COMPARATIVE ANALYSIS OF THE AMINOLYSIS OF POLYETHYLENE TEREPHTHALATE WASTE AND SODIUM DICHROMATE AS CORROSION INHIBITORS FOR MILD STEEL IN 0.5M HCL AND 0.5M H_2SO_4

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ABSTRACT

Waste coca cola plastic bottles were subjected to depolymerization by aminolysis using mono ethanol amine (MEA) in the presence of sodium acetate as catalyst, the product bis(2-hydroxy ethylene terephthalate amide (BHETA) was compared with sodium dichromate ($Na_2Cr_2O_7$) as corrosion inhibitors for mild steel in 0.5M HCl and 0.5M H_2SO_4 at ambient temperature. Results indicated that the rate of corrosion of the mild steel increased in the absence of both inhibitors and decreased with increase in concentration. The effect of temperature on the corrosion behavior of mild steel in the presence of 571, 1142, 1714 and 2285ppm inhibitor concentrations was also studied. The associated activation energy of corrosion and other thermodynamic parameters such as enthalpy of adsorption (ΔH_{ads}), adsorption equilibrium constant (K_{ads}) and standard free energy of adsorption (ΔG_{ads}) were calculated. Highest inhibitor efficiency of BHETA was 84.5% in HCl and 82.9% in H_2SO_4 at 303K and 1714ppm concentration; lowest inhibitor efficiency of 74.8% in HCl and 61.8% in H_2SO_4 was recorded at 333K and 571ppm respectively. $Na_2Cr_2O_7$ had highest inhibitor efficiency of 95.4% in HCl and 79.8% in H_2SO_4 at 303K and concentration of 1714ppm. Lowest inhibitor efficiency of 64.5% in H_2SO_4 and 84% in HCl was recorded at 333K and inhibitor concentration of 571ppm. Inhibitor efficiency increased with increasing concentration and decreased with increasing temperature. The values of activation energy (Ea) and free energy of adsorption indicated that the type of adsorption on the surface of mild steel is physically controlled, exothermic and spontaneous. Optical microscope (OMS) was used to study the surface morphology of mild steel in the absence and presence of both inhibitors. BHETA however surpassed $Na_2Cr_2O_7$ in its corrosion inhibition ability in H_2SO_4, while the corrosion inhibition ability of $Na_2Cr_2O_7$ in HCl was better than BHETA. Nevertheless, BHETA is a good substitute for $Na_2Cr_2O_7$ and it is recommended on the basis of low operational hazard and better inhibition in H_2SO_4.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Metals exhibit a natural tendency of spontaneously reacting with their environment (corrosion) and this produces a destructive effect on their mechanical and physical properties. Corrosion of metals contributes to economic losses, impair the safety of operating equipment and invariably depletes our metal reserves the natural supply which is limited (Njoku, 1998). It has been estimated that approximately five per cent of an industrialized nation's income is spent on corrosion control and prevention or replacement of products lost or contaminated as a result of corrosion reaction (Callister, 1996). As a result of the problems from corrosion, several methods of corrosion control and prevention have been deviced. These include: use of protective coatings, selection of materials, proper design, alloying, cathodic protection and the use of inhibitors. The choice and application of any of the methods are based on their efficiency, economic considerations and the nature of the corrosive environment (Njoku, 1998). Corrosion inhibitors are most effectively utilized in mitigating corrosion of metals in closed cooling systems (motor vehicle radiator), and in corrosion protection of machines, apparatus and other articles in air medium during transportation and storage. Corrosion inhibitors are also extensively used in petroleum, petrochemical, agrochemical and chemical processing plants for protecting metal components operating under corrosive environments. Inhibitors are also appreciably used during pickling (chemical removal of surface oxides from metal by immersion in an acid solution (Taylor, 1964).

A great number of scientific studies have been devoted to the subject of corrosion inhibitors. However, most of what is known has grown from trial and error experiments, both in the laboratories and the

field. Despite continuous resistance of materials to corrosion, the use of chemical inhibitors often remains the most practical and cost effective method of preventing corrosion (Ultiene, 2009).

In this work, corrosion inhibition of low carbon steel by hydrochloric and sulphuric acid solutions was investigated using sodium dichromate and inhibitor gotten from the aminolysis of waste coca-cola bottles. Waste coca-cola bottles made from polyethylene teraphtalate (PET) were chosen due to ecological factors and little research work has been done on its recycling as corrosion inhibitor. Sodium dichromate was chosen for the purpose of comparison and verification of existing results. The choice of low carbon steel was due to their unique qualities which include: excellent formability, comparative cheapness and availability. These properties make low carbon steels to be used in many engineering applications and their subjection to acidic environments is also a common feature during processing and in some areas of application. Thus it has become imperative to investigate the corrosion behavior of low carbon steels in acid solution as well as their response to inhibition in such media (Njoku, 1998). The choice of hydrochloric and sulphuric acids is connected to their predominant use in pickling of metals, cleaning of boilers, oil and gas wells acidizing, acid descaling etc.

1.2 Problem Statement

The pipeline fire in Jesse, Delta State that claimed the lives of many Nigerians (Soyinka, 1998) may not be unconnected to sudden failure (burst) of pipeline due to corrosion attacks, which consequently resulted in spillages that led to the fire inferno. This is one among thousands of cases known around the world in which corrosion attack has resulted to loss of properties and lives. The unfortunate thing about the ugly heads of corrosion is that people tend to be careless in understanding what corrosion entails

and how to eliminate it. In most cases we try to shy away from the fact that corrosion may be a principal cause of such tragedies.

Corrosion does not only destroy useful materials and structures, but may go on so slowly or may occur in inaccessible places that are difficult to detect until they become severe. Corrosion does not only bring about heavy economic losses but may also cause the following:

i. Loss of transported products e.g. oil, gas, water
ii. Loss of efficiency in production process, caused by clogging of pipes with rust.
iii. Contamination of products such as those contain in cans.
iv. Corrosion problems add up to the cost of design and contribute to the depletion of our resources (natural) through increased utilization of replaced corroded materials.

Organic compounds containing nitrogen, sulfur and oxygen have long been used as potential corrosion inhibitors in acid solutions (Mobin et al, 2011). These compounds get adsorbed, form a protective layer or insoluble complex on the metal surface and block the active corrosion sites. However, most of these compounds are synthetic chemicals, expensive and very hazardous to both human beings and the environments and needs to be replaced with nontoxic and eco-friendly compounds. Over the years, numerous classes of organic compounds have been investigated as corrosion inhibitors. However the trend in green chemistry is concentrated towards the replacement of most of these inhibitors with nontoxic, cheap and eco-friendly compounds. In recent years, a number of eco-friendly corrosion inhibitors have been exploited as green alternative to toxic and hazardous compounds (Mobinet al., 2011).

In the 1980s, polyethylene terephthalate, (PET) began to be used popularly for the production of disposable soft drink bottles and in 1987, more than 700 million pounds of PET were consumed in their production (Abd El-Hameed, 2011). As a result of the diversity of its applications in a high volume of consumer products, large amount of PET waste is also generated, which includes polymer manufacture waste as well as the products after the end of their useful life. (PET) is a worldwide used polymer, and packaging is one of its most important applications. Due to its high resistance to the atmospheric and biological agents, this polymer is not considered as biodegradable. PET is not a hazardous product, but its waste quantity increases drastically, with the increasing pressure of keeping the environment clean. Recycling of PET waste in an eco friendly manner is the only solution (Abd El-Hameed, 2011).

1.3 The Present Work

In previous works, glycolysis of PET waste with diethanol amine (DEA) and triethanol amine (TEA) and their modified products and oligomeric surfactants were used as cheap and save corrosion inhibitors for steel in aqueous medium (Abd El-Hameed et al, 2009).

In the present work, mono ethanol amine (MEA) was used to convert PET waste into water soluble amide, the prepared product was compared with sodium dichromate ($Na_2Cr_2O_7.2H_2O$) as corrosion inhibitors for mild steel in 0.5M HCl and 0.5M H_2SO_4.

1.4 Aim and Objectives

The aim of this research is comparative analysis of the aminolysis of polyethylene terephthalate (PET) waste and sodium dichromate as corrosion inhibitors for mild steel in hydrochloric and sulphuric acid media. The specific objectives are:

i. Formulation of inhibitor from PET waste bottles

ii. To carry out corrosion test using weight loss technique

iii. To compare the inhibitive properties of sodium dichromate and PET waste inhibitors

iv. To analyse the efficiencies of both inhibitors at different concentrations and temperature for comparison.

v. To analyse the efficiencies of both inhibitors at different concentrations and temperature for comparison.

vi. To evaluate the surface condition of mild steel in contact with hydrochloric and sulphuric acid solution in the absence and presence of both inhibitors.

1.5 Significance of the Study

1) Enacted environmental laws have imposed severe restriction on the use of chromate in many countries because of its high toxicity and consequent environmental hazards (Friberg et al, 1986). Processing plants using chromate will therefore have to search for new alternatives.

2) Pardo et al. (2006) revealed that alternative corrosion inhibitors have been investigated in recent years to replace chromates in their different fields of application. For example efforts have focused on the search for new corrosion inhibitors and new formulation for both anodizing bath and conversion coating. According to Pardo et al. (2006), the development of viable alternatives to chromates is still in its infancy or experimental stage.

3) Carbon steel is widely used as the constructional material in most of the major industries particularly in food, petroleum, power production, chemical and electrochemical industries, especially due to its excellent mechanical properties and low cost. The major problem of carbon

steel is its dissolution in acidic medium. Corrosion of iron and steel in acidic aqueous solutions is one of the major areas of concern in many industries where acids are widely used for applications such as acid pickling, acid cleaning, acid descaling, and oil well acidizing. Because of general aggressiveness of acid solution the materials of construction are getting corroded easily (Abd El-Hameed, 2011).

1.6 Scope of the Study

The study involved:

i. Depolymerizing waste coca-cola bottles (PET) used for storing carbonated soft drinks by aminolysis, from which an inhibitor was synthesized
ii. Corroding mild steel of known compositions in an aqueous solution of hydrochloric and sulphuric acid, containing either sodium dichromate or the synthesized inhibitor.
iii. Carrying out a gravimetric (weight loss) analysis on the mild steel before and after corrosion in the presence of each of the inhibitors at room temperature
iv. Carrying out weight loss test in the corrosive media at higher temperatures in the presence of both inhibitors.
v. Metallographic examination of the metal surface in contact with both acids solution.

1.7 Definition of Terms

a. Aminolysis: Is any chemical reaction in which a molecule is split into two parts by reacting with a molecule of ammonia or an amine.

b. Adsorption: Is the adhesion of atoms, ions or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate (inhibitor) on the surface of the adsorbent (mild steel).

c. Activation energy (E_a): Is the minimum energy required to start a chemical reaction.

d. Enthalpy *(H)*: Is a measure of the total energy of a thermodynamic system.

CHAPTER TWO

LITERATURE REVIEW

Relevant literatures have been reviewed under as the following subheadings:

2.1 Corrosion

Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals. Metals will also corrode when exposed to gaseous materials like acid vapors, formaldehyde gas, ammonia gas, and sulfur containing gases. Corrosion specifically refers to any process involving the deterioration or degradation of metal components. The best known case is that of the rusting of steel. Corrosion processes are usually electrochemical in nature, having the essential features of a battery (Roberge, 2006).

When metal atoms are exposed to an environment containing water molecules they can give up electrons, becoming themselves positively charged ions. The corrosion process (anodic reaction) of the metal dissolving as ions generates some electrons that are consumed by a secondary process (cathodic reaction), these two processes have to balance their charges. The sites hosting these two processes can be located close to each other on the metal's surface, or far apart (Roberge, 2006). For instance, the hypothetical metal M, which has a valence of n electron, may experience oxidation according to the reaction:

$$M \rightarrow M^{n+} + ne- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.1)$$

In which M becomes an n^{+} positively charged ion and in the process loses its n valence electrons (Roberge, 2006**)**. Typical example is: $Fe \rightarrow Fe^{2+} + 2e-$ …….. (2.2)

2.2 Classification of Corrosion

Corrosion is classified into many different ways. The preferred classification of corrosion is given below (Fontana, 1987).

i. Dry corrosion: This type of corrosion occurs or takes place in the absence of a liquid phase or above the dew point of the environment. Vapours and gases are usually the corrodents. Dry corrosion is often associated with high temperature; a good example is the attack on steel by furnace gases.

ii. Wet corrosion: Wet corrosion takes place when a liquid is present. It usually involves an aqueous solution or electrolyte. This type of corrosion is the common type. This is because most of the harm caused by corrosion around us can be traced to the fact that there is presence of liquid. A good example is corrosion of turbine blade by water.

2.3 Forms of Corrosion

It is convenient to classify corrosion by the form in which it manifests itself, the basis for the classification being the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is helpful or required (Fontana, 1987).

Some of the eight forms of corrosion are unique, but all of them are more or less interrelated. The eight forms are: (1) uniform, or general attack; (2) galvanic, or two metal corrosion; (3) crevice corrosion; (4) pitting; (5) intergranular corrosion; (6) selective leaching or parting; (7) erosion corrosion; and (8) stress corrosion. The forms are not listed in any particular order of importance (Fontana, 1987).

These eight forms of corrosion are discussed viz:

2.3.1 Uniform attack

Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction that proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails. For example, a piece of steel or zinc immersed in dilute sulfuric acid will normally dissolve at a uniform rate over its entire surface. A sheet iron roof will show essentially the same degree of rusting over its entire outside surface (Fontana, 1987).

Rates of uniform attack are reported in various units, with accepted terminologies being millimeters penetration per year (mm/y) and grams per square meter per day (gmd). Other units that are frequently used include inches penetration per year (ipy), mils per year (mpy), and milligrams per square decimeter per day (mdd). These units refer to metal penetration or to weight loss of metal (Revie and Uhlig, 2008).

Uniform attack can be prevented or reduced by:

i. Proper materials, including coatings
ii. Inhibitors
iii. Cathodic protection (Revie and Uhlig, 2008).

2.3.2 Galvanic or two-metal corrosion

A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron flow between them. Corrosion of the less

corrosion resistant metal is usually increased and attack of the more resistant material is decreased, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes anodic and the more resistant metal cathodic. Usually the cathode or cathodic metal corrodes very little or not at all in this type of couple. Because of the electric currents and dissimilar metals involved, this form of corrosion is called galvanic or two-metal, corrosion (Fontana, 1987).Galvanic corrosion also occurs in the atmosphere. The severity depends largely on the type and amount of moisture present. For example, corrosion is greater near the seashore than in a dry rural atmosphere. Condensate near a seashore contains salt and therefore is more conductive (and corrosive) and a better electrolyte than condensate in an inland location, even under equal humidity and temperature conditions. Galvanic corrosion does not occur when the metals are completely dry since there is no electrolyte to carry the current between the two electrode areas (Fontana, 1987).

A number of procedures or practices can be used for combating or minimizing galvanic corrosion. Sometimes one is sufficient, but a combination of one or more may be required. These practices are as follows:

i. Select combination of metals as close together as possible in the galvanic series.
ii. Avoid the unfavourable area effect of a small anode and large cathode. Small parts such as fasteners sometimes work well for holding less resistant materials.
iii. Insulate dissimilar metals wherever practicable. It is important to insulate completely if possible.
iv. Apply coatings with caution. Keep the coatings in good repair, particularly the one on the anode member.
v. Add inhibitors, if possible to decrease the aggressiveness of the environment.

vi. Avoid threaded joints for materials far apart in the series (Fontana, 1987).

