namely 1-morpholinomethyl-3-(1- <i>N</i> -dithiooxamide)iminoisatin (MMTOI) and 1-diphenylaminomethyl-3-(1- <i>N</i> -dithiooxamide)iminoisatin (PAMTOI)	15% HCl	25	91.23% and 84.33%	N80	54
1-(2-oleylamidoethyl)-2-oleylimidazoline (OAEOI) and 1-(2-aminoethyl)-2-oleylimidazoline (AEOI)	15% HCl	25	90.26% and 96.23%	N80	55
Pyridine derivatives, namely 2-amino-6-(2,4-dihydroxyphenyl)-4-(4-methoxyphenyl)nicotinonitrile (ADP) and 2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile (AMP)	15% HCl	35	90.31% and 87.06%	N80	56
Organic compounds (TVE3A, TVE3B, TVE3C,) Containing formaldehyde and phenol.	15% HCl	25-115	62.2% -88.0%	N80	58
Cinnamaldehyde	20% HCl	90	6.3g/m ² h	N80	59
xanthan gum (XG) and xanthangum-graft-poly(acrylamide) (XG-g-PAM)	15% HCl	25	86.82 % and 92.94%	Mild Steel	60

Chapter 3

3. Experimental Work

3.1. Materials and Materials Preparation

All specimens for the electrodes in electrochemical testing and surface analysis were cold cut from mild steel plate. Test coupons were cut in 1.5 X 1.5 X 0.5 cm size and subject to elemental analysis using optical emission spectrometer (OES), ARL 3460. Table 3.1 illustrates the chemical composition results of the analyzed samples, which resembles the typical composition for ASTM A36 steel. Before conducting each experiment, specimens were individually pretreated in a sequential manner by grinding using Silicon Carbide emery papers from 250 to 4000 grit, and then washed using ethanol for 10 minutes in an ultrasonic bath to release and clean off all contaminants. Distilled water was then used to rinse samples before cleaning with acetone and final drying in hot dry air stream.

Table 3.1: Elemental composition analysis for mild steel testing electrodes.

Element	C	Si	Mn	S	P	Cu	Fe
Weight %	0.128	0.25	0.7	0.03	0.04	0.15	Bal.

The experimental work acidic solution was prepared by diluting analytical hydrochloric having concentration of 36 % acid (HCl) grade in distilled water to produce 5 M % HCl solution. Lauramidopropylamine oxide was used as a test green inhibitor, which is obtained from Shanghai Dejun technology Co., Ltd. The repeating unit of the chemical structure for the subject

inhibitor is shown in figure 3.1.

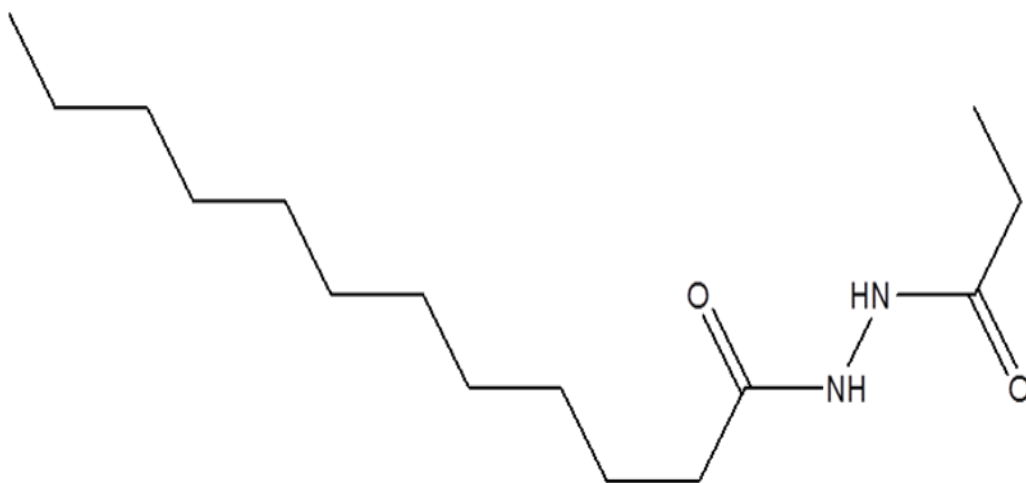


Figure 3.1: Representation of Lauramidopropylamine oxide repeat unit

Viewing of Lauramidopropylamine oxide repeating unit indicates presence of donor atoms i.e. N and O that are important for the adsorption strength and adsorption bond. Presence of these atoms will enhance the overall inhibition efficiency and strengthen the formation of a barrier film [24].

3.2. Electrochemical Measurements

GAMRY Instrument Potentionstat /Galvanostat/ZRA (Reference 3000) was employed to conduct electrochemical measurements using GAMRY frame work, which is based on ESA410. GAMRY system applications include EIS300 for electrochemical impedance spectroscopy (EIS), DC105 for corrosion analysis. A double jacketed corrosion cell with a containment capacity of 250 ml was used. The design of the cell and utilization of Julabo F12 thermostat allowed a precise control of testing temperature starting from 20° C and adding 20 degrees increment until reaching the maximum temperature of 80° C. The testing set up consisted of three electrodes, a counter electrode made of graphite, a working electrode made of mild steel with an exposed area

to the solution of 0.5 cm², , and a saturated calomel reference electrode (SCE). To minimize IR drop the SCE was connected to Luggin capillary. A thermometer was used to monitor temperature of the electrolyte before testing. The open circuit potential (E_{OPC}) of the working electrode is stabilized prior to starting electrochemical testing by placing it in the solutions for 30 minutes. The corrosion behavior of the working electrode was investigated through all temperature with and without the addition of the candidate corrosion inhibitor. Frequencies between the ranges of 0.1 Hz to 100Hz were used to study the corrosion protection offered by inhibitor utilizing electrochemical impedance spectroscopy with 5mV as AC amplitude peak to peak. Potentiodynamic polarization curves were recorded from the cathodic potential value of -250mV to the anodic potential reaching +250mV with respect to the electrode open circuit potential (E_{OPC}). The sweep rate was constant during recording with the value of 0.3mVs⁻¹. After conducting the baseline testing of mild steel substrate in 5M HCl to obtain the data for the blank electrode, Lauramidopropylamine was introduced into the system to study the corrosion protection mechanism in different concentrations 92, 185, 277, and 370 μmol L⁻¹. To ensure reproducibility and accuracy of the measurements all experiments were repeated at least three times and obtained results were averaged out. Figure 3.2 shows the set up of double jacketed corrosion cell with thermostat for temperature control.

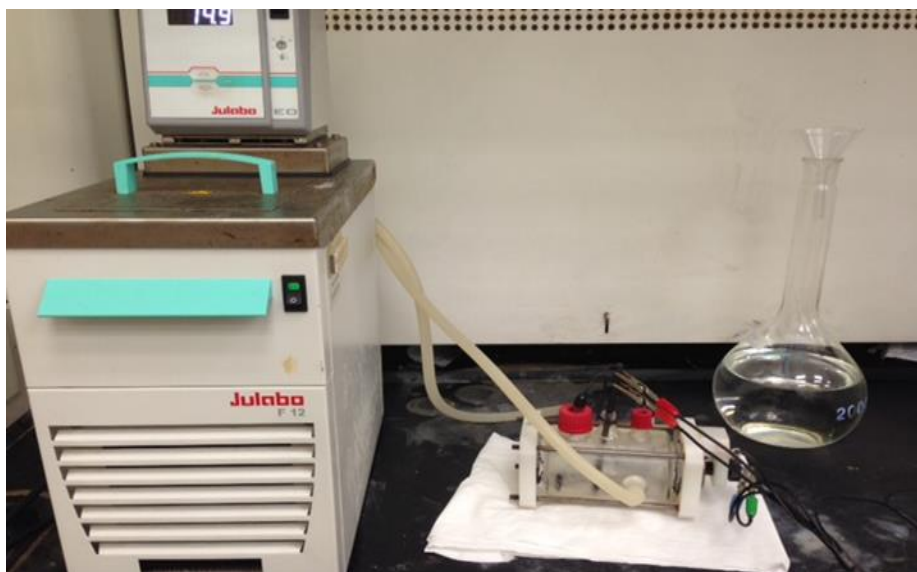


Figure 3.2 Set up of double jacketed corrosion cell with thermostat for temperature control

3.3. Surface Analysis

Surface analysis plays an important role in characterization of surface morphology and in studying inhibitor to substrate interaction and affect. In order to quantify the effect of the corrosive acidic media on the mild steel electrode and study surface topography before and after addition of Lauramidopropylamine inhibitor, immersion tests were conducted. Three mild steel specimens were grinded to 4000 grit and then polished to mirror like appearance using Alumina suspension. The samples were immersed in 5 M HCl solution without the addition corrosion inhibitor for 24 hours at 25°C. Same procedure was repeated but with the addition of 370 $\mu\text{mol L}^{-1}$ of Lauramidopropylamine oxide corrosion inhibitor. The morphology of the samples after immersion in absence of Lauramidopropylamine inhibitor were examined and compared to samples exposed to an inhibited solution using scanning electron microscope (SEM) typically operated with an acceleration voltage of 20kV coupled with energy dispersive spectroscopy (EDS) technique, and atomic force microscopy (AFM).

