**THE INHIBITIVE EFFECT OF ALANINE ON CORROSION OF ALUMINIUM IN 0.5 M HCL SOLUTION USING THE WEIGHT LOSS TECHNIQUE**

**CHAPTER ONE INTRODUCTION**

**1.1 BACKGROUND OF STUDY**

**1.1.1 CORROSION**

Corrosion is defined as a natural process, which converts refined metal to their more stable oxide. It is the gradual destruction or degradation of materials (usually metals) by chemical reaction with their environment which are most likely inevitable. Corrosion is a natural and costly process of destruction like earthquakes, tornados, floods and vocanic eruptions, with one major difference. Whereas we can be only a silent spectator to the above processes of destruction, corrosion can be prevented or at least be controlled.

Despite different definitions, it can be observed that corrosion is basically the result of interaction between materials and their environment. Up to the 1960’s, the term corrosion was restricted only to the metals and their alloys and it did not incorporate ceramics, polymers, composites and semiconductors in its regime. The term corrosion now encompasses all types of natural and man – made materials including biomaterials and nanomaterials, and it is not confined to metals and alloys alone. The scope of corrosion is consistent with the revolutionary changes in materials development witnessed in recent years.

**1.1.1.2 CORROSION AND ITS MECHANISM**

In nature, metals are not found in free state due to their reactivity. Metals are generally in high energy state because some energy is added during their manufacturing process from the ores. Low energy – state ores are more stable than the high energy – state metals. As a result of this uphill thermodynamic struggle, the metals have a strong driving force to release energy and go back to their original form. Hence the metals revert to their parent state or ore under a suitable corrosive environment. The electrochemical process involved in corrosion by nature is opposite to the extractive metallurgy involved in manufacturing of the metals.

According to electrochemistry, the corrosion reaction can be considered as taking place by two simultaneous reactions:

The oxidation of a metal at an anode (a corroded end releasing electrons) and the reduction of a substance at a cathode (a protected end receiving electrons). In order for the reaction to occur, the following conditions must exist:

1. Two areas on the structure must differ in electrical potential.

2. Those areas called anodes and cathodes must be electrically interconnected.

3. Those areas must be exposed to a common electrolyte.

4. An electric path through the metal or between metals be available to permit electron flow.

When these conditions exist, a corrosion cell is formed in which the cathode remains passive while the anode deteriorates by corrosion. As a result of this process, electric current flows through the interconnection between cathode and anode. The cathode area is protected from corrosion damage at the expense of the metal, which is consumed at the anode. The amount of metal lost is directly proportional direct current flow. Mild steel is lost at approximately 20 pounds for each ampere flowing for a year. (Thomas, 1994).

At the anode, metals are oxidized and the electrons are liberated from the metal to form positive metal ions. The liberated electrons dissolve into the electrolyte, and deposition is formed on the cathodic metal. Anode corrodes while the cathode remains intact.

**1.1.1.2.1 ELECTROCHEMISTRY OF CORROSION**

Corrosion occurs by an electrochemical process. The phenomenon is similar to that which takes place when a carbon-zinc “dry” cell generates a direct current. Basically, an anode (negative electrode), a cathode (positive electrode), an electrolyte (environment), and a circuit connecting the anode and the cathode are required for corrosion to occur.

Dissolution of metal occurs at the anode where the corrosion current enters the electrolyte and flows to the cathode. The general reaction or reactions, if an alloy is involved) that occurs at the anode is the dissolution of metal as ions:

M → Mn+ + en-

Where

M = metal involved n = valence of the corroding metal species e = electrons

The basic corrosion cell consists of an anode, a cathode, an electrolyte, and a metallic path for electron flow. Note that the corrosion current (z) enters the electrolyte at the anode and flows to the cathode.

Examination of this basic reaction reveals that a loss of electrons, or oxidation, occurs at the anode. Electrons lost at the anode flow through the metallic circuit to the cathode and permit a cathodic reaction (or reactions) to occur. In alkaline and neutral aerated solutions, the predominant cathodic reaction is

O2 + 2H2O + 4e– → 4(OH) (1.1)

The cathodic reaction that usually occurs in deaerated acids is

2H- + 2e– → H2 (1.2)

In aerated acids, the cathodic reaction could be

O2 + 4H- + 4e– → 2H2O (1.3)

All of these reactions involve a gain of electrons and a reduction process. The number of electrons lost at the anode must equal the number of electrons gained at the cathode. For example, if iron (Fe) was exposed to aerated, corrosive water, the anodic reaction would be

Fe → Fe++ + 2e– (1.4)

At the cathode, reduction of oxygen would occur

O2 + 2H2O + 4e– → 4(OH-) (1.5)

Because there can be no net gain or loss of electrons, two atoms of iron must dissolve to provide the four electrons required at the cathode. Thus, the anodic and cathodic reactions would be

2 Fe → 2Fe++ + 4e– (anodic) (1.6)

O2 + 2H2O + 4e-→ 4(OH-) (cathodic) (1.7)

These can be summed to give the overall oxidation-reduction reaction

2Fe + O2 + 2H2O → 2Fe++ + 4(OH-) (1.8)

After dissolution, ferrous ions (Fe++) generally oxidize to ferric ions (Fe+++); these will combine with hydroxide ions (OH-) formed at the cathode to give a corrosion product called rust.