2.3.3 Pitting

Pitting is a form of extremely localized attack that results in holes in the metal. These holes may be small or large in diameter, but in most cases they are relatively small. Pits are sometimes isolated or so close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth (Fontana, 1987).

Iron buried in the soil corrodes with formation of shallow pits, whereas stainless steels immersed in seawater characteristically corrode with formation of deep pits. Many metals, when subjected to high velocity liquids, undergo a pitting type of corrosion called impingement attack, or sometimes corrosion erosion (Revie and Uhlig, 2008). Prevention and control:

i. Materials that show pitting or tendencies to pit, during corrosion tests should not be used to build plants or equipments.
ii. Adding inhibitors is sometimes helpful, but this may be a dangerous procedure unless attack is stopped completely. If it is not, the intensity of the pitting may increase.

2.3.4 Crevice corrosion

Intensive localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. This type of attack is usually associated with small volumes of stagnant solutions caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. As a result, this form of corrosion is called crevice corrosion or, sometimes, deposit or gasket corrosion. Example of deposits that may produce crevice corrosion (or deposit attack) are sand, dirt,

corrosion products, and other solids, the deposits act as a shield and create a stagnant condition there. Contact between metal and nonmetallic surfaces can cause crevice corrosion as in the case of a gasket. Wood, plastics, rubber, glass, concrete, asbestos, wax, and fabrics are examples of materials that can cause this type of corrosion (Fontana, 1987).

Some methods and procedures for combating or minimizing crevice corrosion are as follows:

i. Use welded butt joints instead of riveted or bolted joints in new equipments. Sound welds and complete penetration are necessary to avoid porosity and crevice on the inside.
ii. Close crevices in existing lap joints by continuous welding or soldering.
iii. Inspect equipment and remove deposits frequently.
iv. Remove solids in suspension early in the process or plant flow sheet, if possible.
v. Remove wet packing materials during long shutdowns.
vi. Use "solid" nonabsorbent gaskets, wherever possible

2.3.5 Intergranular corrosion

If a metal corrodes, uniform attack results since grain boundaries are usually only slightly more reactive than the matrix. However, under certain conditions, grain interfaces are very reactive and interganular corrosion results. Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains, is intergranular corrosion. The alloy disintegrates (grains fall out) and or loses its strength.

Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain boundary areas. Small amount of iron in aluminum, wherein the solubility of iron is low, have been shown to segregate in the grain boundaries and cause intergranular corrosion (Fontana, 1987).

High strength aluminum alloys depend on precipitated phases for strengthening and are susceptible to intergranular corrosion.

2.3.6 Selective leaching

Selective leaching is the removal of one element from a solid alloy by corrosion processes. The most common example is the selective removal of zinc in brass alloys (*dezincification*). Similarly processes occur in other alloy systems in which aluminum, iron, cobalt, chromium, and other elements are removed. Selective leaching is the general term that describes these processes, and its use precludes the creation of terms such as *dealuminumification*, *decobaltification*, etc (Fontana, 1987).

Sometimes selective corrosion of one element in an alloy may be beneficial. Enrichment of silicon observed in the oxide film on stainless steels results in passivity and resistance to pitting (Fontana, 1987).

2.3.7 Erosion corrosion

Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. Generally this movement is quite rapid, and mechanical wear effects or abrasion are involved. Metal is removed from the surface as dissolved ions forms solid corrosion products that are mechanically swept from the metal surface. Sometimes movement of the environment decreases corrosion, particularly when localized attack occurs under stagnant conditions, but this is not erosion corrosion because deterioration is not increased (Fontana, 1987). Erosion corrosion is characterized in appearance by grooves, gullies, waves, rounded holes, and valleys and usually exhibits a directional pattern. In many cases, failures because of erosion corrosion occur in a relatively short time.

Most metals and alloys are susceptible to erosion corrosion damage. Many depend upon the development of a surface film of some sort (passivity) for resistance to corrosion. Examples are aluminum, lead, and stainless steels. Erosion corrosion results when these protective surfaces are damaged or worn and the metal and alloy are attacked at a rapid rate.

Many types of corrosive mediums could cause erosion corrosion. These include gases, aqueous solutions, organic systems, and liquid metals. All types of equipment exposed to moving fluids are subject to erosion corrosion. Some of these are piping systems, particularly bends, elbows, and tees; valves; pumps; blowers etc. (Fontana, 1987).

Five methods for the prevention or minimization of damage due to erosion corrosion are used. In order of importance, or extent of use, they are:

i. Materials with better resistance to erosion corrosion
ii. Design
iii. Alteration of the environment
iv. Coating,
v. Cathodic protection.

2.3.8 Stress corrosion

Stress corrosion cracking (SCC) refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. Many investigators have classified all cracking failures occurring in corrosive mediums as stress-corrosion cracking, including failures due to hydrogen embrittlement. However, these two types of cracking failures respond differently to environmental variables. For instance, cathodic protection is an effective method for preventing stress-corrosion cracking, whereas it

rapidly accelerates hydrogen embrittlement effects. Hence the importance of considering stress corrosion cracking and hydrogen embrittlement as separate phenomena is obvious (Hausler, 1979; Cohen, 1979).

Methods of preventing this type of attack are either general or empirical in nature. Stress-corrosion cracking may be reduced or prevented by application of one or more of the following methods:

i. Lowering the stress below the threshold value if one exists. This may be done by annealing in the case of residual stresses, thickening the section, or reducing the load.
ii. Eliminating the critical environment species by, for example, degasification, demineralization or distillation.
iii. Applying cathodic protection to the structure with an external power supply or consumable anodes. Cathodic protection should only be used to protect installations where it is positively known that stress-corrosion cracking is the cause of the fracture.
iv. Adding inhibitors to the system if feasible. Phosphates and other inorganic and organic corrosion inhibitors have been used to reduce stress-corrosion cracking effects in mildly corrosive mediums.
v. Coatings are sometimes used, and they depend on keeping the environment away from the metal.

2.4 Corrosion Inhibitors

Marcel (1973) defined a corrosion inhibitor as a substance which when added in small quantities to a corroding medium brings about an appreciable reduction in its corrosive action.

Corrosion inhibition is generally described as the interference of a substance foreign to a medium with the corrosion reaction or reactions, and it is visualized that such interference takes place through the following processes (Hausler, 1979; Cohen, 1979).

i. Adsorption of the inhibitor on the metal surface.
ii. Poisoning of the metal surface for hydrogen evolution and/or oxygen reduction
iii. Increasing electronic resistance, and
iv. Interfering with the anodic dissolution process by assisting in the formation and preservation of oxide film.

2.4.1 Classification of corrosion inhibitors

Several substances which have been observed to have corrosion inhibitive properties have often been classified in various ways.

Evans (1960); Brockris and Drazk (1972), simply classified corrosion inhibitors into two: Anodic and Cathodic inhibitors depending on whether their action caused a decrease of the anodic reaction (oxidation – generally termed the corrosion reaction) or of the cathodic reaction (reduction- hydrogen evolution or oxygen reduction reaction).

A more complex classification was advanced by Fisher (1971), based on the specific mechanism by which they achieve inhibition: Interface-Inhibition and electrolyte-layer-Inhibition. According to him, interface inhibition results from substances which are adsorbed at the metal surface and decrease the rates of physical, chemical or electrochemical processes in the corrosion mechanism while electrolyte – layer-inhibitor arises if an inhibitor interferes with processes which are not on the metal surface but in its vicinity such as the electrolyte layer closed to the metal surface.

Antropove (1972); Uhlig (1963), classified corrosion inhibitors as liquid and vapour phase (volatile), depending on their states of use. According to Antropove, the inhibitors most often used for neutral solutions are organic compounds of the anionic type and that corrosion inhibitors for acid solutions are almost exclusively organic substances in the form of amino and carboxyl groups.

Revie and Uhlig (2008), identified the following general classification of inhibitors:

i. Passivators
ii. Organic inhibitors, including slushing compounds and pickling inhibitors
iii. Vapour phase inhibitors

2.4.1.1 Passivators

Passivators are usually inorganic oxidizing substances (such as chromates, nitrites, and molybdates) that have the unique property of reacting only slowly when in direct contact with iron, but they are reduced more rapidly by cathodic currents. For this reason, they can adsorb first on the metal surface, with each site of adsorption adding to the cathodic area. The higher the concentration of passivator, the more readily it adsorbs, and the smaller the residual anodic areas become: this situation obviously favours increased anodic polarization and ultimately passivation (Uhlig and Revie, 2008). In general, the passivating type inhibitors reduce corrosion rates to very low values, being more efficient in this regard than most of the nonpassivating types (pickling inhibitors). They represent, therefore, the best inhibitors available for certain metal-environment combination.

2.4.1.2 Pickling *inhibitors*

Most pickling inhibitors function by forming an adsorbed layer on the metal surface, probably no more than a monolayer in thickness, which essentially blocks discharge of H^+ and dissolution of metal ions. Some inhibitors block the cathodic reaction (raise hydrogen over potential) more than the anodic reaction, or vice versa; but adsorption appears to be general over the entire surface rather than at specific anodic or cathodic sites and both reactions tend to be retarded.

Compounds serving as pickling inhibitors require, by and large, a favourable polar group or groups by which the molecule can attach itself on the metal surface. These include the organic N, amine, S, and OH groups. The size, orientation, shape and electric charge of the molecule play a part in the effectiveness of inhibition.

2.4.1.3 Vapour *phase inhibitors*

Substances of low but significant vapour pressure, the vapour of which has corrosion-inhibiting properties, are called vapour-phase inhibitors. They are used to protect critical machine parts (e. g, ball bearings or other manufactured steel articles) temporary against rusting by moisture during shipping or storage. The mechanism of inhibition has not been studied in detail, but it appears to be one of adsorbed film formation on the metal surface that provides protection against water or oxygen, or both (Revie and Uhlig, 2008).

2.5 Chemical Recycling of Polyethylene Terephthelate (PET) Wastes

Due to upward usage of polymers and plastic materials especially in throw-away applications, wastage generation of these products is daily and relatively in large volume. The plastic materials often are not

resolvable with microorganism and lead to environmental pollutions, so it is necessary to recycle these materials for further application or usage (Vakili and Haghshenas, 2010). Generally, plastics such as: Polyethylene, polystyrene, polyethylene terephthalate, polypropylene and polyvinyl chloride, which are used in packaging industries, are recycled. One of the most important thermoplastic polyesters which is widely used in applications such as textile fibers, films and packaging industries is polyethylene terephthtalate (PET).

There are two global methods for recycling PET waste, mechanical and chemical methods. In mechanical methods, generally beverage bottles can be recycled by chipping them into very fine scraps, heating, melting and remolding to new products. Frequently in the mechanical methods the reground scrap PET is blended with virgin PET. Frouchi, *et al*. (1997) studied mechanical recycling of PET beverage bottle. They blended recycled PET with virgin PET to increase mechanical property of it. They found that mechanical blending can be used for recycling purposes without sacrificing of the virgin PET and to reduce material cost in bottle fabrication. Verney, *et al*. (2005) blended PET waste with polycarbonate (PC) to improve physical properties of mechanically recycled PET. They found that the blends have better properties than neat PET.

Chemical recycling of PET waste consist of depolymerization by hydrolysis, methanolysis, glycolysis and aminolysis to obtain various monomers (Vakili and Haghshenas, 2010). The hydrolysis of PET in presence of acid and base using suitable solvents has been reported by several researchers (Vakili and Haghshenas, 2010). Neutral hydrolysis of waste PET with different amounts of water and different catalysts, in presence of xylene has been studied by Guclu, *et al*. (2003). Thermal hydrolysis depolymerization of PET has also been studied by Sao and Cloyed (1991). Methanolysis of PET waste is used to form monomers, dimethyl terephthalate (DMT) and ethylene glycol (EG). Genta, *et al*.

(2007) used superficial methanol for PET depolymerization instead of vapour methanol. They found that the rate of PET depolymerization in super critical methanol is faster than that of PET depolymerization in vapour methanol.

Shukla, *et al*. (2006) used glycolysis method for recycling waste PET into useful auxiliaries. The advantages of this method were that chemicals used during depolymerization of PET are inexpensive and comparatively less harmful to the environment (Shukla, *et al*. 2006; Vakili and Haghshenas, 2010). Aminolysis is another method of chemical recycling of PET waste, which has been little explored as compared to other technique. Shukla, *et al*. (2006) used this method to produce bis (2-hydroxy ethylene) terephthalate (BHETA). They used excess of ethanolamine in the presence of different simple chemicals, namely glacial acetic acid, sodium acetate and potassium sulphate, as catalyst. Figure 2.1 is the photograph of waste coca cola plastic bottles that were used for this research.



Fig. 2.1: Waste coca cola bottles (PET)

2.6 Review of Past Works

Mclareen et al. (1951), noted from a radiotracer study of the passivation of zinc in chromates solution that chromates act as corrosion inhibitors for metals in aqueous solutions. This work showed that chromate ions have pronounced surface active properties and this propensity is responsible for their

inhibiting capability, the subsequent formation of oxide layer being merely incidental. Njoku (1998), studied the effects of inhibitors on corrosion of low carbon steel in hydrochloric acid pickling solution. He found out that organic compounds inhibit both the corrosion and hydrogen evolution rates while the inorganic salts stimulate the corrosion but inhibit hydrogen evolution rate. Anafi and Obi (2004), investigated the corrosion inhibition of mild steel in simulated media by a methanolic extract of bitter leaf. The solvent extract of bitter leaf was compared with sodium benzoate with mild steel immersed in sea water, 0.3M H_2SO_4 and 0.3M HCl media at ambient temperature using weight loss method. They found out that the inhibition ability of bitter leaf against corrosion was best in sea water where it exhibited an inhibitive efficiency of 61.19%. Sodium benzoate however surpassed bitter leaf in its corrosion inhibition ability in all test media used in the investigation. Yawas (2005), made a suitability assessment of neem, mahagony, cashew, locust bean husk, and acacianolitica pod extracts as corrosion inhibitors. Neem, sesame, mahogany, soyabean, cotton, and groundnut seed oils were also analyzed. Inhibition efficiencies increased with increase in inhibitor concentrations and temperature but decreased in the case of cotton seed and sesame oil. This work also showed the ability of the inhibitors to reduce stress corrosion cracking of carbon steel in acidic media.