Chapter 4

4. Results and Discussion:

4.1. Potentiodynamic polarization studies

Figure 4.1 illustrates the potentiodynamic curves of mild steel exposed to 5 M hydrochloric acid solution in absence and in presence of lauramidopropylamine oxide corrosion inhibitor at different concentrations and at different temperatures

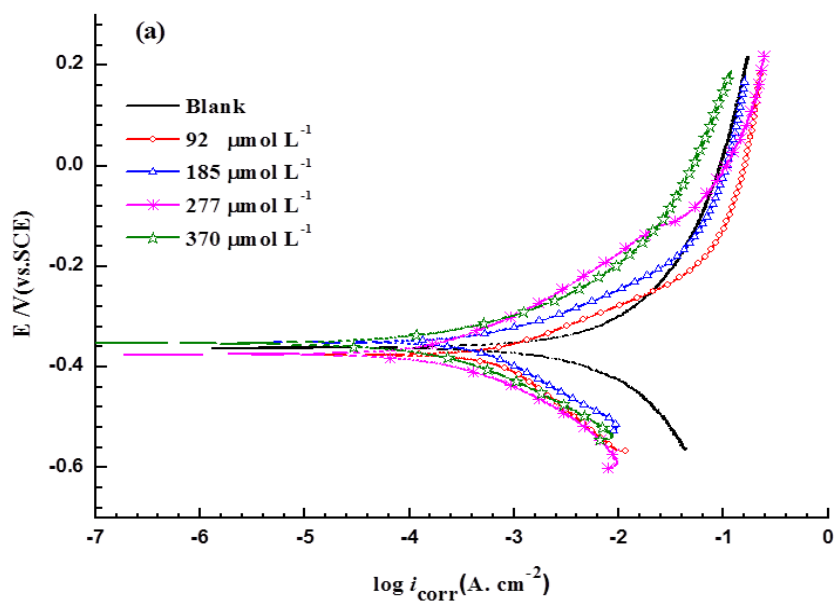


Figure 4.1(a): Representation of mild steel in 5M HCl solution potentiodynamic polarization curves before and after addition of lauramidopropylamine oxide corrosion inhibitor at 20 °C.

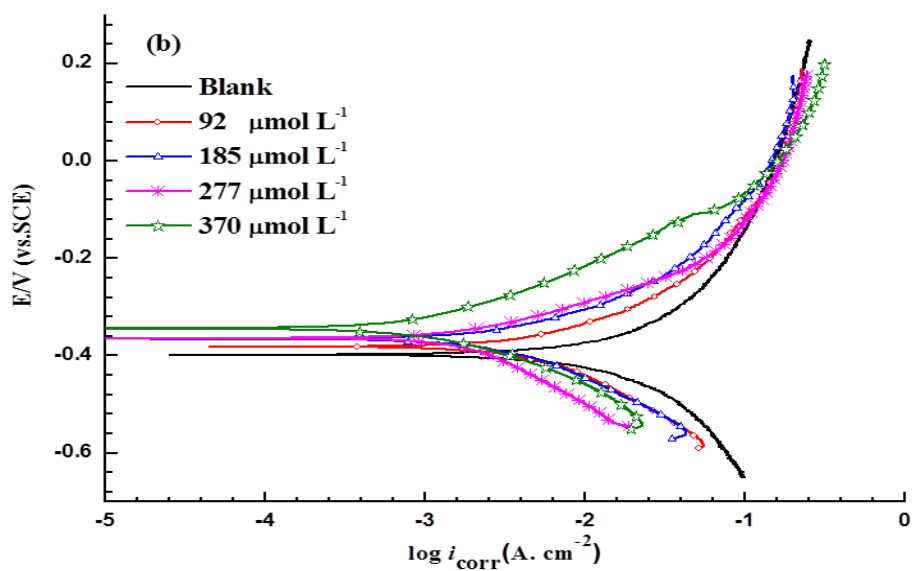


Figure 4.1(b): Representation of mild steel in 5M HCl solution potentiodynamic polarization curves before and after addition of lauramidopropylamine oxide corrosion inhibitor at 40 °C.

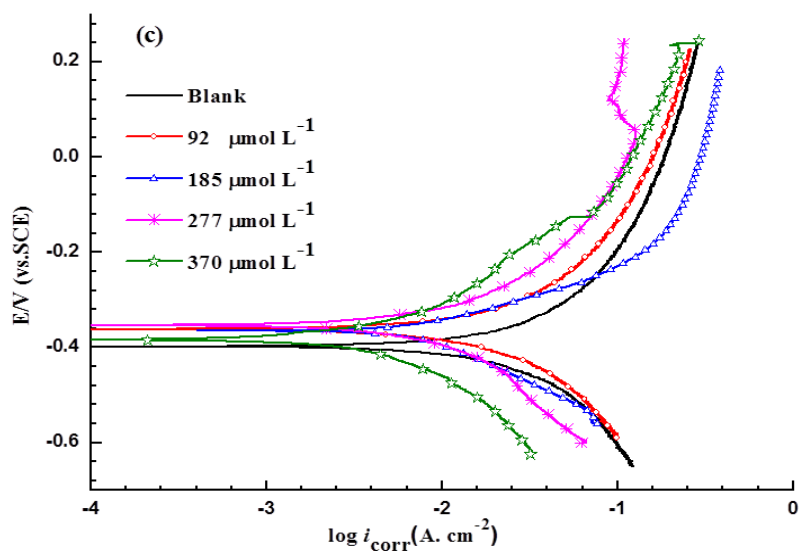


Figure 4.1(c): Representation of mild steel in 5M HCl solution potentiodynamic polarization curves before and after addition of lauramidopropylamine oxide corrosion inhibitor at 60 °C.

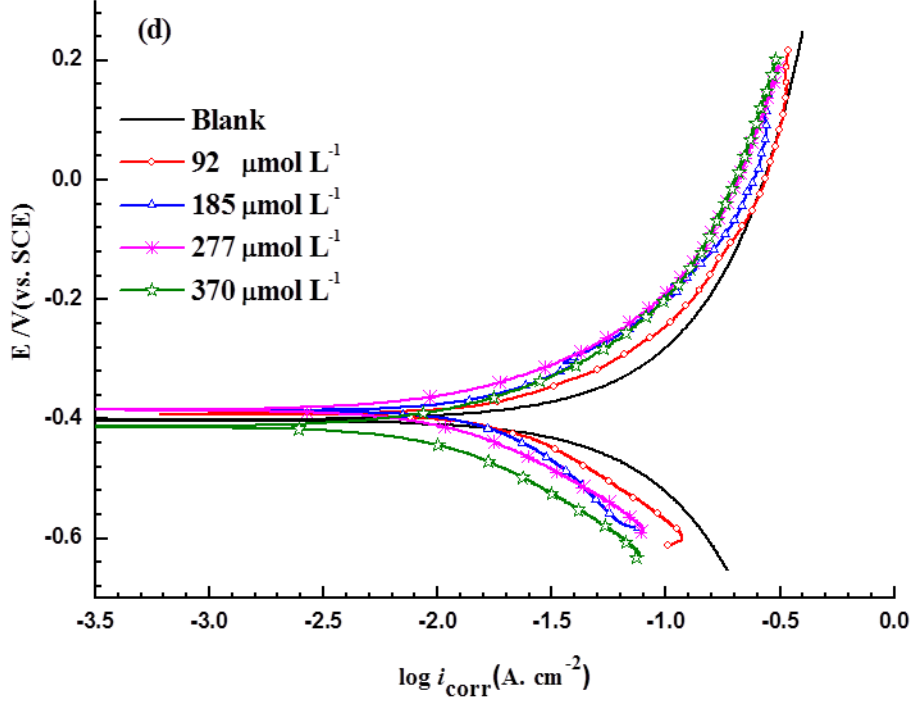


Figure 4.1(d): Representation of mild steel in 5M HCl solution potentiodynamic polarization curves before and after addition of lauramidopropylamine oxide corrosion inhibitor at 80 °C.

After extrapolation of the above linear logarithmic Tafel plots and intersecting them, important electrochemical corrosion parameters as corrosion current (i_{corr}), corrosion potential (E_{corr}) were obtained. Cathodic Tafel slope (β_c), and anodic Tafel slope (β_a) were also calculated and presented in Table 4.1.

Inhibition efficiency percentage (IE%) as well as degree of surface coverage in Table 4.1 were calculated using equation (1), and (2) respectively.

$$IE\% = \left(\frac{i_1 - i_2}{i_1} \right) \times 100 \quad (1)$$

$$\theta = \frac{IE\%}{100} \quad (2)$$

Where i_1 and i_2 represent respectively the corrosion currents obtained before the addition of the inhibitor to the environment and after adding tested corrosion inhibitor.

Stern-Geary below equation was utilized to calculate the polarization resistance for the test specimens in the 5 M HCl solution in presence and absence of corrosion inhibitor [57].

$$R_p = \frac{b_c b_a}{2.303 i_{\text{corr}}(b_c + b_a)} \quad (3)$$

Table 4.1: Potentiodynamic polarization parameters for mild steel in 5 M HCl solution in absence and presence of lauramidopropylamine oxide corrosion inhibitor at different temperatures.