Shetty *et al*. (2006), investigated the corrosive behaviour of mild steel in 0.05 M and 0.1 M HCL, 0.025 M and 0.05 M H_2SO_4 solutions containing different concentrations of N-(2-thiophenyl)-$N^{/}$ -phenyl thiourea (TPTU) using potentiodynamic technique. The results reveal that TPTU is an efficient anodic inhibitor in the acid environment and it is more effective for reducing corrosion of mild steel in HCL than in H_2SO_4 media. The thermodynamics parameters of adsorption deduced revealed a strong interaction and spontaneous adsorption of TPTU on the mild steel surface. Ita (2006), studied the inhibition of corrosion of mild steel in hydrochloric acid by Isatin glycin (ING) and Isatin (IN) at 30-

60^{o}C and concentrations of 0.0001 M to 0.0005 M via weight loss method. At the highest inhibitor concentration studied ING exhibited inhibition efficiency of 87% while IN exhibited 84% at 60^{o}C. The difference in the inhibitory properties of the inhibitors was explained in terms of the difference in their molecular structures and solubility rather than difference in molecular weights alone. Dubey and Singh (2007), studied the corrosion inhibition of mild steel in sulphuric acid solution by using Polyethylene Glycol Methyl Ether (PEGME) in relation to the concentration of the inhibitor as well as the temperature using electrochemical polarization techniques. The results were supplemented with scanning electron microscopy and infra-red spectroscopy. Adsorption of PEGME was found to follow the Langmuir's adsorption isotherm. PEGME is a mixed type of inhibitor.

Umoren*et al*. (2008), investigated the corrosion inhibition of mild steel in 1 M H_2SO_4 by Polyvinyl pyrrolidone (PVP) and the synergistic effect of iodide ions using weight loss and hydrogen evolution methods in the temperature range of 30-60^{o}C. The corrosion rates of mild steel decreased with the increasing concentration of PVP, while the inhibition efficiency (%IE) increased. The inhibition efficiency of PVP decreased with rise in temperature suggesting a physical adsorption mechanism. Zhang and Hua (2009), investigated the acid corrosion inhibition process of mild steel in 1M HCl by 1-butyl-3-methylimidazolium chlorides(BMIC) and 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO_4) using electrochemical impedance, potentiodynamic polarization and weight loss measurements. Potentiodynamic polarization studies indicated that the inhibitors investigated are mixed type inhibitors. For both inhibitors, the inhibition efficiency increased with increase in the concentration of the inhibitor and the effectiveness of the two inhibitors are in the order ([BMIM]HSO_4)> BMIC. The adsorption of the inhibitors on mild steel surface obeyed the Langmuir's adsorption isotherm. The effect of temperature on the corrosion behavior in the presence of 5×10−3M of inhibitors was studied in the temperature range of 303–333 K.

Sathiq and Abdul Nasser (2010), studied the influence of N-[morpholin-4-yl (phenyl) methyl]benzamide (MPB) on corrosion inhibition of mild steel in 1M HCl by weight loss, effect of temperature, potentiodynamic polarization and electrochemical impedance spectroscopy. The experimental results showed that the inhibition efficiency increases with increasing of MPB concentrations but decreases with increasing temperatures. The adsorption of MPB on the mild steel surface obeyed the Temkin's adsorption isotherm. Potentiodynamic polarization curves showed that MPB acted as a cathodic inhibition predominantly in hydrochloric acid. Ndibe *et al*. (2011), studied the corrosion inhibition of mild steel using acid extract of *Vernonia amygdalina* (VA) in HCl and HNO_3 using standard weight loss method. The studies were carried out at 30-60^{o}C temperatures range in 0.1-0.5M concentrations of the acids using 0.01 – 0.03g/l concentrations of inhibitor. The results indicated that the rate of corrosion of the metal in the media increased with an increase in the concentration of the acid and decreased with an increase in the concentration of the inhibitor. VA is an adsorption inhibitor and its adsorption on the surface of mild steel is physically controlled, exothermic, spontaneous and sufficiently fits with Langmuir adsorption isotherm.

Abd El-Hameed (2011), evaluated pol(bis(2-hydroxythylene)terephthal amide from PET waste as corrosion inhibitor for C-Steel in 1 MHCl by using weight loss, open circuit potential and potentiodynamic polarization measurement, the polarization curves indicate that this compound act as mixed type inhibitor. The inhibitor efficiency increased with increasing concentrations of the inhibitor and decrease with increasing the temperatures. Kuburi (2011), investigated the effect of flow velocity and exposure time on the corrosion rate of low carbon steel in crude oil. The study was performed using neem oil and locust bean husk extract as inhibitors. Results obtained showed a decrease in corrosion rate with time in unhibited and inhibited systems but corrosion rate increases with increase in

Reynolds number. Hmimou *et al*. (2012), tested 2-propargyl-5-p chlorophenyltetrazole (PCPT) as corrosion inhibitor for mild steel in 1M HCl solution using electrochemical and weight loss measurements. Results obtained showed that this compound has a good inhibiting properties for mild steel corrosion in acidic medium, with inhibition efficiencies values reach 98% at 5×10-4 M . The inhibition was assumed to occur via adsorption of the PCPT molecules on metallic surface. Adsorption of inhibitor molecules on steel surface showed Langmuir adsorption isotherms fit in acidic media. Potentiodynamic polarization curves showed that the inhibition is a cathodic nature. In addition, results obtained by weight loss and electrochemical measurements are in good agreement.

CHAPTER THREE

EQUIPMENT, MATERIALS AND EXPERIMENTAL PROCEDURE

3.1 Equipment

The equipment used for this research are: beakers which contained acids solution into which the mild steel samples were immersed, analytical mass balance for weight measurements, hotplate and stirrer for heating test solution, and a metallurgical microscope for surface examination.

3.2 Materials

The materials used for this research are as follow:

a. Mild steel bar3mm thick with chemical compositions shown in Table 3.1 was analyzed at Universal Steel Limited, Lagos, Nigeria.
b. Coca-cola bottles (PET) collected from municipal waste in Samaru-Zaria
c. Emery cloth of different grit sizes
d. Sodium dichromate ($Na_2Cr_2O_7$)
e. Mono ethanolamine (MEA)
f. Analytical grade Hydrochloric (HCl) and Sulphuric (H_2SO_4) acids
g. Sodium acetate
h. Distilled water
i. Acetone
j. Ethanol.

Table 3.1: Elemental composition of mild steel

Element	Average Content
%C	0.175
%Mn	0.214
%P	0.098
%S	0.012
%Si	0.036
%Cu	0.018
%W	0.0275
%Cr	0.015
%Ti	0.012
%V	0.0278
%Nb	0.0197
%Co	0.042
%Mo	0.0144
%Al	0.0001
%Fe	balance

3.2.1 Area and density of specimen

For use in this work, flat mild steel bar was cut into rectangular coupons. The area of the specimens was obtained from the relation:

$$A = 2(xy + yz + xz) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.1$$

Where A = area of specimen

x = breadth of specimen = 19mm

y = length of specimen = 37.14mm

z = thickness of specimen = 3mm

Thus,

$A = 2[(19mm \times 37.14mm) + (37.14mm + 3mm) + (19mm \times 3mm)]$

$= 174.8mm^2 \equiv 17.48cm^2$

The density of mild steel is $7.87g/cm^3$ (Yawas, 2005).

3.2.2 Preparation of 0.5M HCl acid solution

The concentrated HCl acid used for this research has a density of 1.18g/cm^3, a percentage purity of 37% and molar mass of 36.5g/mol.

To obtain the molarity of the concentrated HCl acid, the following relation was used (Yawas, 2005):

Molarity ———— 3.2

Where concentration standard volume density percentage purity

For 1 liter (1000cm^3) of standard HCl acid,

Concentration 1000 1.18 37%

Hence, the molarity is given by:

Molarity ———— 11.96 M

From the relation C_1V_1 C_2V_2 ..... 3.3

Where C concentration, and V volume

Since 350ml of 0.5M HCl acid is required,

Hence, 11.96 V_1 0.5 350

V_1 ——— 14.63ml

Therefore, 14.63ml of HCl acid was dissolved in 350ml of distilled water in a standard flask to obtain the desired concentration.

3.2.3 Preparation of 0.5M H_2SO_4 acid solution

Standard concentrated H_2SO_4 acid has a density of 1.84g/cm^3 and percentage purity of 98%. It has a molar mass of 98g/mol.

As in section 3.2.2.1, we obtain the molarity of H_2SO_4 acid as:

Molarity ———————— 18.40M

Similarly, the volume of standard H_2SO_4 acid required for 350ml of o0.5M H_2SO_4 can be obtained as follows:

18.4 V_1 0.5 350

Hence, V_1 ——— 9.51ml

Therefore, 9.51ml of H_2SO_4 acid was dissolved in 350ml of distilled water in a standard flask to obtain the desired concentration.

3.3 Experimental Procedure

3.3.1 Aminolysis of PET waste

This was carried out at the multi user research Laboratory, Chemistry Department, Ahmadu Bello University, Zaria, Nigeria. Coca cola plastic bottles sourced from post consumer wastes were cleaned. The cleaning process was done manually. It involved: removal of plastic cap, removal of label and rinsing. The cleaned bottles were cut with a knife into 1mm × 1mm to 6mm × 6mm flakes. 200g PET flakes and 100ml mono ethanolamine (MEA) were charged into a 500ml conical flask. Then 2g of sodium acetate was added to the mixture, sodium acetate was to act as catalyst. The mixture was heated on a hotplate and stirrer with vigorous stirring at temperature of 180^oC for 4 hrs and at 200^oC for 3 hrs. The temperature of the reaction was then lowered to 100^oC for 1 hr. the mixture was allowed to cool to room temperature. At the end of the reaction, distilled water was added in excess to the mixture with vigorous shaking to precipitate out poly (bis (2-hydroxy ethylene) terephthal) amide (PHETA), in accordance with (Abd El-Hameed, 2011 and Shukla *et al*, 2006). White powder (BHETA) was obtained by recrystallization. This was done by heating PHETA at 80^oC on a hot water bath until all the solids were dissolved; the solution was cooled to room temperature to crystallize the product. Vacuum

filtration was used to isolate BHETA which was subsequently dried in air. Figure 3.1 below shows heated PET and MEA mixture.



Fig. 3.1: Heated PET flakes and MEA mixture in a fume cupboard

3.3.2 Weight loss measurements

Gravimetric experiments were conducted with rectangular coupons having dimension of 19 ×37.14 × 3mm. The total geometric surface area was 17.48cm^2. Subsequently, each coupon was polished using different grades of silicon carbide impregnated emery paper of 120, 400, 800, and 1000 grits, degreased in ethanol, dipped in acetone, removed and allowed to dry in air before use. Test was carried out with 10 coupons as control. 5 of the coupons were immersed in350ml blank solution of hydrochloric acid, another 5 in 350ml blank solution of sulphuric acid. 0.2g, 0.4g, 0.6g and 0.8g of BHETA were dissolved into 350ml0.5MHCl and0.5M H_2SO_4acidssolutions to obtain concentrates of 571, 1142, 1714 and 2285ppm.In each experiment, 5 cleaned coupons were weighed (m_1) and immersed completely in the inhibited acids solutions. At ambient temperature (30^{o}C), the coupons were retrieved at intervals of 7days progressively for 35 days; this is to allow for a measurable amount of the specimen that reacted in the solution. Finally the samples were washed with running water to remove any corroded

product(s), dipped in acetone, dried and re-weighed (m_2). The weight loss (W) was taken as the difference between the weight at a given time and the initial weight of the test coupon. The experiment was repeated using $Na_2Cr_2O7.2H_2O$; the concentration of the inhibitor was also varied as in with BHETA.

It is worthy of note here that part per million (ppm) is a term used to denote a very, very low concentration of a solution. The inhibitors concentration in ppm was obtained using the relationship.

1ppm = 1mg/l (De Lloyd, 2000)

For 0.2g inhibitor concentration in 350ml acid solution, we know that 1g = 1000mg

Therefore 0.2g = 200mg. Similarly, 1000ml = 1liter therefore 350ml = 0.35 liters.

Concentration (ppm) = mass in milligrams/ volume in liters

= ——— = 571.42ppm

The above calculation was repeated for 0.4g, 0.6g and 0.8g in 350 ml acids solutions to obtain 1142,1714 and 2285 ppm inhibitor concentrations respectively.

3.3.3 Effect of temperature

To elucidate the mechanism of inhibition and to determine the kinetic parameters of the corrosion process, weight loss measurements were performed at 303, 313, 323 and 333K. In this case, the coupons were retrieved from the solution after 24 hours of immersion, according to the method discussed by Zhang and Hua (2009), using hot water bath. The difference in weight of the coupons was again taken as the weight loss (Yawas, 2005). The rate of corrosion (CR), inhibition efficiency (IE), degree of surface coverage (Θ), film attractive free energy (ΔG_{ads}), activation energy (E_a),equilibrium constant of adsorption (K) and film heat of attraction were determine from the used inhibitors.

3.3.4 Microstructure examination

In order to evaluate the surface condition of the coupons in contact with 0.5M HCL and 0.5MH_2SO_4 acid solutions in the absence and presence of both inhibitors, surface analysis of the coupons were carried out using an optical metallurgical microscope at a magnification of 100. This was done at the Metallurgical Engineering Department, Ahmadu Bello University, Zaria.

3.4 Corrosion Rate and Inhibitor Efficiency

The corrosion rate (C.R) in millimeters penetration per year (mm/y) was calculated, from equation 3.4 (Callister, 1996).

Where W is the weight loss (mg), A is the total surface area of sample, T is time of exposure in hours and ρ is the density of mild steel.

The inhibitor efficiency ( ) was computed using equation 3.5 (Khaled, 2008).

Where (*C.R*)o and(*C.R*) are the corrosion rates in (mm/y) without and with different concentrations of $Na_2Cr_2O_7$ and PHETA additives respectively.

The degree of surface coverage of mild steel by molecules of PHETA and Sodium dichromate was calculated using equation 3.6 (Khaled, 2008).

3.5 Kinetic and Thermodynamics Analysis

The apparent activation energies for mild steel in 0.5M HCL and 0.5M H_2SO_4 solutions in the absence and presence of both inhibitors were calculated using the logarithm form of Arrhenius equation below (Nnabuk *et al*, 2010).

where E_a is the activation energy of the reaction, A is the Arrhenius pre exponential factor, *R* is the gas constant, *CR* is the corrosion rate, and *T* is the absolute temperature.

In order to study the adsorption characteristics of BHETA and Sodium dichromate on the surface of the coupons at a given concentration and temperature, the equilibrium constant of adsorption was computed from the following equation given by Umoren *at al*, (2008) as;

Where K_{ads} is the equilibrium constant of adsorption, θ is the degree of surface coverage, and C is the inhibitor concentration (*mol/l*).

Free energy of adsorption (ΔG_{ads}): Is a measure of the energy which is available to do work outside a system. It is the driving force behind a process and determines the spontaneity of a reaction (Yawas, 2005).The K_{ads} values are related to the standard free energy of adsorption (ΔG_{ads} of both inhibitors as follows (Zhang and Hua, 2009).

$$\Delta G_{ads} = -RT \ln (55.5\ K_{ads}) \quad \text{(3.9)}$$

Where T is the Absolute temperature in Kelvin (K), R is the Universal gas constant (0.00831447 KJ),

ΔG_{ads} is the Gibbs energy of adsorption (*KJ/mole*). The constant value 55.5 is the concentration of water in solution in *mol/l*.

Enthalpy of adsorption (ΔH_{ads}): Is a measure of the total energy of a thermodynamic system. The enthalpy of adsorption (ΔH_{ads}) of the inhibitors was calculated using Van't Hoff equation given in equation 3.10

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results

Results of this work are shown in tables 4.1 – 4.28 and figures 4.1 – 4.26 below:

Table 4.1: Corrosion rate for mild steel in 0.5 M HCl in the absence of inhibitor

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr)×10^{-3}
7	38.1661	37.4261	0.7400	2.8049
14	37.7316	36.9279	0.8037	1.5232
21	38.2727	37.3930	1.1797	1.2905
28	38.2813	37.0585	1.2228	1.1587
35	38.2993	36.9565	1.3428	1.0179

Table 4.2: Corrosion rate for mild steel in 0.5 M HCl in the presence of 571ppm BHETA

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) ×10^{-3}	Θ	IE (%)
7	38.0979	37.9161	0.1818	0.6892	0.7543	75.4
14	39.7985	39.5891	0.2094	0.3969	0.7394	73.9
21	37.8986	37.5932	0.3054	0.3859	0.7010	70.1
28	39.1423	38.7417	0.4006	0.3796	0.6724	67.2
35	39.0234	38.5592	0.4642	0.3519	0.6543	65.4

Table 4.3: Corrosion rate for mild steel in 0.5 M HCl in the presence of 1142ppm BHETA

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) ×10^{-3}	Θ	IE (%)
7	39.9444	39.7895	0.1549	0.5871	0.7907	79.1
14	38.1640	37.9712	0.1928	0.3654	0.7601	76.0
21	38.5569	37.2990	0.2579	0.3259	0.7475	74.8
28	37.4394	37.0987	0.3407	0.3228	0.7214	72.1
35	39.1952	38.8062	0.3890	0.2949	0.7103	71.0

Table 4.4: Corrosion rate for mild steel in 0.5 M HCl in the presence of 1714ppm BHETA

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	37.2051	37.0735	0.1316	0.4989	0.8221	82.2
14	37.7819	37.6247	0.1572	0.2979	0.8044	80.4
21	39.0639	38.8583	0.2056	0.2598	0.7987	79.9
28	39.4908	39.2229	0.2679	0.2539	0.7809	78.1
35	39.0840	38.7571	0.3233	0.2451	0.7592	75.9

Table 4.5: Corrosion rate for mild steel in 0.5 M HCl in the presence of 2285ppm BHETA

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	38.7819	38.6805	0.1014	0.3842	0.8645	86.5
14	37.8478	37.7227	0.1251	0.2370	0.8444	84.4
21	37.9827	37.8113	0.1714	0.2165	0.8322	83.2
28	39.1434	38.9170	0.2264	0.2145	0.8149	81.5
35	38.1130	37.2118	0.2809	0.2129	0.7908	79.1

Table 4.6: Corrosion rate for mild steel in 0.5 M HCl in the presence of 571ppm $Na_2Cr_2O_7$

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	37.8159	37.7073	0.1086	0.4117	0.8532	85.3
14	38.2854	38.1256	0.1598	0.3028	0.8012	80.1
21	38.1077	37.8823	0.2254	0.2848	0.7793	77.9
28	38.6706	38.3755	0.2951	0.2796	0.7587	75.9
35	37.5520	37.2044	0.3476	0.2635	0.7411	74.1

Table 4.7: Corrosion rate for mild steel in 0.5 M HCl in the presence of 1142ppm $Na_2Cr_2O_7$

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	38.3724	38.2917	0.0807	0.3060	0.8909	89.1
14	39.3197	39.1972	0.1225	0.2322	0.8475	84.8
21	38.3593	38.1951	0.1642	0.2075	0.8392	83.9
28	38.2186	38.0108	0.2078	0.1969	0.8301	83.0
35	37.9737	37.7330	0.2407	0.1825	0.8207	82.1

Table 4.8: Corrosion rate for mild steel in 0.5 M HCl in the presence of 1714ppm $Na_2Cr_2O_7$

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	39.1645	39.1140	0.0505	0.1913	0.9318	93.2
14	40.2981	40.2075	0.0907	0.1718	0.8872	88.7
21	37.9217	37.7941	0.1276	0.1612	0.8751	87.51
28	38.4396	38.2794	0.1602	0.1518	0.8690	86.9
35	37.9860	37.7949	0.1911	0.1449	0.8576	85.8

Table 4.9: Corrosion rate for mild steel in 0.5 M HCl in the presence of 2285ppm $Na_2Cr_2O_7$

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	37.9066	37.8632	0.0434	0.1644	0.9414	96.14
14	37.8821	37.8171	0.0650	0.1232	0.9191	91.9
21	38.4212	38.3271	0.0941	0.1189	0.9079	90.8
28	39.9316	39.8089	0.1227	0.1163	0.8996	90.0
35	38.7529	38.6110	0.1419	0.1076	0.8943	89.4

Table 4.10: Corrosion rate for mild steel in 0.5 M H_2SO_4 in the absence of inhibitor

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$
7	38.2323	37.3390	0.8933	3.3859
14	38.0282	36.3883	1.6399	3.1079
21	37.8546	35.6314	2.2232	2.8089
28	38.5598	36.2041	2.3557	2.2322
35	37.7564	35.3185	2.4379	1.8481

Table 4.11: Corrosion rate for mild steel in 0.5 M H_2SO_4 in the presence of 571ppm BHETA

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	38.5316	38.2827	0.2489	0.9433	0.7214	72.1
14	37.6769	37.1794	0.4975	0.9429	0.6966	69.7
21	38.1094	37.3998	0.7096	0.8966	0.6808	68.1
28	38.8872	36.1087	0.7785	0.7377	0.6695	67.0
35	39.1033	38.2257	0.8776	0.6653	0.6400	64.0

Table 4.12: Corrosion rate for mild steel in 0.5 M H_2SO_4 in the presence of 1142ppm BHETA

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	38.4917	38.2886	0.2031	0.7699	0.7726	77.3
14	37.9199	37.5245	0.3954	0.7493	0.7589	75.9
21	38.2375	37.6566	0.5809	0.7340	0.7387	73.9
28	37.6787	37.0205	0.6582	0.6237	0.7206	72.06
35	39.0909	36.9947	0.7356	0.5576	0.6983	69.8

Table 4.13: Corrosion rate for mild steel in 0.5 M H_2SO_4 in the presence of 1714ppm BHETA

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	40.8107	40.6412	0.1695	0.6426	0.8102	81.0
14	38.6381	38.3093	0.3288	0.6231	0.7995	80.0
21	38.9520	38.4705	0.4815	0.6084	0.7834	78.3
28	37.9124	37.3689	0.5435	0.5150	0.7693	76.9
35	38.9620	38.3308	0.6312	0.4785	0.7411	74.1

Table 4.14: Corrosion rate for mild steel in 0.5 M H_2SO_4 in the presence of 2285ppm BHETA

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	37.6095	37.4913	0.1182	0.4480	0.8677	86.8
14	39.6162	39.3847	0.2315	0.4388	0.8588	85.9
21	38.1858	37.8434	0.3424	0.4326	0.8460	84.6
28	38.9097	38.4643	0.4455	0.4221	0.8109	81.1
35	38.8867	38.3738	0.5129	0.3888	0.7896	79.0

Table 4.15: Corrosion rate for mild steel in 0.5 M H_2SO_4 in the presence of 571ppm $Na_2Cr_2O_7$

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	39.2276	38.9644	0.2632	0.9975	0.7054	70.5
14	37.8600	37.3641	0.4959	0.9398	0.6976	69.8
21	37.5845	36.8622	0.7223	0.9126	0.6751	67.5
28	40.7464	39.9238	0.8226	0.7795	0.6508	65.1
35	38.5626	37.7020	0.8606	0.6524	0.6470	64.7

Table 4.16: Corrosion rate for mild steel in 0.5 M H_2SO_4 in the presence of 1142ppm $Na_2Cr_2O_7$

Exposure Time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	39.4208	39.1708	0.2500	0.9477	0.7201	72.0
14	38.8591	38.3890	0.4701	0.8910	0.7133	71.3
21	38.0568	37.3783	0.6785	0.8573	0.6948	69.5
28	38.5105	37.7353	0.7752	0.7346	0.6709	67.1
35	39.6548	38.8303	0.8245	0.6250	0.6618	66.2

Table 4.17: Corrosion rate for mild steel in 0.5 M H_2SO_4 in the presence of 1714ppm $Na_2Cr_2O_7$

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	39.1440	38.9104	0.2336	0.8854	0.7385	73.9
14	38.8975	38.4380	0.4595	0.8708	0.7198	72.0
21	37.5585	36.8962	0.6623	0.8368	0.7021	70.2
28	39.1758	38.4346	0.7412	0.7023	0.6854	68.5
35	38.8724	38.0874	0.7850	0.5951	0.6780	67.8

Table 4.18: Corrosion rate for mild steel in 0.5 M H_2SO_4 in the presence of 2285ppm $Na_2Cr_2O_7$

Exposure time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mm/yr) $\times 10^{-3}$	Θ	IE (%)
7	38.3790	38.1651	0.2139	0.8109	0.7605	76.1
14	39.4780	39.0528	0.4252	0.8059	0.7407	74.1
21	37.9897	37.3883	0.6014	0.7598	0.7295	73.0
28	38.4434	37.7636	0.6798	0.6442	0.7114	71.1
35	39.6112	38.8659	0.7453	0.5650	0.6943	69.4

Table 4.19-4.22 shows the degree of surface coverage (Θ) and percentage inhibition efficiency (%IE) of $Na_2Cr_2O_7$ and PHETA in 0.5M HCl and H_2SO_4 at 303-333K.

Table 4.19: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of BHETA in 0.5M HCl at 303-313 K, obtained from weight loss measurement after 24hrs.

Temp *(k)*	Inhibitor conc.	Initial weight(*g*)	Final weight(*g*)	Weight Loss(*g*)	*C.R* (*mm/yr*) 10^{-3}	Θ	*I.E* (%)	*Log CR*
303	Blank	37.4795	37.4060	0.0735	1.95	0	0	-2.7100
	571ppm	38.3550	38.3401	0.0149	0.3961	0.7969	79.7	-3.4023
	1142ppm	40.7195	40.7061	0.0134	0.3567	0.8171	81.7	-3.4478
	1714ppm	37.3515	37.3401	0.0114	0.3017	0.8453	84.5	-3.5205
313	Blank	39.6930	39.5648	0.1282	3.4	0	0	-2.4685
	571ppm	38.9052	38.8771	0.0281	0.7456	0.7807	78.1	-3.1275
	1142ppm	38.2826	38.2570	0.0256	0.6780	0.8006	80.1	-3.1688
	1714ppm	38.2880	38.2658	0.0222	0.5886	0.8269	82.7	-3.2302
323	Blank	38.2906	38.0747	0.2159	5.7280	0	0	-2.2420
	571ppm	39.7691	39.7182	0.0509	1.3499	0.7643	76.4	-2.8697
	1142ppm	38.3283	38.2816	0.0467	1.2385	0.7838	78.4	-2.9071
	1714ppm	40.0532	40.0117	0.0415	1.1021	0.8076	80.8	-2.9578
333	Blank	38.5136	38.1611	0.3525	9.3519	0	0	-2.0291
	571ppm	38.3894	38.3005	0.0889	2.3580	0.7479	74.8	-2.6275
	1142ppm	39.1825	39.1002	0.0823	2.1824	0.7666	76.7	-2.6611
	1714ppm	39.5508	39.4759	0.0749	1.9869	0.7875	78.8	-2.7018

Table 4.20: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of $Na_2Cr_2O_7$ in 0.5M HCl at 303-313 K, obtained from weight loss measurement after 24hrs.

Temp *(k)*	Inhibitor conc.	Initial weight(*g*)	Final weight(*g*)	Weight loss(*g*)	*CR* (*mm/yr*) 10^{-3}	*Θ*	*IE* (%)	*Log CR*
303	Blank	37.9210	37.8253	0.0957	2.54	0	0	-2.5951
	571ppm	37.2485	37.2381	0.0104	0.2748	0.8918	89.2	-3.5609
	1142ppm	37.2262	37.2192	0.0070	0.1869	0.9264	92.6	-3.7283
	1714ppm	39.0119	39.0075	0.0044	0.1176	0.9537	95.4	-3.9295
313	Blank	38.2024	38.0427	0.1597	4.2384	0	0	-2.3728
	571ppm	37.6217	37.6019	0.0198	0.5265	0.8758	87.6	-3.2786
	1142ppm	37.7499	37.7348	0.0151	0.4011	0.9054	90.5	-3.3967
	1714ppm	38.9429	38.9325	0.0104	0.2763	0.9348	93.5	-3.5586
323	Blank	38.5644	38.3062	0.2582	6.8502	0	0	-2.1643
	571ppm	38.3508	38.3143	0.0365	0.9687	0.8586	85.9	-3.0138
	1142ppm	40.1391	40.1082	0.0309	0.8209	0.8802	88.0	-3.0857
	1714ppm	38.8542	38.8310	0.0232	0.6156	0.9101	91.0	-3.2107
333	Blank	37.2923	36.8870	0.4053	10.7547	0	0	-1.9684
	571ppm	38.5577	38.4929	0.0648	1.7183	0.8402	84.0	-2.7649
	1142ppm	39.1076	39.0469	0.0607	1.6095	0.8503	85.0	-2.7933
	1714ppm	38.6601	38.6108	0.0493	1.3071	0.8785	87.9	-2.8837

Table 4.21: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of BHETA in 0.5M H_2SO_4 at 303-313 K, obtained from weight loss measurement after 24hrs.

Temp *(k)*	Inhibitor conc.	Initial weight*(g)*	Final weight*(g)*	Weight loss(*g)*	*CR* (*mm/yr*) 10^{-3}	*Θ*	*IE* (%)	*Log CR*
303	Blank	38.8832	38.7769	0.1063	2.82	0	0	-2.5498
	571ppm	38.6469	38.6197	0.0272	0.7216	0.7441	74.4	-3.1417
	1142ppm	38.1921	38.1693	0.0228	0.6035	0.7860	78.6	-3.2193
	1714ppm	37.4021	37.3840	0.0181	0.4814	0.8293	82.9	-3.3175
313	Blank	39.4393	39.2627	0.1766	4.6849	0	0	-2.3293
	571ppm	37.3275	37.2571	0.0521	1.3817	0.7051	70.5	-2.8596
	1142ppm	38.0665	38.2754	0.0459	1.2170	0.7402	74.0	-2.9147
	1714ppm	38.0078	37.9703	0.0375	0.9950	0.7876	78.8	-3.0022
323	Blank	38.9866	38.7023	0.2843	7.5440	0	0	-2.1224
	571ppm	37.0312	36.9354	0.0958	2.5416	0.6631	66.3	-2.5949
	1142ppm	37.5178	37.4292	0.0886	2.3496	0.6886	68.9	-2.6290
	1714ppm	39.9308	39.8567	0.0741	1.9661	0.7394	73.9	-2.7064
333	Blank	38.0024	37.5574	0.4450	11.8059	0	0	-1.9279
	571ppm	37.0898	36.9199	0.1699	4.5066	0.6183	61.8	-2.3461
	1142ppm	38.0159	37.8515	0.1644	4.3614	0.6306	63.1	-2.3604
	1714ppm	37.0731	36.9325	0.1406	3.7296	0.6841	68.4	-2.4283

Table 4.22: Degree of surface coverage (θ) and percentage inhibition efficiency (% IE) of $Na_2Cr_2O_7$ in 0.5M H_2SO_4 at 303-313 K, obtained from weight loss measurement after 24hrs.