T (°K)	C_{inh} $\mu\text{mol L}^{-1}$	b_a (V decade ⁻¹)	$-b_c$ (V decade ⁻¹)	R_p $\Omega \text{ cm}^2$	E_{corr} (mV) SCE	i_{corr} (mA cm ⁻²)	$IE\%$	θ
293	--	0.14	0.19	25.1	358	1.4	--	--
	92	0.1	0.162	51.6	376	0.52	62	0.62
	185	0.08	0.153	76.1	349	0.3	78	0.78
	277	0.06	0.146	97.2	380	0.19	86	0.86
	370	0.03	0.131	117.7	354	0.08	94	0.94
313	--	0.21	0.261	9.7	399	5.2	--	--
	92	0.184	0.241	18.8	380	2.4	53	0.53
	185	0.179	0.221	25.2	362	1.7	67	0.67
	277	0.165	0.211	34.6	358	1.16	77	0.77
	370	0.153	0.209	51.8	342	0.74	86	0.86
333	--	0.23	0.298	4.8	396	11.7	--	--
	92	0.188	0.285	6.9	360	7.1	39	0.39
	185	0.18	0.281	8.2	364	5.8	50	0.5
	277	0.171	0.276	10.7	354	4.3	63	0.63
	370	0.165	0.269	14.3	347	3.1	73	0.73
353	--	0.242	0.302	3.4	398	17.2	--	--
	92	0.197	0.32	3.8	390	13.9	19	0.19
	185	0.185	0.298	4.5	386	11.1	35	0.35
	277	0.181	0.287	5.4	382	8.9	48	0.48
	370	0.173	0.278	7.1	412	6.6	61	0.61

Table 4.1 when analyzed reveals a direct relation between inhibitor concentration and corrosion reduction tendency. A gradual increase in inhibition efficiency in correspondence to the increase in inhibitor's dosage is evident. A maximum inhibition efficiency of 94% was attained at a testing temperature of 25°C and with the addition of 370 $\mu\text{mol L}^{-1}$ from the tested corrosion inhibitor. The corrosion current density (i_{corr}) decreases appreciably in line with the increase dosage of corrosion inhibitor reaching a minimum value of less than 0.08 mAcm^{-2} at the same dosage of maximum efficiency, which validates the high inhibition and film forming capability of lauramidopropylamine oxide [12]. The parallel anodic and cathodic Tafel lines and the relatively constant slopes suggest that Hydrogen evolution reaction is primarily activation controlled [15]. Related literature survey indicated that if the shift in corrosion free potential E_{corr} after addition of inhibitor is more than 85mVSCE in the anodic or cathodic direction, then the inhibitor can be classified as anodic or cathodic respectively. Otherwise the inhibitor is considered influential for both reactions. The overall shift in E_{corr} in this study after the addition of corrosion inhibitor was found insignificant i.e. less than 85mV versus SCE in polarization direction. This proves that the inhibitor suppresses both the anodic as well as the cathodic reactions and hence can be categorized as a mixed type- inhibitor [13, 14]. The E_{corr} displacement is in the positive direction suggesting that the inhibitor is mixed- inhibitor but dominated by anodic reaction.

Figure 4.1 a) shows a kink in the anodic polarization curve at 20°C and at low concentration of corrosion inhibitor, that could be attributed to the following: (i) Alteration in the surface area covered with the corrosion inhibitor due to the rearrangement of the adsorbed inhibitor molecules to the electrode surface and/or (ii) destabilization and delamination of the thin

protective film formed over the substrate. Similar kinks witnessed at higher temperature and inhibitor concentration could be caused by either the desorption of the inhibitor from the surface or to a local change in inhibition mechanism for the anodic reaction [16].

4.2. EIS Studies

Electrochemical impedance spectroscopy is another crucial electrochemical technique employed widely to investigate and provide deep insight into the protection against corrosion by using corrosion inhibitors. It provides useful information about kinetic and mechanistic of electrochemical systems [24]. A small potential perturbation having the range of 5 to 50 mV is utilized along a range of frequencies starting from 100 kHz to 10 mHz. Impedance values represented in Real Z' and imaginary Z'' numbers are obtained from the corresponding frequency to develop a mathematical relation, which is represented in a form of Nyquist plot. Taking into account the shape of the plotted Nyquist, the system under study that consist of working electrode, electrolytic solution, and adsorbed inhibitor can be modeled in a form of equivalent circuit comprises number of important element include charge-transfer resistance R_{ct} , electrochemical solution resistance R_s , and double layer capacitance C_{dl} . Corrosion protection mechanism while using corrosion inhibitors can be analyzed reliably through interpretation of equivalent circuit components. Corrosion inhibition efficiency increases in direct relation to the value of charge transfer resistance R_{ct} , whereas the double layer capacitance at the interface C_{dl} decreases with better inhibition [10]. Corrosion inhibition efficiency is analyzed by comparing impedance curves in absence and in presence of tested corrosion inhibitor. Figure 4.2 shows a typical equivalent electrical circuit used to analyze the measured impedance of an electrolyte

subject to uniform corrosion. The circuit as indicated above comprises charge transfer resistance R_{ct} , electrochemical solution resistance R_s , and CPE which is the constant phase element used to describe the non-ideal behavior of the double layer attributed mainly to insufficient surface coverage and surface roughness. Below circuit has been used previously to model iron- acid interface corrosion [25].

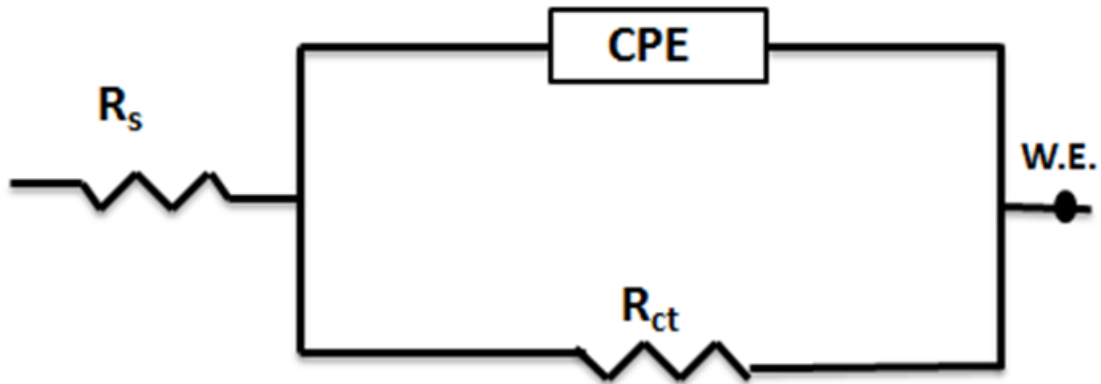


Figure 4.2: Representation of equivalent circuit used to analyze and fit Electrochemical Impedance Spectroscopy EIS spectra for mild steel in 5 M HCl.

The impedance of the constant phase element was analyzed using below equation [26]:

$$Z_Q = [Y_0 (j\omega)^n]^{-1} \quad (4)$$

Where Z_Q represent the constant phase element CPE impedance ($\Omega \text{ cm}^{-2}$), Y_0 is CPE constant, ω is the frequency in radians / sec (rad s^{-1}) and the values n falls between 0 and 1 defining the diverging from capacitance linearity. When $n = 1$, then the CPE constant Y_0 behaves as an ideal capacitor. When $n = 0$, Y_0 becomes equivalent to that of a resistor.

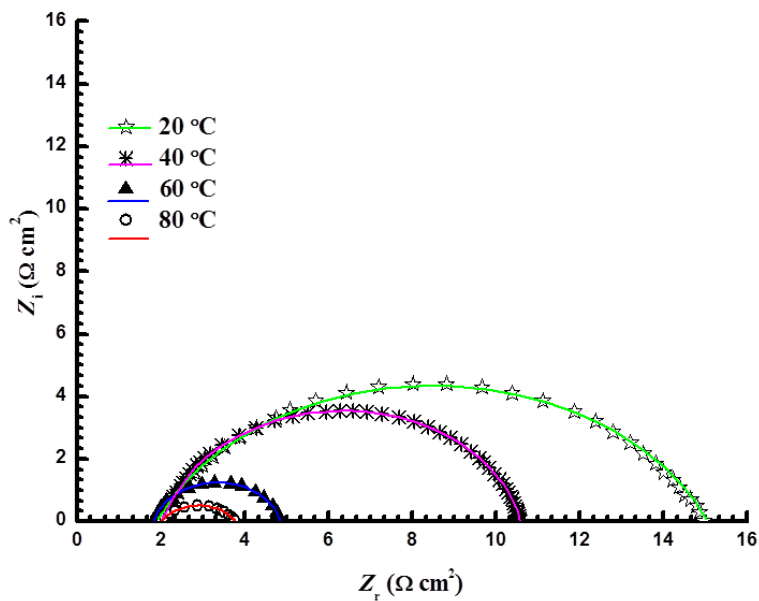


Figure 4.3: (a) Representation of mild steel in 5 M HCl Nyquist plots at different temperatures in absence of tested corrosion inhibitor.

The measured (Broken lines) and fitted (Solid lines) of electrochemical impedance spectroscopy spectra are shown in figure 4.3 (a) in a form of Nyquist. Different curves for the mild steel in 5 M HCl in absence of corrosion inhibitor at 20, 40, 60, 80 °C were established and fitted using electrochemical equivalent circuit explained in figure 4.2. By viewing 4.3 (a) it is apparent that the size of Nyquist semicircle plot decreases as temperature incrementally increases from 20 to 80 °C.