Temp *(k)*	Inhibitor Conc.	Initial weight(*g*)	Final weight(*g*)	Weight loss(*g*)	*CR* (*mm/yr*) 10^{-3}	*Θ*	*IE* (%)	*Log C.R*
303	Blank	39.3085	39.1732	0.1353	3.59	0	0	-2.4449
	571ppm	40.6932	40.6583	0.0349	0.9255	0.7422	74.2	-3.0336
	1142ppm	38.2569	38.2257	0.0312	0.8268	0.7697	77.0	-3.0826
	1714ppm	38.5285	38.5012	0.0273	0.7245	0.7982	79.8	-3.1399
313	Blank	38.5068	38.2981	0.2087	5.5361	0	0	-2.2568
	571ppm	37.5253	37.4651	0.0602	1.5985	0.7113	70.1	-2.7963
	1142ppm	37.8460	37.7907	0.0553	1.4679	0.7348	73.4	-2.8333
	1714ppm	39.4885	39.4394	0.0491	1.3026	0.7647	76.0	-2.8852
323	Blank	38.0924	37.7791	0.3133	8.3119	0	0	-2.0803
	571ppm	37.9911	37.8905	0.1006	2.6693	0.6789	67.9	-2.5736
	1142ppm	38.9222	38.8274	0.0948	2.5159	0.6973	69.4	-2.5993
	1714ppm	38.0710	37.9859	0.0851	2.2579	0.7284	72.0	-2.6463
333	Blank	39.7674	39.3084	0.4590	12.1787	0	0	-1.9144
	571ppm	38.1609	37.9980	0.1629	4.3227	0.6451	64.5	-2.3643
	1142ppm	38.2216	38.0643	0.1573	4.1741	0.6573	65.7	-2.3794
	1714ppm	40.2138	40.0711	0.1427	3.7870	0.6891	68.9	-2.4217

Table 4.23: Values of activation parameters of BHETA on the surface of mild steel in HCl and H_2SO_4

Concentration	E_a (*KJ/mol*)		ΔH_{ads} (*KJ/mol*)	
	HCl	H_2SO_4	HCl	H_2SO_4
Blank	43.85	40.05	-	-
571ppm	49.90	51.23	-0.0078	-0.0162
1142ppm	50.66	55.31	-0.0085	-0.0212
1714ppm	52.72	57.26	-0.0108	-0.0224

Table 4.24 Values of activation parameters of $Na_2Cr_2O_7$ on the surface of mild steel in HCl and H_2SO

Concentration ( )	E_a (*KJ/mol*)		ΔH_{ads} (*KJ/mol*)	
	HCl	H_2SO_4	HCl	H_2SO_4
Blank	40.36	34.16	-	-
571ppm	51.26	43.10	-0.0124	-0.0128
1142ppm	60.21	45.28	-0.0221	-0.0154
1714ppm	67.35	46.25	-0.0291	-0.0161

Table 4.25: Values of thermodynamic parameters for the adsorption of BHETA in 0.5M HCl on the mild steel samples at different concentrations and temperatures

Temperature (*K*)	Concentration	K_{ads} (*mol/l*)	ΔG_{ads} (*KJ/mol*)
303	571ppm	1961.94	-29.22
	1142ppm	1116.82	-27.80
	1714ppm	910.66	-27.29
313	571ppm	1779.99	-29.93
	1142ppm	1003.71	-28.45
	1714ppm	796.18	-27.84
323	571ppm	1621.27	-30.64
	1142ppm	906.37	-29.07
	1714ppm	699.59	-28.38
333	571ppm	1483.24	-31.34
	1142ppm	821.09	-29.70
	1714ppm	617.63	-28.91

Table 4.26: Values of thermodynamic parameters for the adsorption of $Na_2Cr_2O_7$ in 0.5M HCl on mild steel samples at different concentrations and temperatures

Temperature (*K*)	Concentration	K_{ads} (*mol/l*)	ΔG_{ads} (*KJ/mol*)
303	571ppm	4115.23	-31.09
	1142ppm	3146.74	-30.41
	1714ppm	3433.05	-30.63
313	571ppm	3521.13	-31.71
	1142ppm	2392.71	-30.70
	1714ppm	2389.57	-30.69
323	571ppm	3036.07	-32.32
	1142ppm	1836.81	-30.97
	1714ppm	1687.25	-30.74
333	571ppm	2628.91	-32.92
	1142ppm	1420.01	-31.22
	1714ppm	1205.07	-30.76

Table 4.27: Values of thermodynamic parameters for the adsorption of BHETA in 0.5M H_2SO_4 on mild steel samples at different concentrations and temperatures

Temperature (*K*)	Concentration	K_{ads} (*mol/l*)	ΔG_{ads} (*KJ/mol*)
303	571ppm	1453.91	-28.46
	1142ppm	918.19	-27.31
	1714ppm	809.72	-26.99
313	571ppm	1195.46	-28.89
	1142ppm	712.30	-27.55
	1714ppm	618.01	-27.18
323	571ppm	984.16	-29.29
	1142ppm	552.82	-27.75
	1714ppm	472.88	-27.33

333	571ppm	809.91	-29.66
	1142ppm	426.77	-27.89
	1714ppm	360.92	-27.42

Table 4.28: Values of thermodynamic parameters for the adsorption of $Na_2Cr_2O_7$ in 0.5M H_2SO_4 on the mild steel samples at different concentrations and temperatures

Temperature (K)	Concentration	K_{ads} (mol/l)	ΔG_{ads} (KJ/mol)
303	571ppm	1439.47	-28.44
	1142ppm	835.56	-27.07
	1714ppm	659.24	-26.47
313	571ppm	1231.83	-28.97
	1142ppm	692.66	-27.47
	1714ppm	541.65	-26.83
323	571ppm	1057.19	-29.49
	1142ppm	575.90	-27.86
	1714ppm	446.99	-27.18
333	571ppm	908.84	-29.98
	1142ppm	479.50	-28.21
	1714ppm	369.41	-27.49

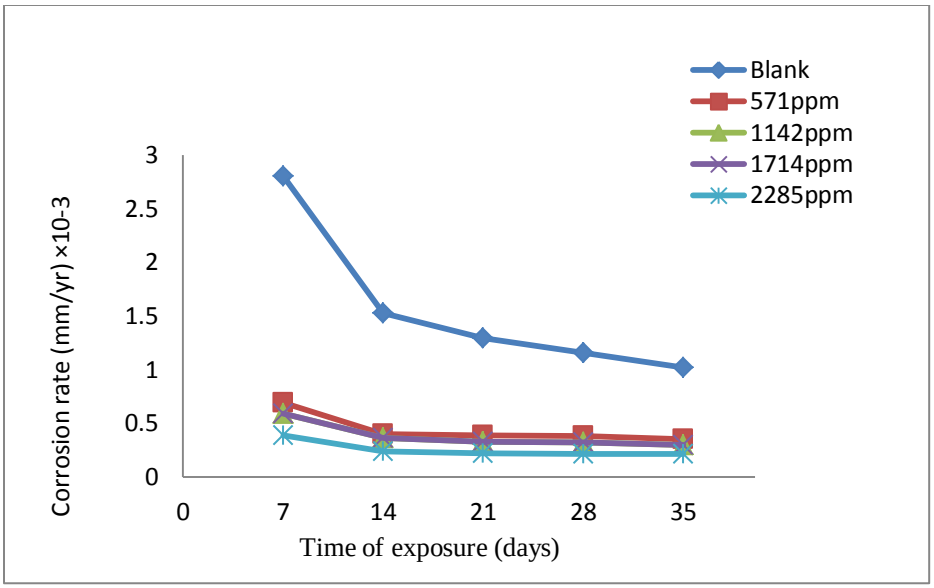


Fig. 4.1: Corrosion rate-time curve of mild-steel in 0.5M HCl in absence and presence of different concentrations of BHETA

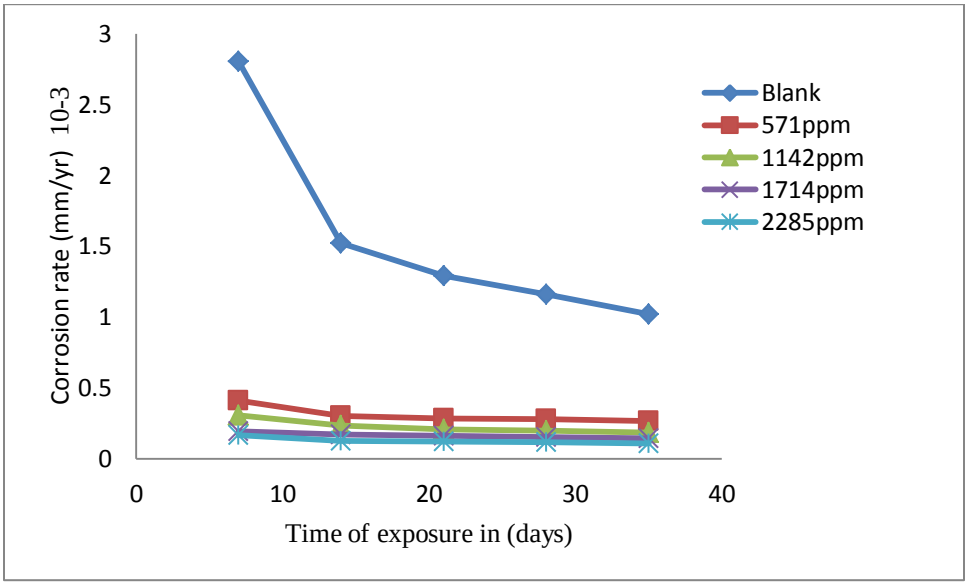


Fig. 4.2: Corrosion rate-time curve of mild-steel in 0.5M HCl in absence and presence of different concentration $Na_2Cr_2O_7$

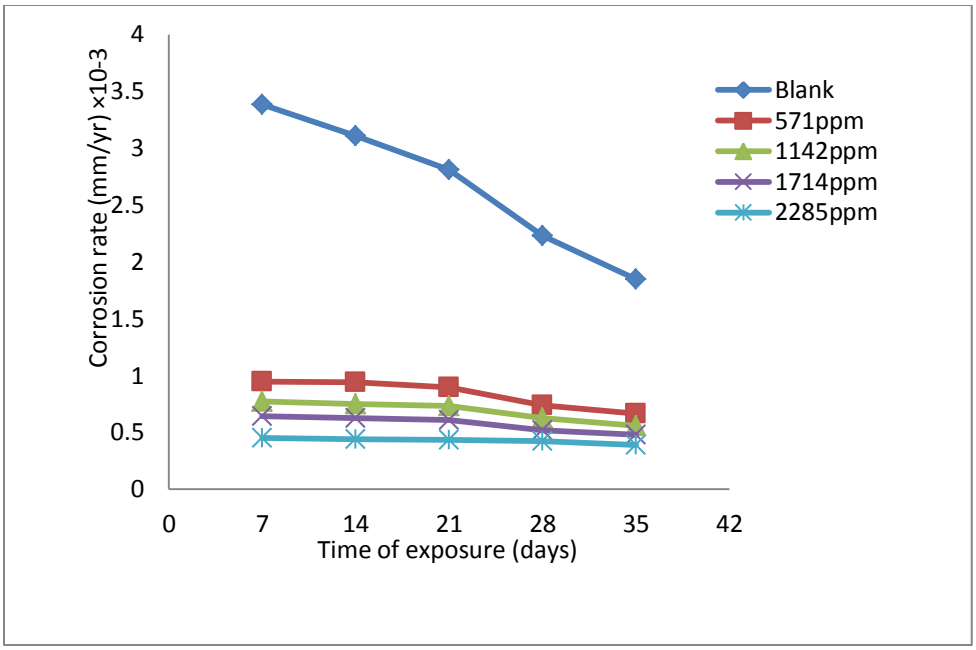


Fig. 4.3: Corrosion rate-time curve of mild steel in 0.5M H_2SO_4 in absence and presence of different concentration of BHETA

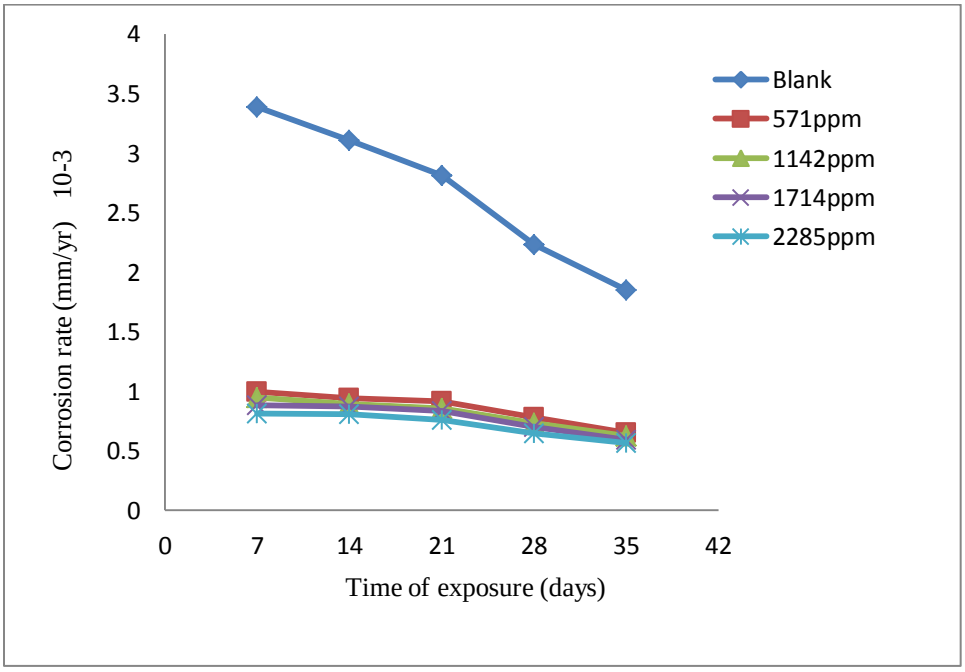


Fig. 4.4: Corrosion rate-time curve of mild steel in 0.5M H_2SO_4 in absence and presence of different concentration $Na_2Cr_2O_7$