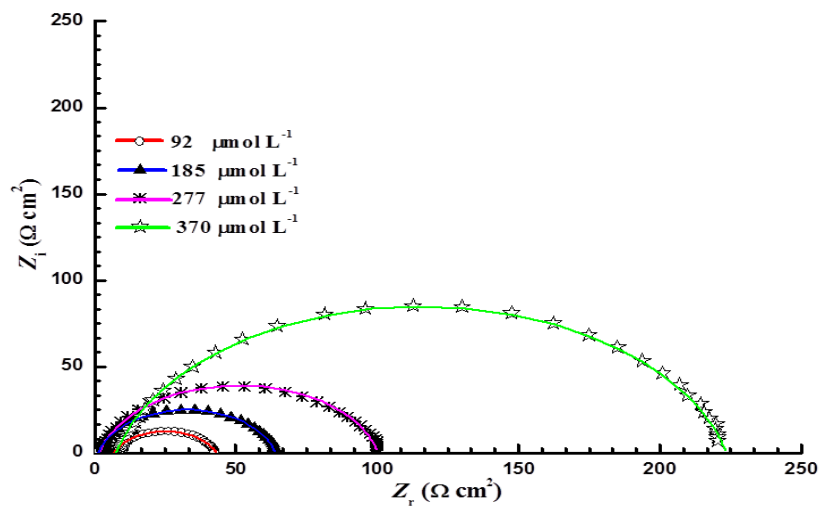


Figure 4.3: (b) Representation of mild steel in 5 M HCl Nyquist plots in presence of different concentrations of lauramidopropylamine oxide corrosion inhibitor at 20 °C

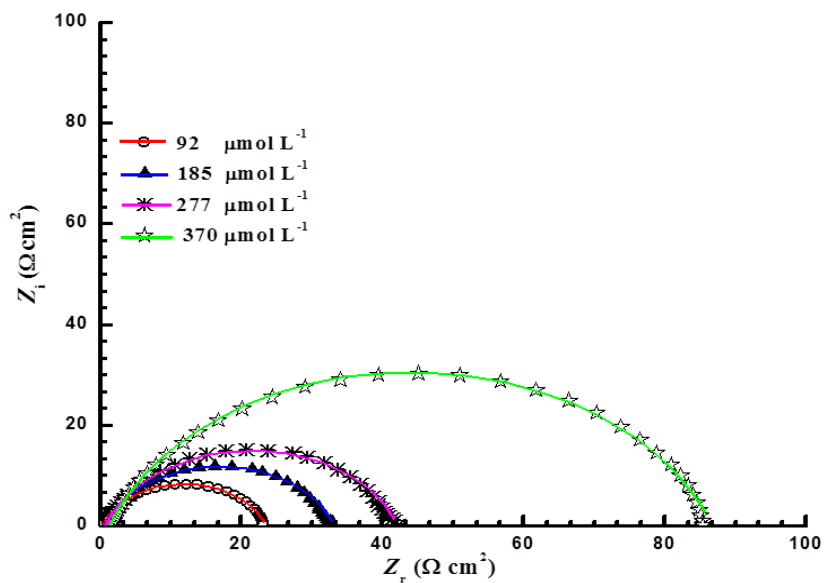


Figure 4.3: (c) Representation of mild steel in 5 M HCl Nyquist plots in presence of different concentrations of lauramidopropylamine oxide corrosion inhibitor at 40 °C

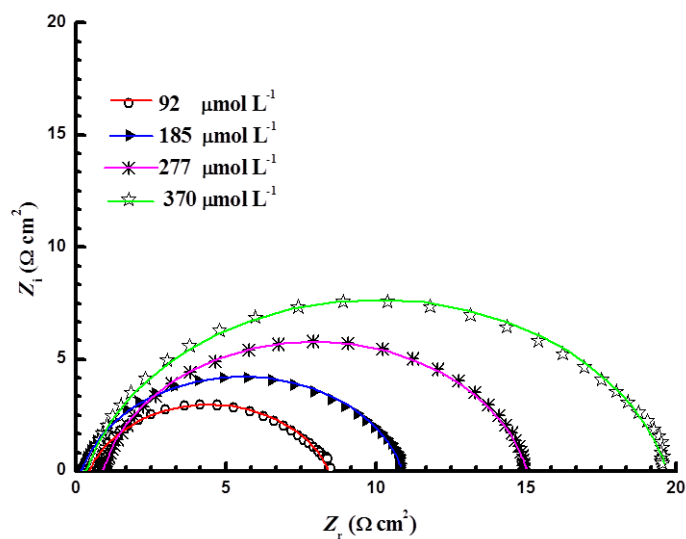


Figure 4.3: (d) Representation of mild steel in 5 M HCl Nyquist plots in presence of different concentrations of lauramidopropylamine oxide corrosion inhibitor at 60 °C

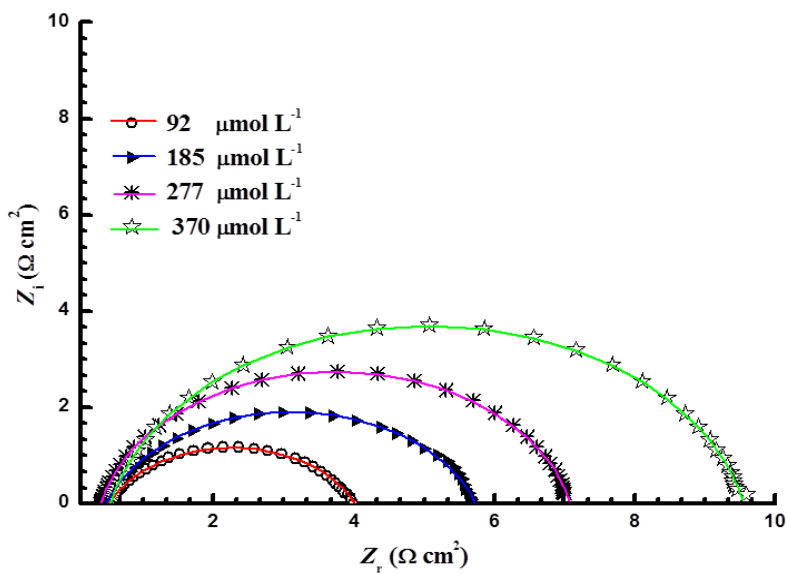


Figure 4.3: (e) Representation of mild steel in 5 M HCl Nyquist plots in presence of different concentrations of lauramidopropylamine oxide corrosion inhibitor at 80 °C

Similar to figure 4.3 (a), figures 4.3 (b), 4.3 (c), 4.3 (d), and 4.3 (e) represent the Nyquist plots of mild steel exposed to 5 M HCl solution in presence of different concentrations of lauramidopropylamine oxide corrosion inhibitor at (b) 20, (c) 40, (d) 60, (e) 80 °C, The range of the frequency was between 0.1 Hz to 100 kHz with 5mV as AC amplitude peak to peak. The low impedance modulus (Z) increases in line with the increase in inhibition concentration as an indication of increased adsorption of the inhibitor molecules to the metallic substrate [27].

Table 4.2 tabulates the electrochemical parameters gained from fitting of the measured data from Nyquist plots including charge transfer resistance R_{ct} , constant phase element (CPE), Y_0 and n parameters.

Using the charge transfer resistance obtained from the impedance measurements before and after addition of lauramidopropylamine oxide corrosion inhibitor to the 5 M HCl, the inhibition efficiency is calculated using the following equation:

$$IE\% = \left(\frac{R_{ct1} - R_{ct2}}{R_{ct1}} \right) \times 100$$

Where, R_{ct1} and R_{ct2} represent the charge transfer resistance with and without the addition of lauramidopropylamine oxide corrosion inhibitor respectively. The extent of surface coverage (Θ) by corrosion inhibitor was calculated using equation (2).

Charge transfer resistance (R_{ct}), and constant phase parameters (Y_0 and n) were used to calculate the metal solution interface double layer capacitance (C_{dl}) using following expression:

$$C_{dl} = (Y_0 R_{ct}^{1-n})^{1/n} \quad (6)$$

Y_0 and n were identified before as CPE constant and exponent respectively. (n) is an important

exponent the defines the deviation from idealism and it varies from 0-1.

Table 4.2 when examined reveals that the charge transfer resistance increases with respect to the increase in the concentration of corrosion inhibitor as compared to the baseline value in absence of the inhibitor. This increase in resistance is attributed to the adsorption of a barrier film of the metallic substrate. On the contrary to the charge transfer resistance increase the interface double layer capacitance (C_{dl}) gradually decreases on increasing the concentration of lauramidopropylamine oxide corrosion inhibitor. The decrease in interface capacitance is primarily caused by the following (i) A reduced value of the dielectric parameter (ϵ) due to replacement of water species by inhibitor's molecules , (ii) Thickness increase of the double layer (δ) because of the adsorption of the inhibitor to the surface as indicated by Helmholtz equation

$$C_{dl} = \frac{\epsilon \epsilon_0 A}{\delta} \quad (7)$$

Where, A represents the cross sectional area of the electrode and ϵ_0 the dielectric constant for air.

The inhibition efficiency $IE\%$ increases as the concentration of the corrosion inhibitor increases as seen in table 4.2.

It is important to note that the value CPE exponent n has increased with the addition of lauramidopropylamine oxide corrosion inhibitor than without. The higher positive values for n parameter indicate that the CPE reaches the condition of an ideal capacitor with respect to the concentration increase of corrosion inhibitor. This is primarily attributed to the homogeneity in surface coverage of the substrate with the dosed corrosion inhibitor in addition to the uniformity

of the corrosion rate exerted upon increase of corrosion inhibitor concentration. The measurements obtained from EIS are apparently consistent with the Tafel results summarized in table 4.1.

Table 4.2: EIS corrosion parameters for Mild Steel in 5 M HCl solution at different temperatures in absence and in presence of lauramidopropylamine oxide corrosion inhibitor.

T (°C)	C_{inh} $\mu\text{mol L}^{-1}$	R_{ct} $\Omega \text{ cm}^2$	CPE		$Cdl, \mu F$	$IE\%$	θ
			$Y_0 \times 10^{-6} \text{ s}^n \text{ ohm}^{-1} \text{ cm}^{-2}$	n			
20	0	15.1	751	0.810	--	--	--
	92	44.2	641	0.743	65.83	65.83	0.658
	185	62.3	610	0.720	75.76	75.76	0.757
	277	100.2	550	0.697	84.93	84.93	0.849
	370	210.4	524	0.625	93.0	92.82	0.928
40	0	10.5	772	0.826	--	--	--
	92	23	656	0.784	54.34	54.34	0.543
	185	33	621	0.766	68.18	68.18	0.682
	277	42	566	0.758	75	75	0.75
	370	85	533	0.734	87.64	87.64	0.876
60	0	4.8	818	0.857	--	--	--
	92	8.5	781	0.827	43.52	43.52	0.435
	185	10.8	761	0.801	55.55	55.55	0.556
	277	15.2	732	0.789	68.42	68.42	0.68
	370	19.5	714	0.761	75.38	75.38	0.754
80	0	3.4	885	0.894	--	--	--
	92	4	826	0.864	15	15	0.15
	185	5.5	806	0.839	38.18	38.18	0.38
	277	7	784	0.816	51.42	51.42	0.514
	370	9.6	764	0.792	64.58	64.58	0.646

4.3. Adsorption isotherm and thermodynamic calculations

Adsorption isotherms are used extensively to illustrate and describe the interaction between the applied corrosion inhibitor and the metallic substrate. The effectiveness and characteristics of the corrosion inhibitors adsorption to the surface is a key step in the overall inhibition process.

Dependence of the inhibitor's efficiency on the inhibitor dosed concentration is well described using isotherms. The adsorption of an organic inhibitor to the metal surface in an aqueous solution is usually considered as a quasi-substitution process in which inhibitor molecules replaces number of solvent atoms e.g. water in a fixed size ratio [17].

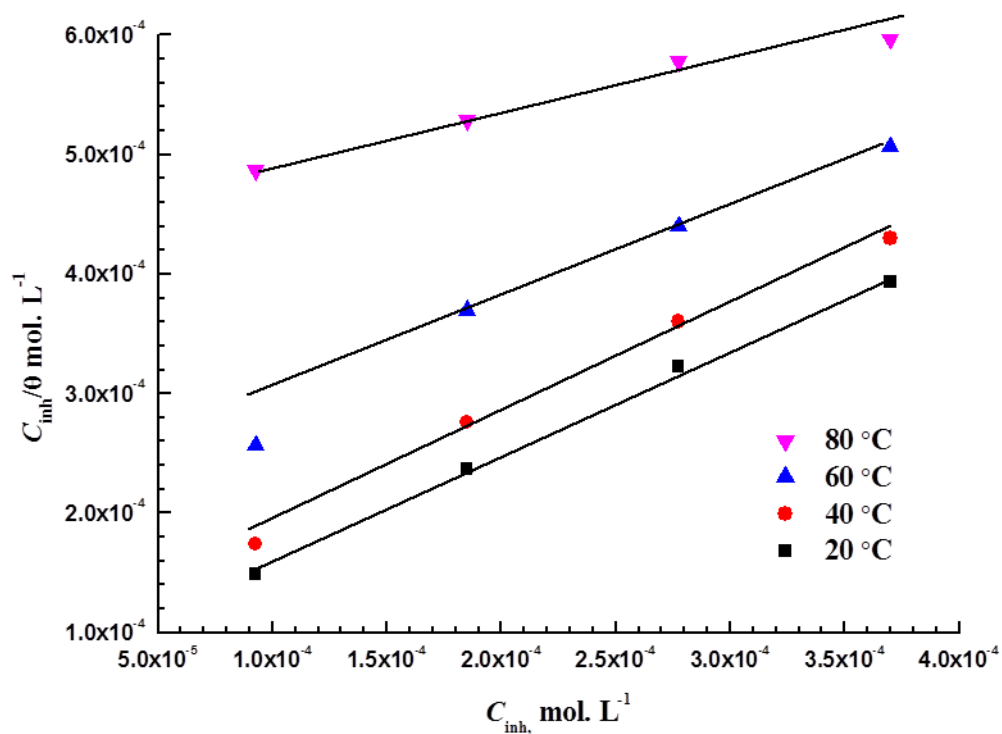


Figure 4.4: Representation of mild steel in 5 M HCl Langmuir adsorption plots at different temperatures

In order to define the best fit isotherm that describes the inhibition process, the relationship between the inhibitor concentration (C_{inh}) and the degree of inhibitor surface coverage (θ) should be determined. It is appropriately assumed that the surface coverage does not differ

substantially from the inhibition efficiency (IE%) [18]. Number of isotherms were evaluated including Langmuir, Frumkin, and Temkin. Langmuir was by far the best fit aligned with the experimental data collected for the tested corrosion inhibitor. The Langmuir isotherm relates C_{inh} and Θ as follows:

$$\frac{C_{inh}}{\Theta} = \frac{1}{K_{ads}} + C_{inh} \quad (4)$$

Where C_{inh} is the concentration of the inhibitor; Θ is the extent of surface coverage; and K_{ads} is the adsorption process equilibrium constant.

Figure 4.2 shows the dependence of the C_{inh}/Θ against C_{inh} at different temperatures.

The standard Gibbs free energy change of adsorption (ΔG_{ads}^0) can be readily calculated using equation (5) after calculating the constant of adsorption (K_{ads}) by interpolation of the straight lines $C_{inh}/\Theta - axis$.

$$K_{ads} = \frac{1}{55.5} e^{-\frac{\Delta G_{ads}^0}{RT}} \quad (5)$$

Where R is the universal gas constant, T is the temperature in Kelvin, The 55.5 value represents the concentration of water molecules in the solution in mol/l [20].

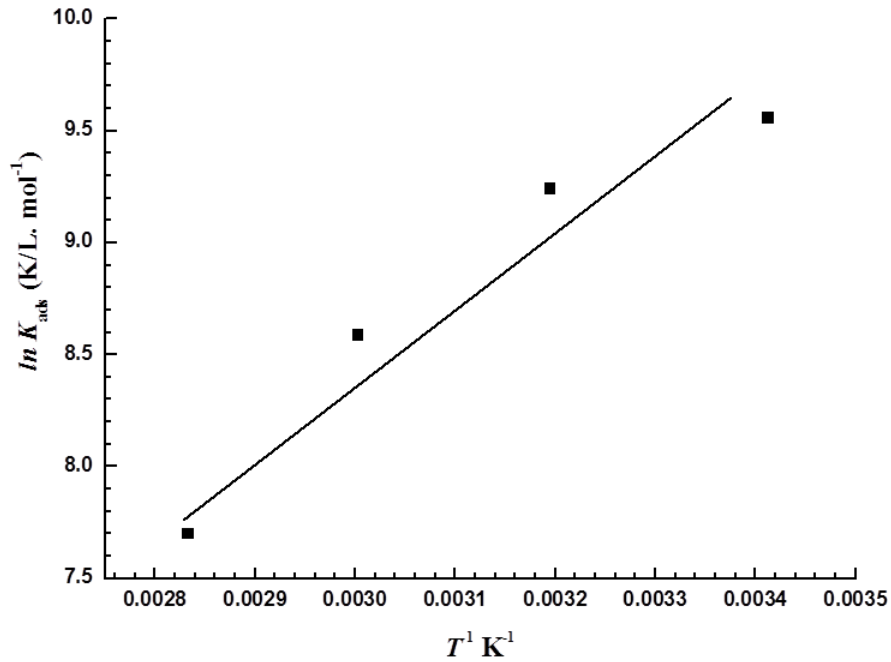


Figure 4.5: Relationship between $\ln K_{\text{ads}}$ and $1/T$ for the lauramidopropylamine oxide corrosion inhibitor at mild steel surface in 5 M HCl solution.

By plotting $\ln K_{\text{ads}}$ versus $1/T$ as shown in figure 4.5, a straight line was obtained, that follows the Van't Hoff equation (6) [19]

$$\ln K_{\text{ads}} = \frac{-\Delta H^{\circ}_{\text{ads}}}{RT} + \frac{\Delta S^{\circ}_{\text{ads}}}{R} \quad (6)$$

Where, $\Delta S^{\circ}_{\text{ads}}$ and $\Delta H^{\circ}_{\text{ads}}$ are the entropy changes and the standard enthalpy of adsorption, respectively.

By getting $\Delta H^{\circ}_{\text{ads}}$ from the slope of equation (6), the entropy change of adsorption $\Delta S^{\circ}_{\text{ads}}$ was calculated utilizing equation (7);

$$\Delta G^{\circ}_{\text{ads}} = \Delta H^{\circ}_{\text{ads}} - T \Delta S^{\circ}_{\text{ads}} \quad (7)$$

Table 4.3 lists the values of thermodynamic parameters $\Delta H^{\circ}_{\text{ads}}$, $\Delta S^{\circ}_{\text{ads}}$, K_{ads} , and $\Delta G^{\circ}_{\text{ads}}$, for the lauramidopropylamine oxide corrosion inhibitor at the mild steel surface in 5 M HCl.