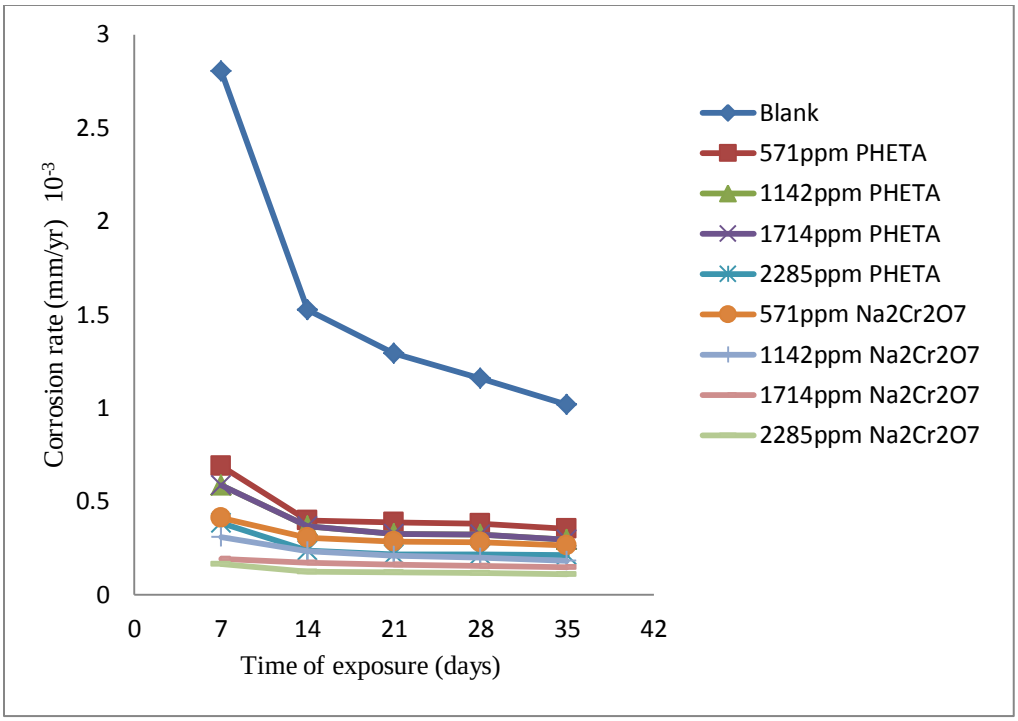


Fig. 4.5: Variation of corrosion rate with time of exposure for mild steel in 0.5M HCl containing BHETA and $Na_2Cr_2O_7$

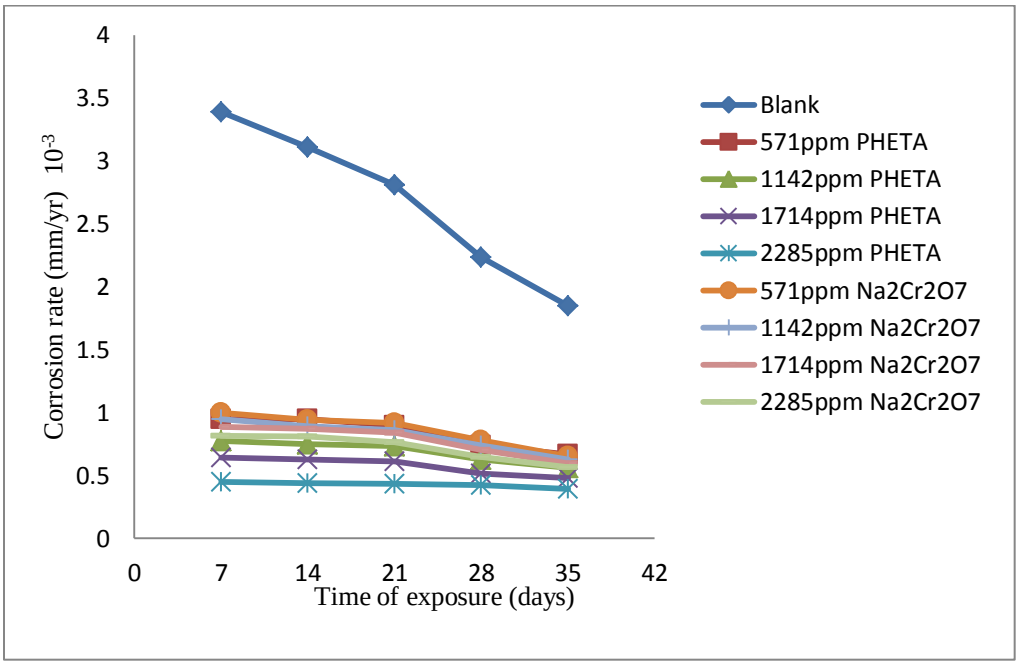


Fig. 4.6: Variation of corrosion rate with time of exposure for mild steel in 0.5M H_2SO_4 containing BHETA and $Na_2Cr_2O_7$

Figures 4.7-4.10 below show the plots of inhibitor efficiency against concentration.

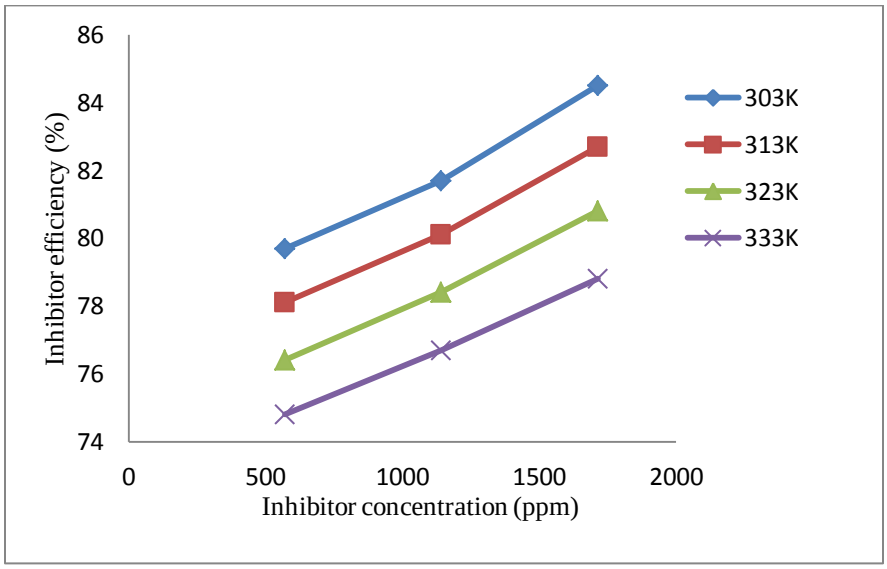


Fig.4.7: Variation of %IE with inhibitor concentration in 0.5M HCl containing BHETA at different temperatures

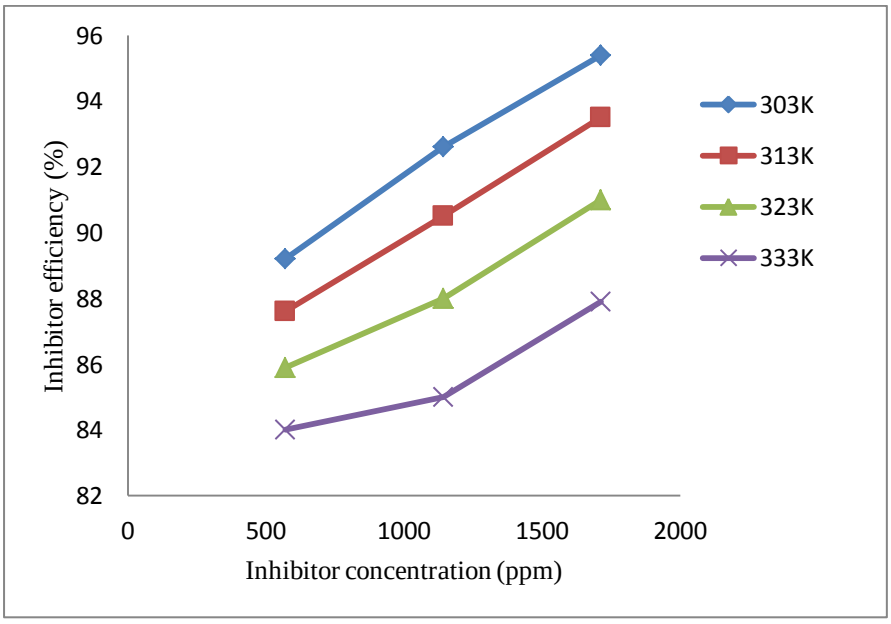


Fig.4.8: Variation of %IE with inhibitor concentration in 0.5M HCl containing $Na_2Cr_2O_7$ at different temperatures

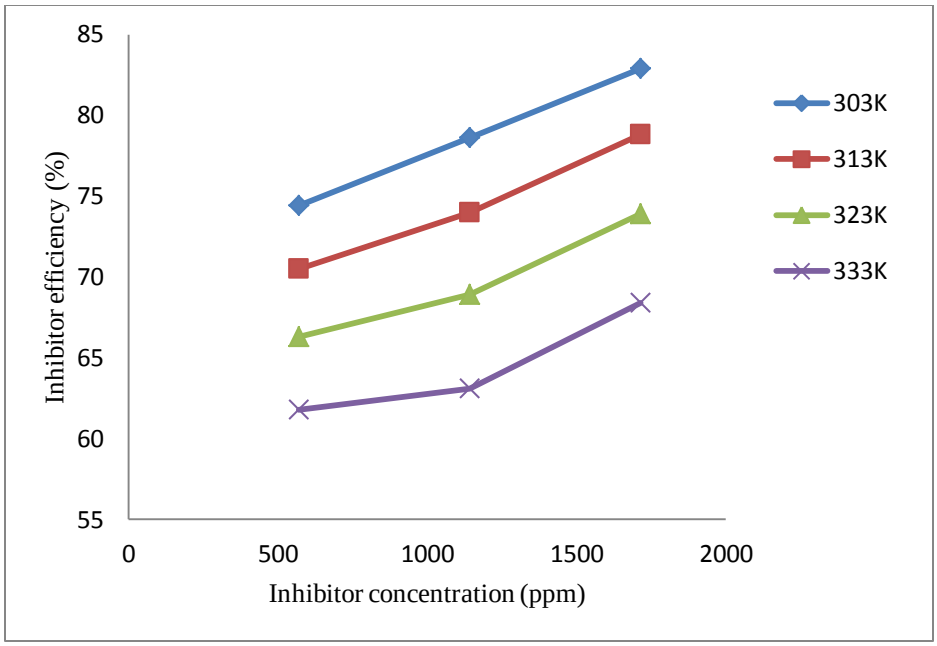


Fig.4.9: Variation of %IE with inhibitor concentration in 0.5M H_2SO_4 containing BHETA at different temperatures

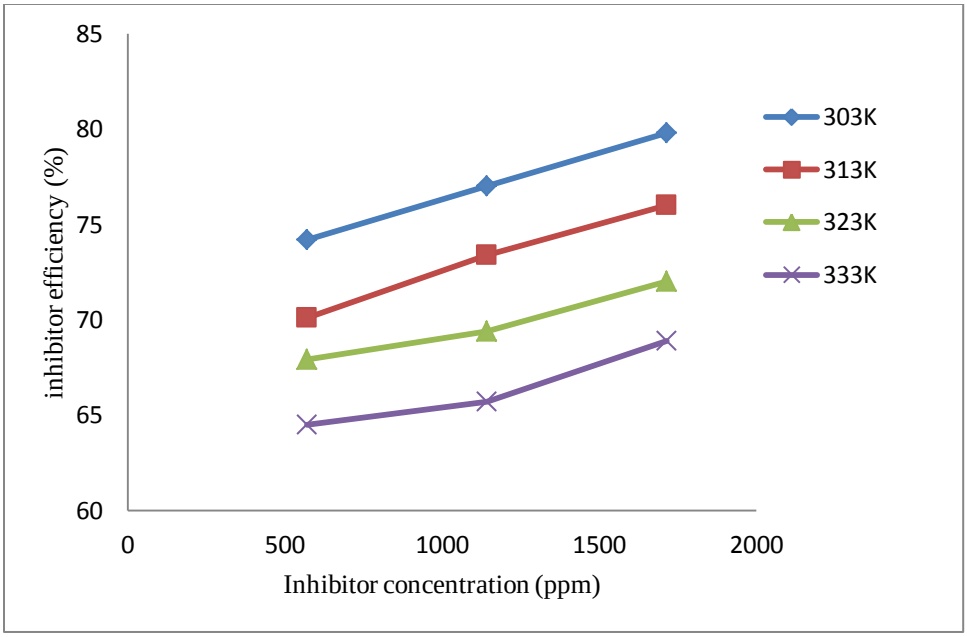


Fig.4.10: Variation of %IE with concentration in 0.5M H_2SO_4 containing $Na_2Cr_2O_7$ at different temperatures

Figure 4.11 and 4.12 below show a comparison of the efficiencies of both inhibitors in the aggressive solutions.

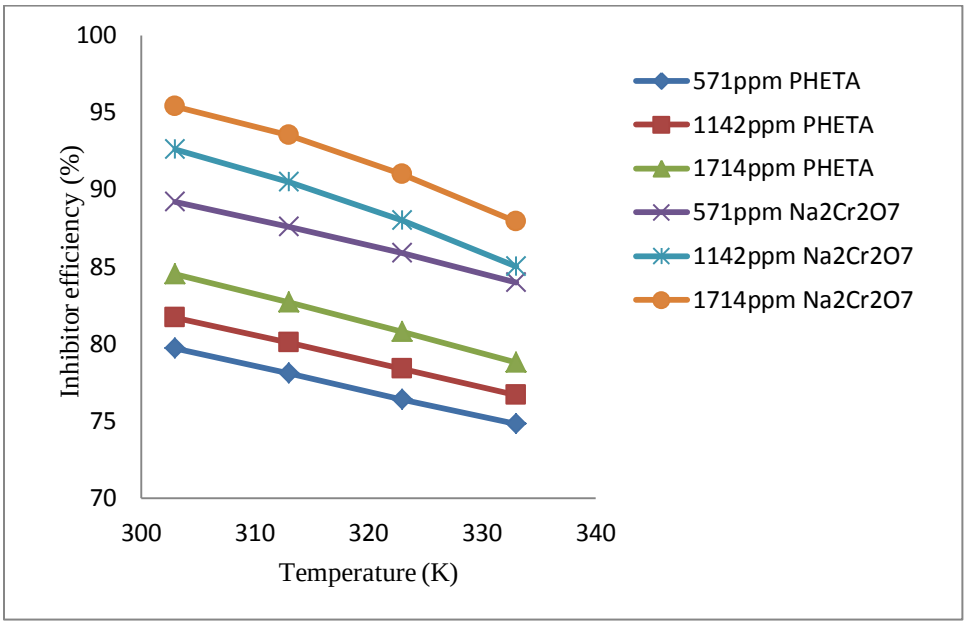


Fig.4.11: Variation of %IE with temperature for mild steel in 0.5M HCl containing BHETA and Na_2Cr_2O

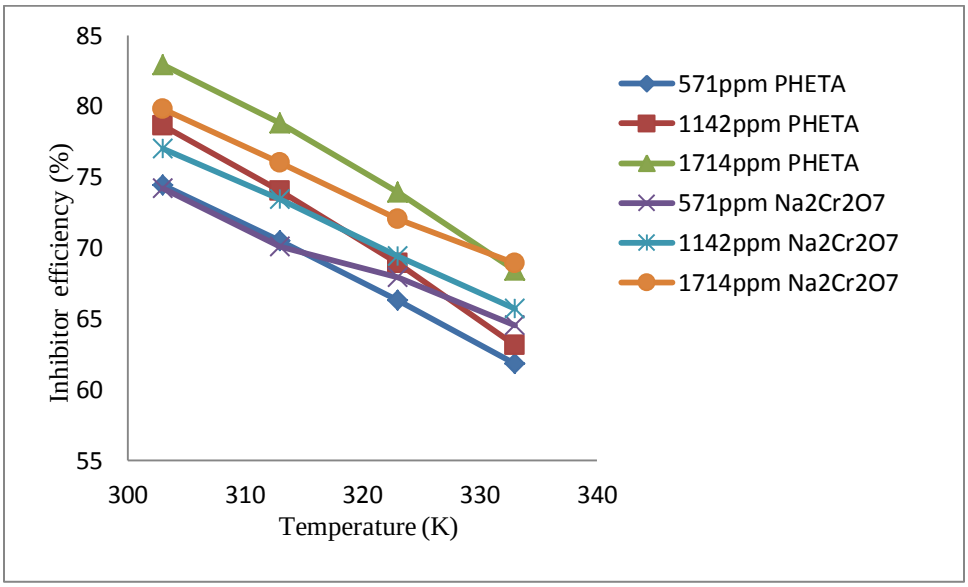


Fig.4.12: Variation of %IE with temperature for mild steel in 0.5M H_2SO_4 containing BHETA and $Na_2Cr_2O_7$

A plot of the logarithm of corrosion rate against the reciprocal of the absolute temperature figures 4.13-4.16 gave linear graphs with slope equal to E_a/R.

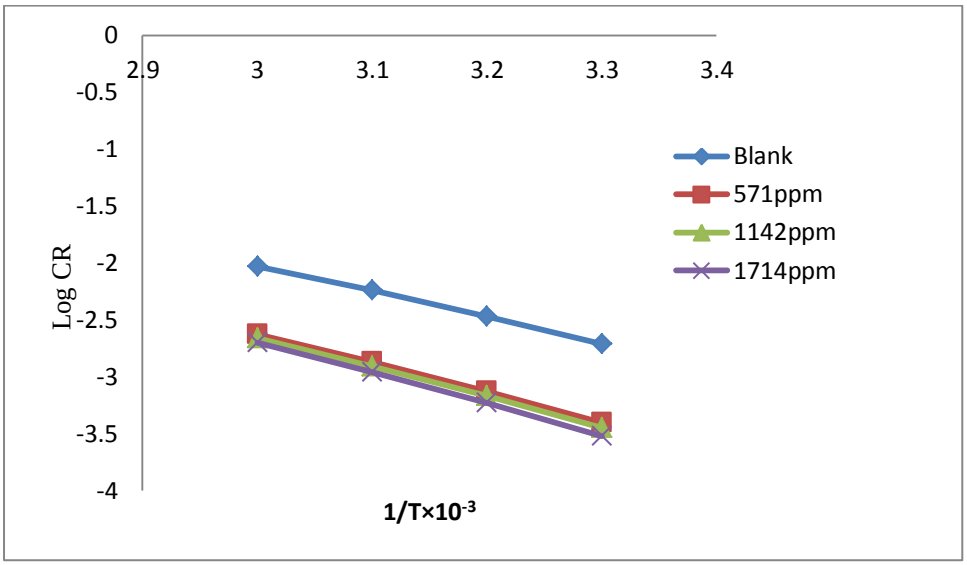


Fig. 4.13: Arrhenius plot for mild steel in 0.5M HCl in the absence and presence of BHETA

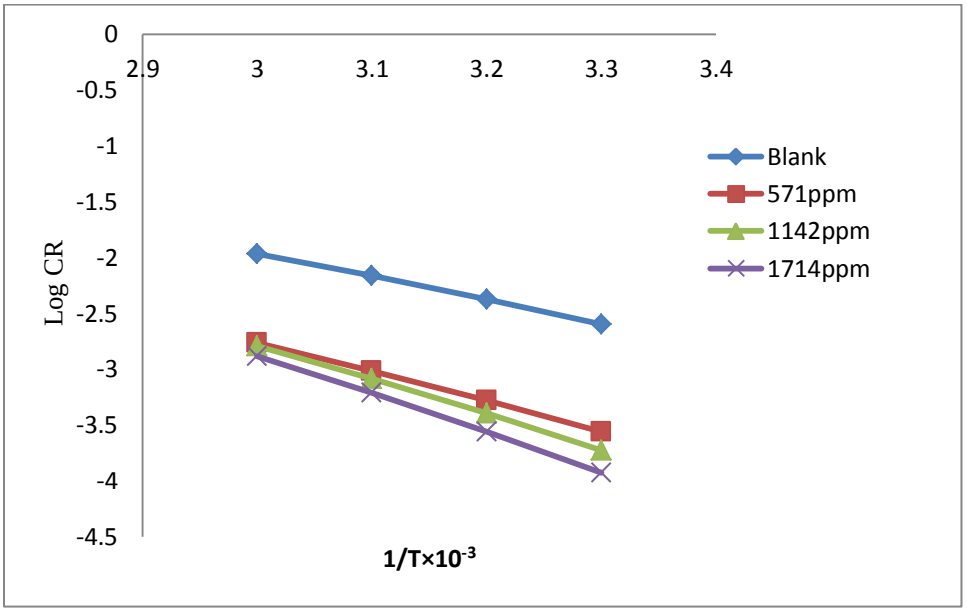


Fig. 4.14: Arrhenius plot for mild steel in 0.5M HCl in the absence and presence of $Na_2C_2rO_7$

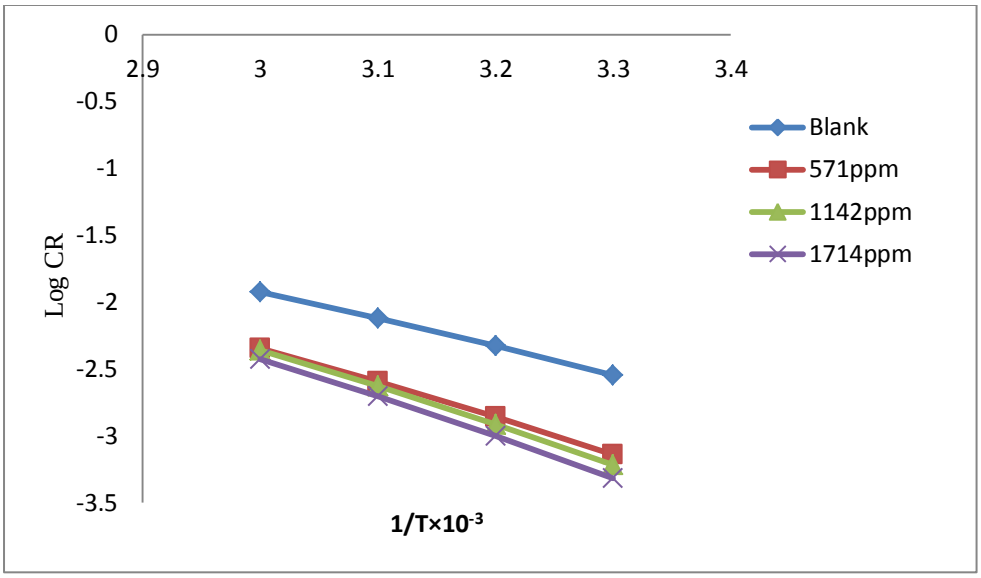


Fig. 4.15: Arrhenius plot for mild steel in 0.5M H_2SO_4 in the absence and presence of BHETA

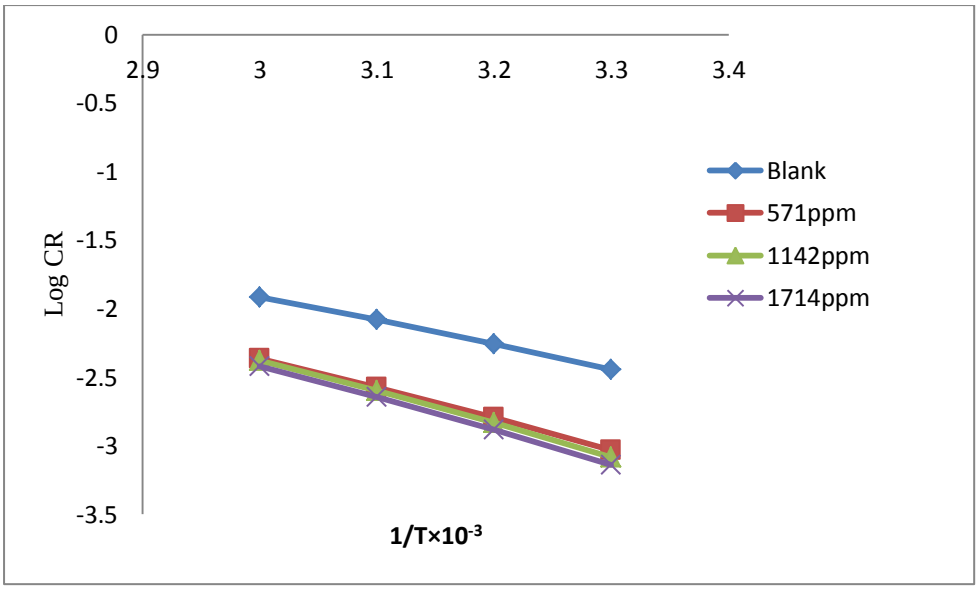


Fig. 4.16: Arrhenius plot for mild steel in 0.5M H_2SO_4 in the absence and presence of $Na_2C_2rO_7$

Figures 4.17-4.20 shows the linear regression of lnK_{ads} against 1/T from 571 to 2285ppm inhibitor concentration.

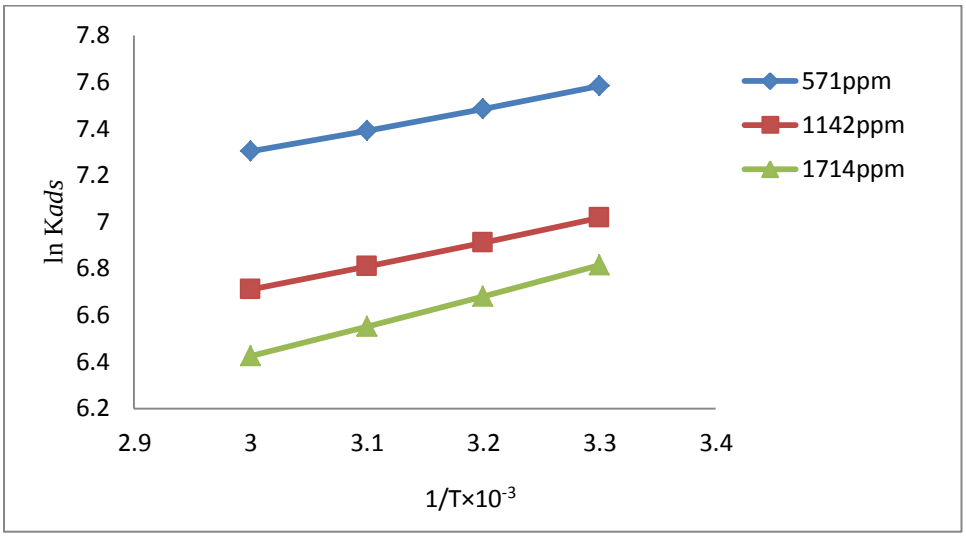


Fig 4.17: Variation oflnK*ads* and 1/T of BHETA in 0.5M HCl on mild steel surface

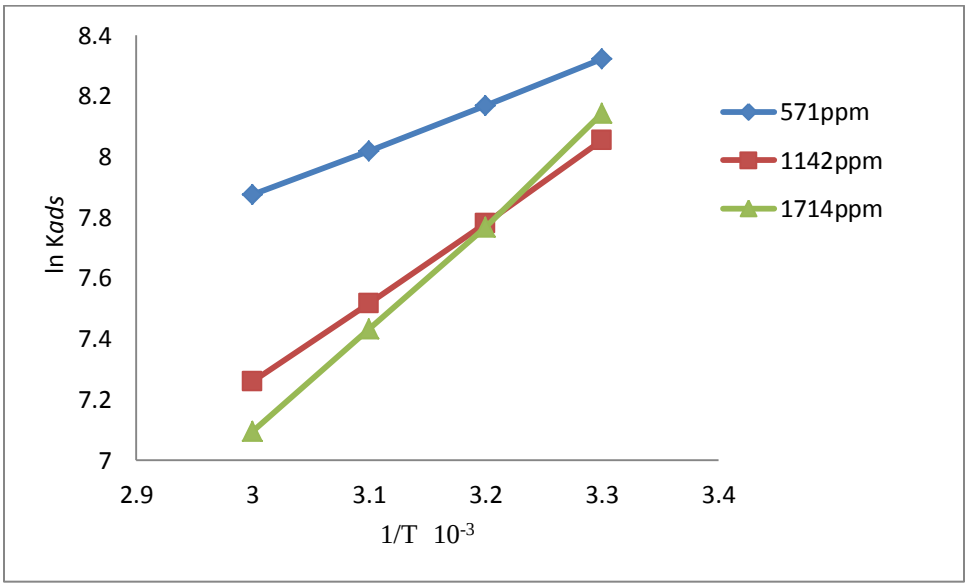


Fig 4.18: Variation of ln K*ads* and 1/T of $Na_2Cr_2O_7$ in 0.5M HCl on mild steel surface

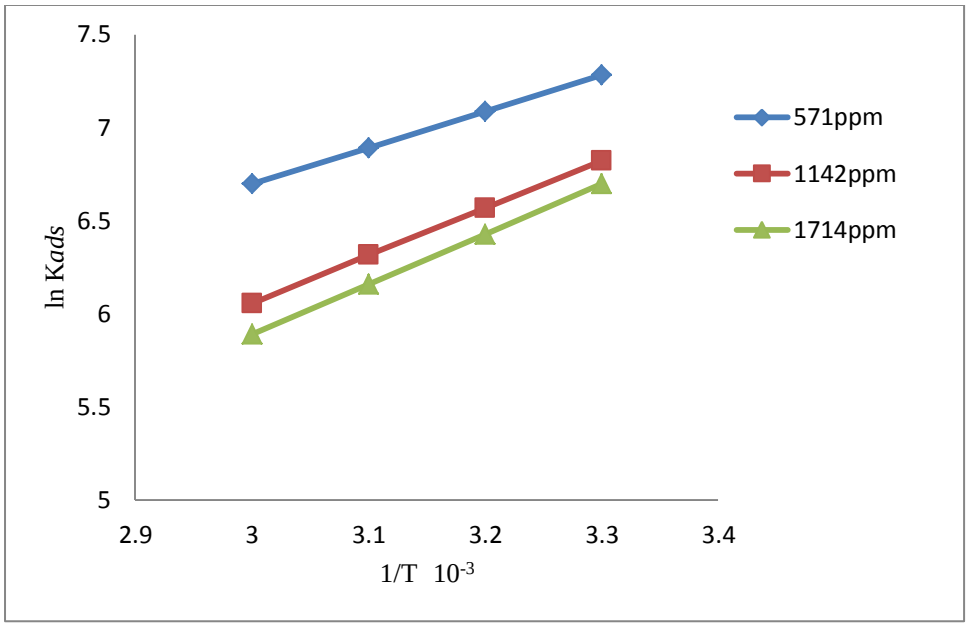


Fig 4.19: Variation of *ln* K*ads* and 1/T of BHETA in 0.5M H_2SO_4on mild steel surface

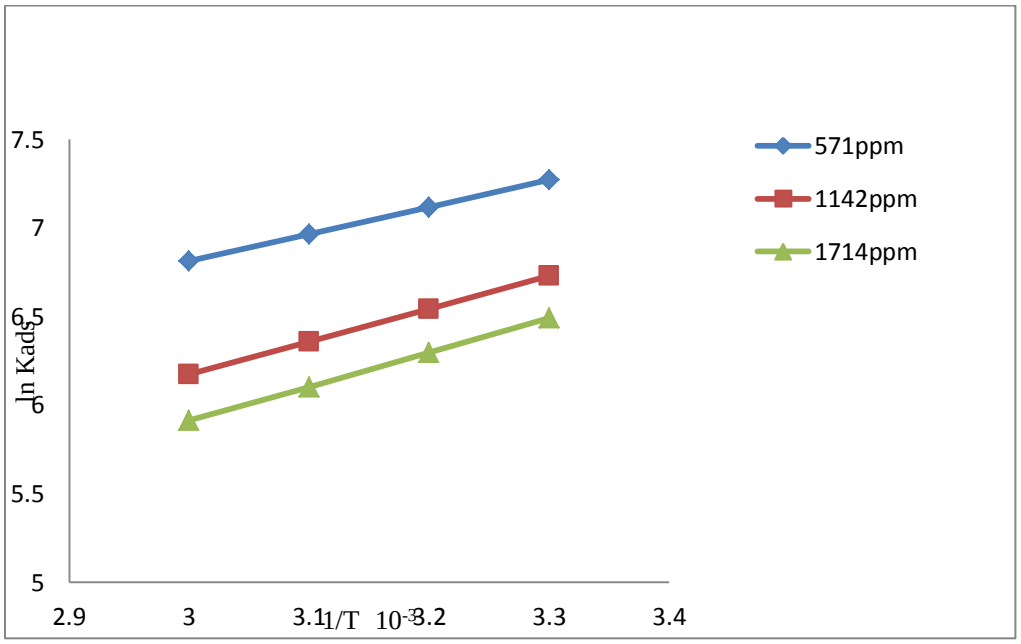


Fig 4.20: Variation of *ln* K_{ads} and 1/T of $Na_2Cr_2O_7$ in 0.5M H_2SO_4 on mild steel surface

Optical micrographs of mild steel samples (100 magnification) are shown in figure 4.21- 4.26.