Table 4.3: Thermodynamic parameters derived and calculated from Langmuir model at different temperatures

Temperature, K	K_{ads} (L/ mole)	$\Delta G^{\circ}_{\text{ads}}$ (kJ mol ⁻¹)	$\Delta H^{\circ}_{\text{ads}}$ (kJ mol ⁻¹)	$\Delta S^{\circ}_{\text{ads}}$ (J mol ⁻¹ K ⁻¹)
293.15	14139	-33.1	-27.7	18.5
313.15	10337	-34.5	-27.7	21.8
333.15	5354	-34.8	-27.7	21.4
353.15	2211	-34.4	-27.7	19.1

The positive values of entropy change of adsorption $\Delta S^{\circ}_{\text{ads}}$ indicate that the adsorption of the corrosion inhibitor to the mild steel surface is accompanied by an increase in the system entropy. This is attributed to the absorption process, which is exothermic in nature as seen from the negative value of standard enthalpy of adsorption $\Delta H^{\circ}_{\text{ads}}$.

The high value for the constant of adsorption (K_{ads}), particularly at 25° C, for the studied lauramidopropylamine oxide corrosion inhibitor indicate signs of strong adsorption to the mild steel substrate. Large K_{ads} values suggest strong adsorption tendency, hence better inhibition performance. This is explained by the presence of π -electrons in the inherent inhibitor's molecular structure [21].

The negative values of calculated $\Delta G^{\circ}_{\text{ads}}$ are aligned with the spontaneity of the inhibitor adsorption to the metal as well as indicate strong bond between them. $\Delta G^{\circ}_{\text{ads}}$ values are usually interpreted in relation to the nature of the adsorption process, whether it is physisorption or chemisorption. Generally if the values of $\Delta G^{\circ}_{\text{ads}}$ are up to - 20 kJ mol⁻¹ then physisorption

mechanism is favored, while if the values of $\Delta G^{\circ}_{\text{ads}}$ are around -40 kJ mol^{-1} or higher, then the adsorption process is consistent with chemisorption. The latter adsorption process involves charge sharing or transfer from the inhibitor's molecule to the protected surface to form a coordinated bond.

As seen in table 4.3, the obtained $\Delta G^{\circ}_{\text{ads}}$ for inhibition of mild steel corrosion in 5 M hydrochloric acid solution using lauramidopropylamine oxide corrosion inhibitor ranges from -33.1 to $-34.8 \text{ kJ mol}^{-1}$, which is higher than -20 kJ mol^{-1} but less than -40 kJ mol^{-1} . Thus, cannot be classified as neither chemisorption nor physisorption typical adsorption process. This implies that the adsorption process involved in this work is a mix of both chemisorption and physisorption.

4.4 Effect of activation energy and temperature on corrosion rate

Inhibition mechanism and efficiency are directly influenced by the apparent activation energy (E_a) [22]. The rate of almost all chemical reactions tends to increase as the temperature increases [1]. It is of paramount importance to calculate the activation energy in presence and absence of lauramidopropylamine oxide corrosion inhibitor at different temperatures. The effect of temperature on corrosion rate of mild steel can be evaluated using the Arrhenius equation:

$$\log CR = \log A - \frac{E_a}{2.303 RT} \quad (8)$$

Where CR is the corrosion rate expressed in corrosion current density (i) of the metal in the acidic solution at a specific temperature (T), (E_a) is the activation energy, R is the universal gas constant, and A is the Arrhenius constant that is affected by the metal type and electrolyte

composition.

Arrhenius plot of the mild steel logarithmic current density ($\log i$) versus $1/T$ in absence and in presence of corrosion inhibitor are given in figure 4.6 with a linear regression rate that is close to unity.

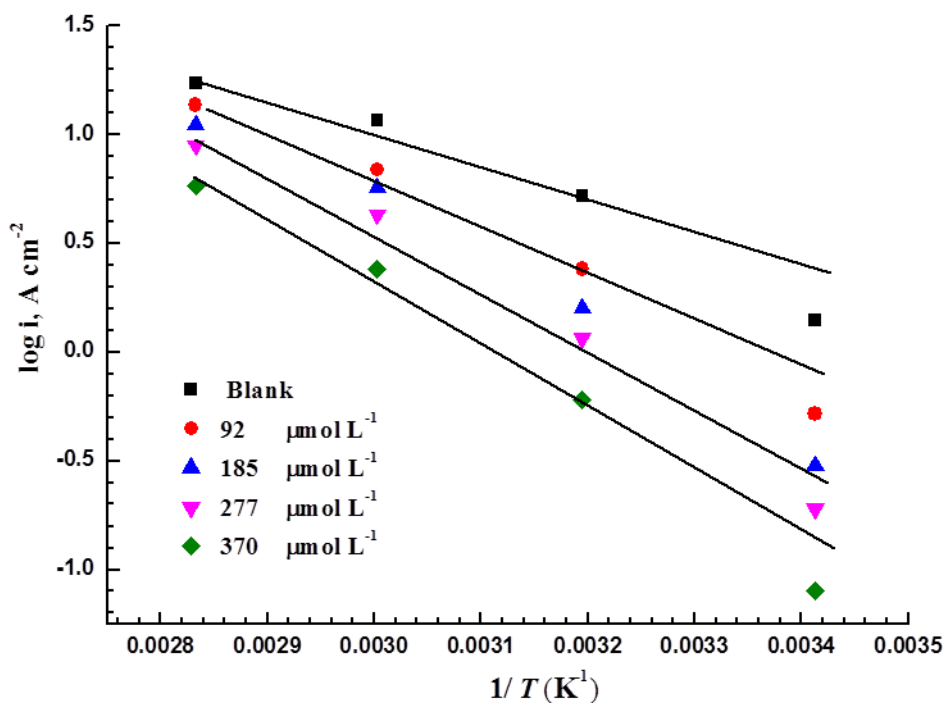


Figure 4.6: Arrhenius plots for the corrosion current densities ($\log i$) versus $1/T$ for mild steel at different concentrations of the lauramidopropylamine oxide corrosion inhibitor in 5 M HCl

The apparent activation energy (E_a) calculated from the inclination of the above Arrhenius plots in 5M HCl are listed in table 44. It is apparent from the table that activation energy (E_a) increases as the inhibitor dosage is increased. The higher value of (E_a) is attributed to the corrosion

inhibitor attachment and formation of barrier film at the surface of the mild steel.

The entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*) due to the dissolution of mild steel in 5 M HCl were calculated using Arrhenius equations:

$$CR = \frac{RT}{Nh} \exp \frac{\Delta S^*}{R} \exp \frac{-\Delta H^*}{RT} \quad (8)$$

Where h is Planck's constant, R is universal gas constant (8.314 J mol⁻¹ K⁻¹) N is Avogadro's number and ΔH^* and ΔS^* are the enthalpy and entropy of activation, respectively.

As in figure 4.4 straight lines were obtained by plotting log i/T versus 1/T at different concentrations of lauramidopropylamine oxide corrosion inhibitor. The slope of ($\Delta H^*/2.303R$) and the intercept of [$\log (R/ Nh) + ((\Delta S^*) / 2.303R)$] were used to calculate the enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) respectively.

The positive values of the calculated enthalpy of activation (ΔH^*) in table 4.4 indicate an evidence of endothermic nature of the mild steel dissolution, which suggests suppression of metallic dissolution after introduction of corrosion inhibitor to the solution. In addition to this, the average difference between apparent activation energy (E_a) and calculated enthalpy of activation (ΔH^*) falls around 2.6 kJ mol⁻¹ for each test, which is almost equal to the value of RT (2.63 kJ mol⁻¹). This finding aligns with the suggestion that the dissolution of mild steel in this environment is a unimolecular reaction [23].

Table 4.4: Activation Energy (E_a), regression coefficient (r^2), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) for mild steel in 5 M HCl in the absence and presence of different concentrations of lauramidopropylamine oxide corrosion inhibitor.

Conc. of inhibitor $\mu\text{mol L}^{-1}$	E_a (kJ mol^{-1})	r^2	ΔH^* (kJ mol^{-1})	ΔS^* ($\text{J mol}^{-1} \text{K}^{-1}$)
0	36.3	0.95	33.6	-126
92	47.1	0.97	44.4	-97
185	52.5	0.97	49.8	-84
277	55.7	0.97	53.1	-76
370	61.7	0.98	59	-63

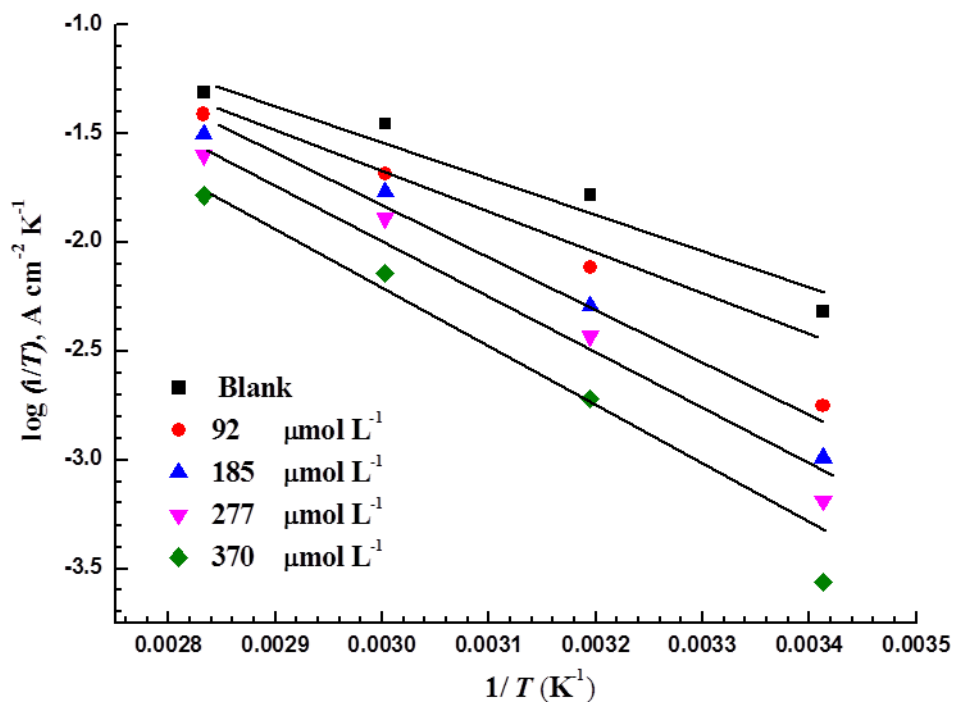


Figure 4.5: Transition-state plots of $\log(i/T)$ versus $1/T$ for mild steel in 5 M HCl in the absence and presence of different concentrations of the lauramidopropylamine oxide corrosion inhibitor

4.5. Surface Topography and Characterization

4.5.1. Scanning electron microscope (SEM) analysis

Figure 4.7 (a)-(C) depicts the SEM images under 5000X magnification for studying the mild steel surface (a) just after grinding with 4000 SiC paper, (b) in 5MHCl without the addition of corrosion inhibitor and (c) in the presence of $370 \mu\text{mol L}^{-1}$ of lauramidopropylamine oxide corrosion inhibitor. The testing temperature was maintained at 20°C while conducted all experiments. The morphology of the SEM image for the sample before immersion (Fig. 4.7(a)) shows a smooth surface with no visible signs of corrosion under 5000X magnification. Upon retrieving the sample from the uninhibited 5 Molar hydrochloric acid solution the surface was examined using scanning electron microscope and found severely deteriorated as depicted in SEM image (Fig. 4.7(b)). When immersion test was repeated in the presence of $370 \mu\text{mol L}^{-1}$ of lauramidopropylamine oxide corrosion inhibitor, significant corrosion suppression was noted with a relatively smooth surface (Fig. 4.7(c)) suggesting formation of barrier film. Therefore, the enhancement of the surface morphology while decreasing 5M HCl attach both support the inhibition capabilities of lauramidopropylamine oxide corrosion inhibitor

EDX was conducted to examine the elemental composition of the samples with and without the addition of lauramidopropylamine oxide corrosion inhibitor at 20°C . Presence of Nitrogen on the metallic substrate was detected during analysis, which validates the adsorption and attachment of the corrosion inhibitor molecules onto the surface. The results of EDX analysis are summarized in table 4.5

Table 4.5: Elemental composition breakdown of blank mild steel electrode in absence and in presence of $370 \mu\text{mol L}^{-1}$ of lauramidopropylamine oxide corrosion inhibitor after immersion period of 24 h, at 20°C .

EDX results sample/Spectrum	%C	%Fe	%Cl	%Mn	%N
Mild Steel	4.54	89.00	0.00	6.46	0.00
Mild Steel immersed in 5M HCl	4.95	87.30	0.69	7.06	0.00
Mild Steel immersed in 5M HCl + $370 \mu\text{mol L}^{-1}$ of Inhibitor	5.31	85.80	0.84	6.18	1.87

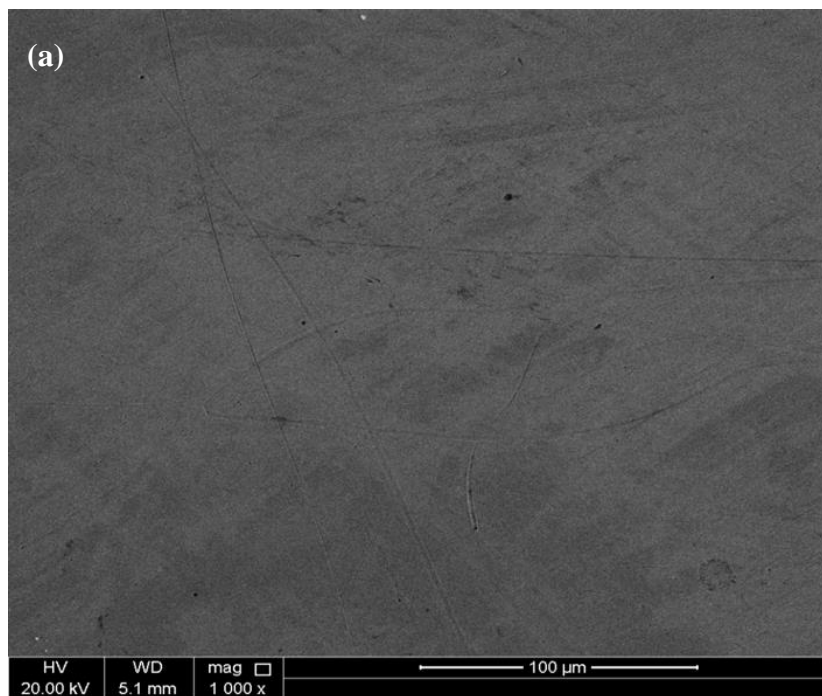


Figure: 4.6 (a): SEM surface analysis micrograph for blank mild steel surface at 20°C .

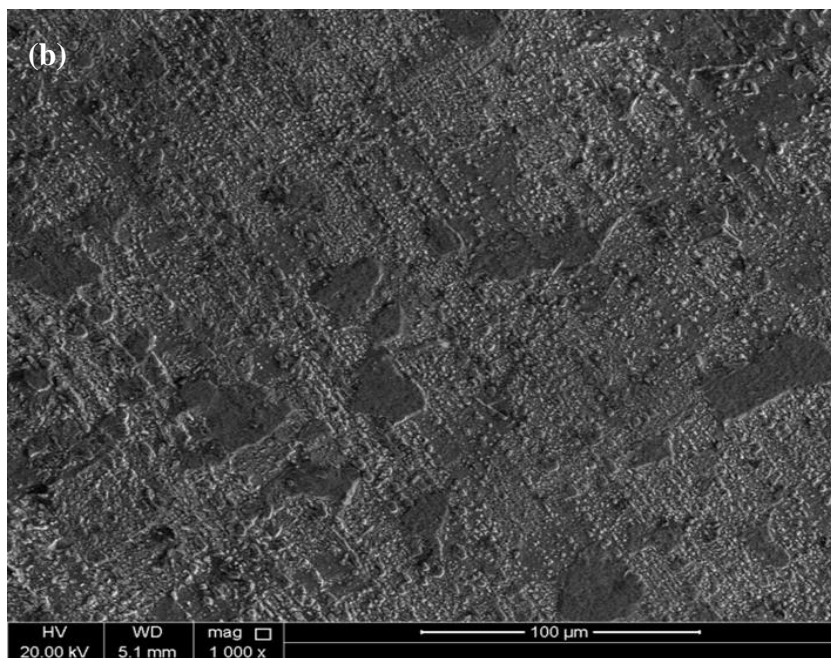


Figure:4.6 (b): SEM surface analysis micrograph for mild steel surface in 5MHCl for 24 h at 20°C.

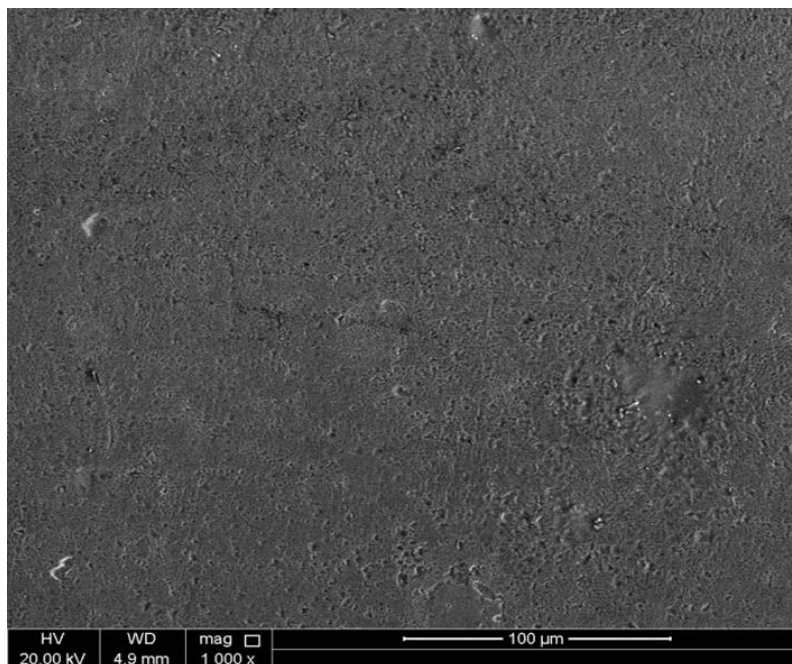


Figure: 4.6 (c): SEM surface analysis micrographs for mild steel surface for 24 h in 5MHCl in presence of $370 \mu\text{mol L}^{-1}$ of lauramidopropylamine oxide corrosion inhibitor at 20 °C.