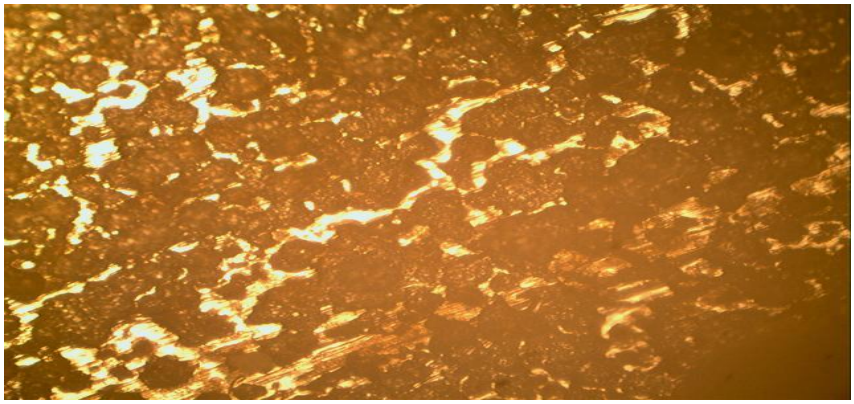


Fig. 4.21: after immersion in 0.5M H_2SO_4 for 35 days (100 magnification)

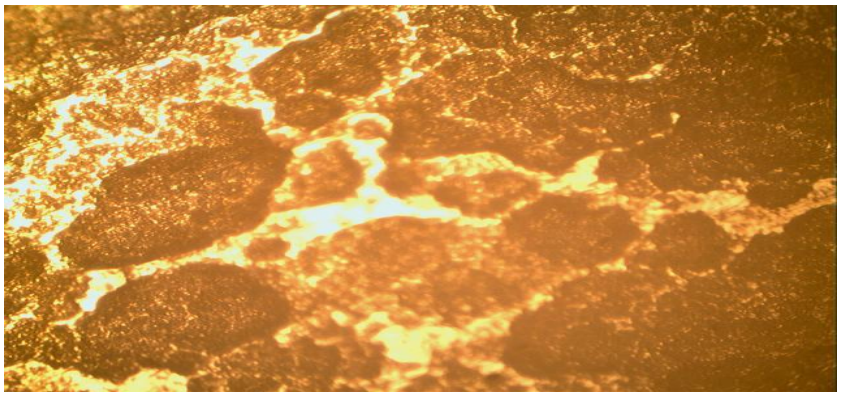


Fig. 4.22: after immersion in 0.5M HCl for 35days (100 magnification)

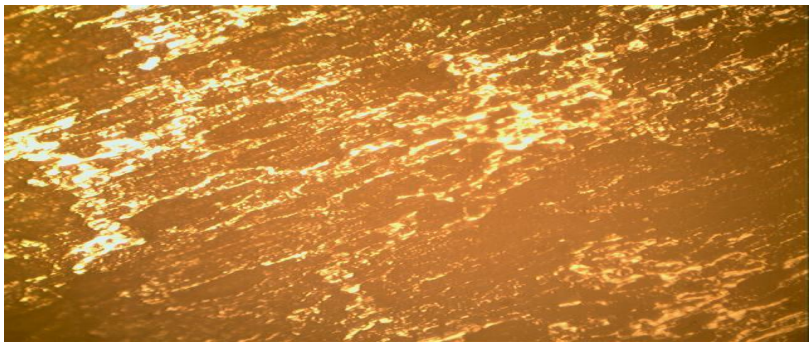


Fig. 4.23: after immersion in 0.5M H_2SO_4 + 1714ppm BHETA for 35 days (100 magnification)

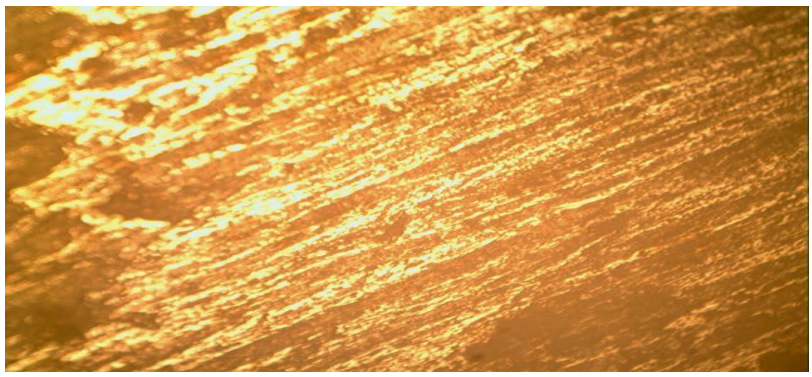


Fig. 4.24: after immersion in 0.5M HCl + 1714ppm BHETA for 35 days (100 magnification)

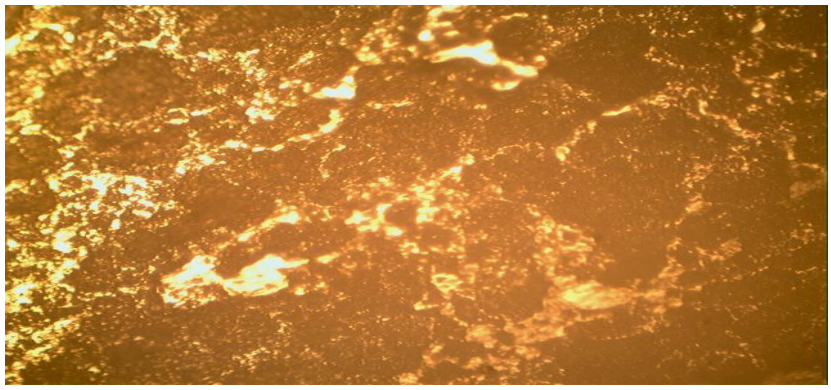


Fig. 4.25: after immersion in 0.5M H_2SO_4 + 1714ppm $Na_2Cr_2O_7$ for 35 days (100 magnification)

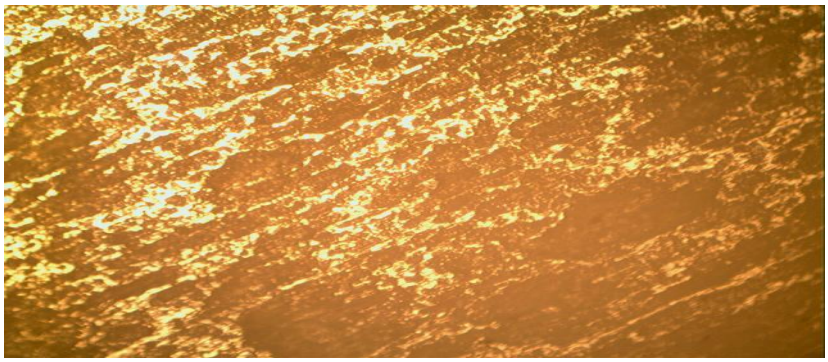


Fig. 4.26: after immersion in 0.5M HCl + 1714ppm $Na_2Cr_2O_7$ for 35 days (100 magnification)

4.2 Discussion of Results

Figure 4.1-4.4 show the effect of inhibitors concentration on the exposure time of mild steel in 0.5M HCl and 0.5M H_2SO_4 at concentrations of 571, 1142, 1714 and 2285ppm. Results showed higher corrosion rate for uninhibited solutions and better performance in inhibited solutions. As the concentration of inhibitors increases, the rate of corrosion decreased which indicates that a protective layer is formed at the surface of the coupons which prevents serious damage. This is in agreement with the works of Yawas (2005) and Divakara *et al*. (2006). On the corrosion rate with time of exposure for mild steel in HCl and H_2SO_4 containing BHETA and $Na_2Cr_2O_7$, Fig. 4.5 and 4.6 show lower corrosion rates for coupons immersed in H_2SO_4 in the presence of BHETA, however, $Na_2Cr_2O_7$ had a better inhibitive propensity in HCl.

Figures 4.7- 4.10 show the plots of inhibitor efficiency against concentration. Figures 4.11 and 4.12 show a comparison of the efficiencies of both inhibitors in the aggressive solution at temperatures of 303 to 333K. Highest inhibitor efficiency of BHETA was 84.5% in HCl and 82.9% in H_2SO_4 at 303K and 1714ppm concentration; lowest inhibitor efficiency of 74.8% in HCl and 61.8% in H_2SO_4 was recorded at temperature and concentration of 333K and 571ppm respectively. $Na_2Cr_2O_7$ had highest inhibitor efficiency of 95.4% in HCl and 79.8% in H_2SO_4 at 303K and concentration of 1714ppm. Lowest inhibitor efficiency of 64.5% in H_2SO_4 and 84% in HCl was recorded at 333K and inhibitor concentration of 571ppm. Hence, it is evident that inhibitor efficiency decreased with increase in temperature but increases with inhibitor concentration as observed in this work.

A plot of the logarithm of corrosion rate against the reciprocal of the absolute temperature (Figs. 4.13 - 4.16) gave linear graphs with slope equal to $-E_a/R$. Hence, the activation energy (E_a) was calculated and

tabulated in table 4.23 and 4.24.These values were found to range from 43.85-52.72KJ/mol and 40.05-57.26KJ.molfor BHETA in HCl and H_2SO_4 respectively. Values of E_a for$Na_2Cr_2O_7$ in HCl and H_2SO_4 ranged from 40.36-67.35KJ/mol and 34.16-46.25KJ/mol respectively. This results that the adsorption of these inhibitors is consistent with the mechanism of physical adsorption. For physical adsorption mechanism, the activation energy should be less than 80KJ/mol (Ndibe et al, 2011). Also, the values of E_a obtained in the presence of BHETA and $Na_2Cr_2O_7$ were higher than the values obtained for the blank solutions, indicating that the inhibitors retarded the corrosion of mild steel in HCl and H_2SO_4. The heat of adsorption (H_{ads}) of BHETA and $Na_2Cr_2O_7$ on the surface of mild steel was calculated from the slope of z -$\Delta H_{ads}/R$ obtained from figure 4.17-4.20. Values of H_{ads} calculated are recorded in table 4.23 and 4.24. These values are negative, indicating that the adsorption of the inhibitors on mild steel is exothermic. These values are relatively low indicating that the heat of adsorption is also low.

The Gibbs free energy of adsorption (G_{ads}) was calculated from equation 3.9, and tabulated in tables 4.25-4.28. These values are negative, indicating spontaneous adsorption of the inhibitor on the surface of the mild steel. Generally, the magnitude of G_{ads} fall around -20KJ/mol or less negative indicates electrostatic interactions between inhibitor and the charged metal surface (i.e.physisorption). Those around -40KJ/mol or more negative indicates charge shearing transfer from organic species to the metal surface to form coordinate type of bond (i.e chemisorptions) in accordance with Abd El-Hammed, (2011). In the present work, the calculated values are negatively lower than the threshold value of -40KJ/mol required for chemical adsorption; hence the adsorption of both inhibitors in HCl and H_2SO_4 on the surface of mild steel is spontaneous and favours the mechanism of physical adsorption. It was observed in this study that the more negative the value of G_{ads} the stronger the strength of adsorption.

Figures 4.21 and 4.22 show micrographs of mild steel exposed in 0.5M HCl and 0.5M H_2SO_4 for 35 days without inhibitors, pronounced grain sizes were observed. Inspection of the figures reveals that there is severe damage, clear pits and cavities on the surface of mild steel were seen. However, figures 4.23-4.26 show finer grain sizes of samples, surface corrosion of mild steel decreased remarkably in the presence of both inhibitors. This confirms that the metal surface was fully covered with adsorbed inhibitor molecules. On comparison BHETA acts as a good inhibitor in H_2SO_4 than in HCl while $Na_2Cr_2O_7$ is better in HCl than in H_2SO_4, which is in agreement with results obtained from weight loss measurement.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The following conclusions can be drawn from this research work:

i. BHETA was successfully formulated from waste PET bottles as corrosion inhibitor

ii. BHETA and $Na_2Cr_2O_7$have high significant effects on the corrosion of mild steel by forming films on the substrate subsequently displacing water molecules. However, BHETA is more effective in reducing corrosion loss in H_2SO_4 than in HCl while $Na_2Cr_2O_7$ is more effective in HCl.

iii. Protection efficiency of these compounds was seen to increase with increased inhibitor concentration but decreased with increase in temperature. Leading to the conclusion that the protective film of these compounds formed on the carbon steel surface is less stable at higher temperature.

iv. Activation energies were higher in the presence of the inhibitors suggesting physisorption mechanism in both acid media.

v. The negative sign of the G_{ads} and H_{ads} indicates that the adsorption process is spontaneous and exothermic.

vi. Results obtained from the metallurgraphical examination carried out on the mild steel specimen have shown that both inhibitors displayed an effective inhibitive tendency against stress corrosion cracking of the materials in the acidic solutions considered.

5.2 Recommendations

i. Present constraint in the availability of equipments has subjected this research to weight loss methods. However, subsequent investigation can be carried out using A.C Impedance and Linear polarization methods. Further analysis can be done using X-ray diffractometry (XRD).

ii. Further analyses into the chemical structure of BHETA should be carried out.

iii. More work could be done on the corrosion rate of non ferrous alloys with both inhibitors.

iv. Further studies can be carried out on the solvolysis of pure water sachet (LDPE) as corrosion inhibitor in order to convert waste to useful products and alleviate environmental pollution

v. Mediums such as crude oil, distillate fuels etc. could be use to characterize the inhibition propensity of these inhibitors.

vi. BHETA is a good substitute for $Na_2Cr_2O_7$ and it is recommended on the basis of low operational hazard and better inhibition in H_2SO_4.

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