4.5.2. Atomic –Force Microscopy analysis

Surface roughness and topography is reliably analyzed using Atomic Force Microscopy. Three dimensional images were taken for two mild steel samples grinded by using SiC to 4000 and immersed in 5M HCl for four (4) hours with and without the addition of $370 \mu\text{mol L}^{-1}$ of lauramidopropylamine oxide corrosion inhibitor as shown in figure 4.7 (a) and (b) respectively. The average roughness of mild steel sample after being exposed to the uninhibited acidic environment was found around 43.356 nm, while the roughness of the mild steel sample after immersion in the inhibited acidic medium was about 16.409 nm. The appreciable decrease in roughness in presence of inhibitor as compared to the roughness obtained from the uninhibited sample suggest a good inhibition capability of lauramidopropylamine oxide corrosion inhibitor in 5 M HCl attributed to the adsorption of the inhibitor to the surface.

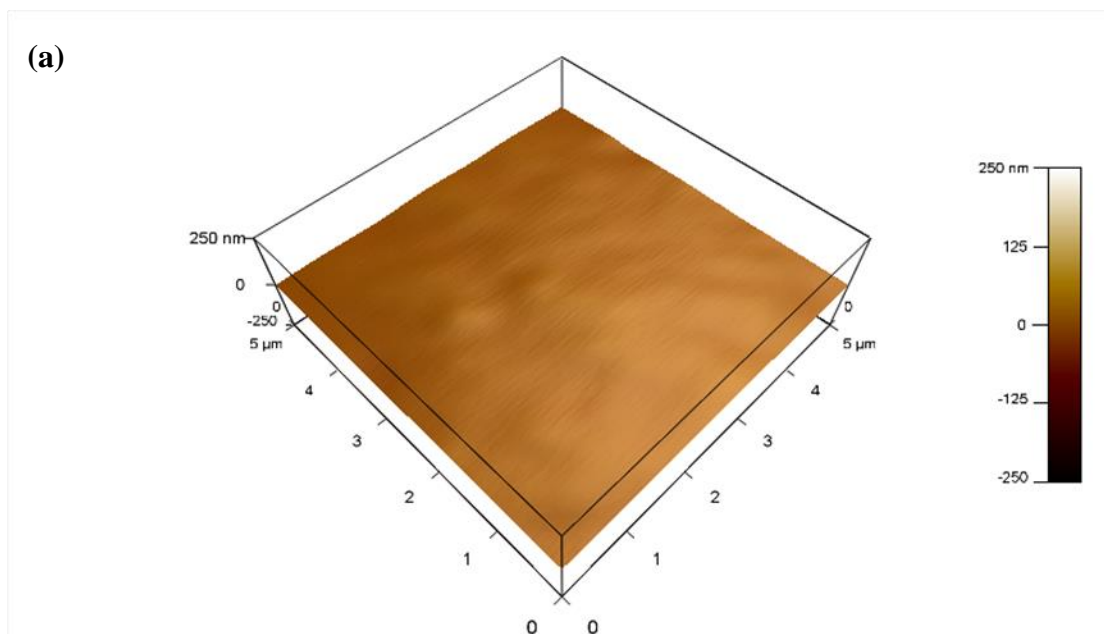


Figure: 4.7 (a): AFM image for blank mild steel at 20 °C before immersion in 5 M HCl.

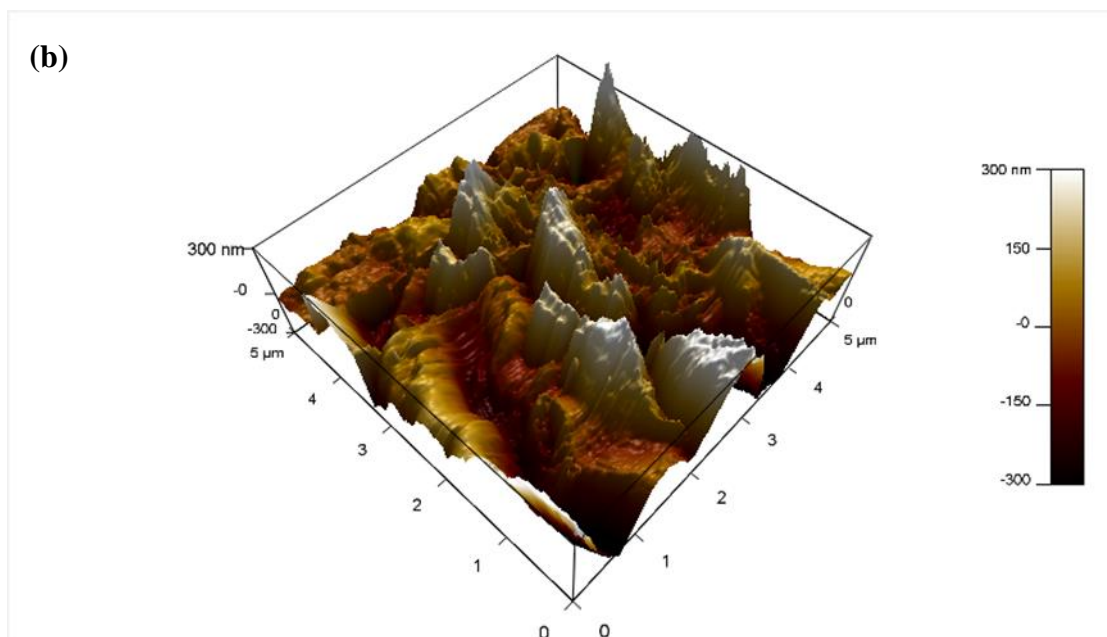


Figure: 4.7 (b): AFM images for mild steel in 5MHCl in absence of corrosion inhibitor for 24 h at 20 °C.

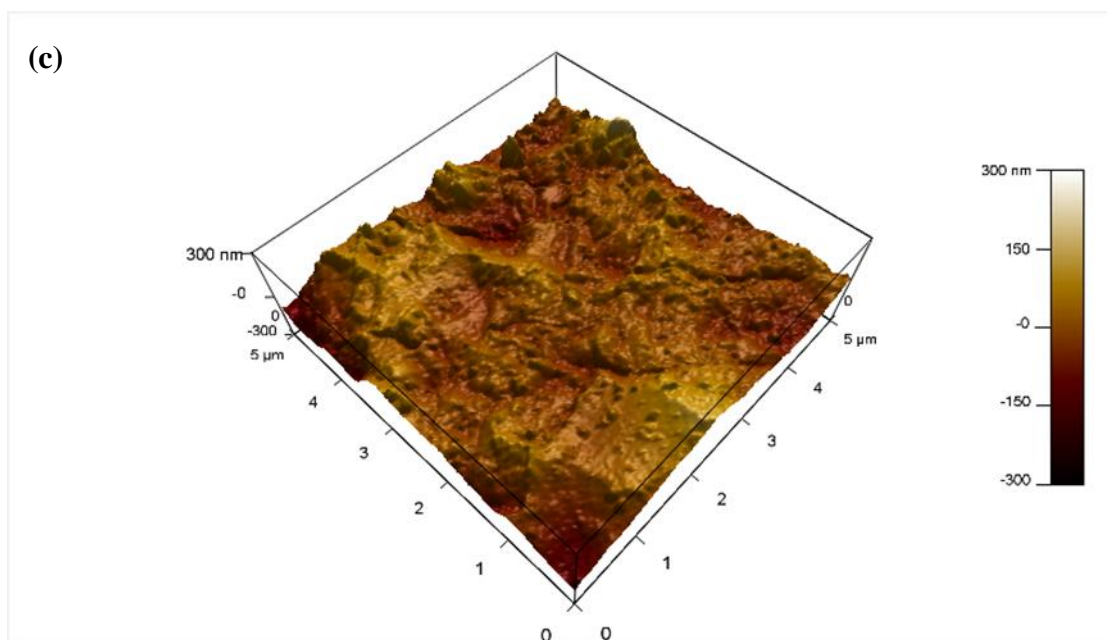


Figure: 4.7 (c): AFM images for mild steel in 5MHCl for 24 h at 20 °C with the addition of 370 μmol L⁻¹ of lauramidopyramine oxide corrosion inhibitor.

Chapter 5

Conclusion

The lauramidopropylamine oxide corrosion inhibitor at elevated temperatures has shown extraordinary performance in inhibiting corrosion of mild steel in 5 Molar Hydrochloric acid. The efficiency was found to increase as inhibitor's concentration increased. While increasing the testing temperature up to 80°C a slight decline in efficiency was noted due to the increased rate of iron dissolution in acidic brine as well as to the expected desorption of the attached inhibitor from the metallic substrate. More than 94 % of inhibition efficiency was successfully achieved upon addition of only 370 $\mu\text{mol L}^{-1}$ from the candidate inhibitor. The relationship between surface coverage and inhibitor concentration is consistent with Langmuir's adsorption isotherm. The acidic deterioration of steel in acidic environment was reduced by suppressing of oxidation and reduction reactions. Therefore, the inhibitor can be classified as a mixed type inhibitor dominated by anodic reaction.

The adsorption of the inhibitor to the steel was proven to be chemi-physisorption, which is confirmed by the calculated standard Gibbs free energy ($\Delta G^{\circ}_{\text{ads}}$). AFM analyses revealed a significant decrease in surface roughness under inhibited condition compared to immersion testing with no inhibitor added. Additionally, EDS revealed presence of Nitrogen on the mild steel which validates the adsorption of the corrosion inhibitor molecules onto the surface

Lauramidopropylamine oxide as green corrosion inhibitor showed excellent inhibition capability for mild steel in acidic environment at elevated temperatures. Application of this inhibitor in mitigating acidic corrosion in oil and gas industry will definitely add value to a safer operation as

well as contribute to significant cost savings. Further qualification testing of the candidate inhibitor under dynamic conditions is recommended to get more assurance and gain more confidence of the inhibition capabilities.

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