(FeOH or Fe2O3.H2O) (1.9)

Similarly, zinc corroding in aerated, corrosive water (i.e., Zn → Zn++ + 2e-) will form the corrosion product Zn(OH)2. The important issue to remember is that anodic dissolution of metal occurs electrochemically; the insoluble corrosion products are formed by a secondary chemical reaction.

**1.1.1.3 CLASSIFICATION OF CORROSION**

Corrosion based on the appearance of the corroded metal can be classified as uniforrm or localized. Corrosion is either uniform i.e the metal corrodes at the same rate over the entire surface,or it is localized, in which case only small areas are affected.

Classification by appearance, which is particularly useful in failure analysis, is based on identifying forms of corrosion by visual observation with either the naked eye or magnification.The morphology of attack is the basis for classification. Figure 1.5 illustrate some of the most common forms of corrosion.

There should be vivid distinction between macroscopically localized corrosion and microscopic local attack. In the latter case, the amount of metal dissolved is minute (minimal), and considerable damage can occur before the problem becomes visible to the naked eye or can be viewed with the aid of a low – power magnifying device (Schweitzer, 1998).

**1.1.1.4 CORROSION PREVENTION**

Some corrosion prevention methods include material selection, conditioning the corrosive environment, electrochemical control, protective coating and use of corrosion inhibitors. The most common and easiest way of preventing corrosion is through the judicious selection of material once the corrosion environment has been characterized. Standard corrosion references are helpful in this respect. Here, cost may be a significant factor and it is not always economically feasible to employ the material that provides the optimum corrosion resistance; sometimes, either another alloy or some other measure must be used.

Conditioning the corrosive environment if possible may also significantly influence corrosion. Lowering the fluid temperature and/or velocity usually produces a reduction in the rate at which corrosion occurs. Many times increasing or decreasing the concentration of some species in the solution will have a positive effect; for example, the metal may experience passivation.

**CORROSION INHIBITORS:**

Corrosion inhibitors are chemicals that react with the metal’s surface or the environmental gases causing corrosion, thereby, interrupting the chemical reaction that causes corrosion. Inhibitors can work by adsorbing themselves on the metal’s surface and forming a protective film. These chemicals can be applied as a solution or as a protective coating via dispersion techniques.

The inhibitors process of slowing corrosion depends upon:

• Changing the anodic or cathodic polarization behavior

• Decreasing the diffusion of ions to the metal’s surface

• Increasing the electrical resistance of the metal’s surface

Major end-use industries for corrosion inhibitors are petroleum refining, oil and gas exploration, chemical production and water treatment facilities.

The benefit of corrosion inhibitors is that they can be applied in-situ to metals as a corrective action to counter unexpected corrosion.

**1.1.1.5 ECONOMIC IMPORTANCE OF CORROSION**

The problems of metallic corrosion is one significant propotion, it has been estimated that appoximatly 5% of an industrial nation’s income is spent on corrosion prevention and its maintenance or preplacement of products lost or contaminated as a result of corrosion reaction. The consequences of corrosion are many and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failure of various kinds of equipment and the need for expensive replacement may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarized as follows:

• Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.

• Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.

• Mechanical damage to valves, pumps, etc., or blockage of pipes by solid corrosion products.

• Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

• Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localized zones so as to give a crack on the structure, very considerable weakening may result from quite a small amount of metal loss.

• Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).

• Reduced value of goods due to deterioration of appearance.

Corrosion processes are occasionally used to advantage. For example, etching procedures makes use of the selective chemical reactivity of grain boundaries or various micro-structural constituent. Also, the current development in dry cell is as a result of corrosion processes.

**1.1.2 ALUMINIUM**

Aluminium always finds very regular and diversified uses in domestic appliances, chemical reactions and storage bottles, vessels and containers, buildings, bridges, packaging foils, automobiles, aircrafts, ships and many others. It is used for variety of applications due to its light weight, very high strength, good thermal and electrical conductivities, good heat and light reflectivity, its non-rusty nature, non-toxicity and attractive appearance. It is highly electropositive and resistant to corrosion because a hard, tough film of oxide is formed on the surface. The surface film is amphoteric, hence the metal could dissolve readily in both strong acid and alkaline media. Despite these great properties of aluminium, it is not a perfect material for engineering applications in all environments as they suffer corrosion caused by chemical interactions with their surroundings (Khandelwal et al., 2010). Aluminium is used in industries like shipping, offshore petroleum exploration, power and coastal industrial plants (for cooling), fire-fighting, oil fuel water injection and desalination plants.

**1.2 STATEMENT OF PROBLEM**

The failure of aluminum equipment and aluminum materials due to acid corrosion in industries is widely reported (Abiola et al, 2012), as such there is a need to minimize this common effect. In virtually all situations, aluminum failure through corrosion can be managed, slowed or even stopped by using the proper techniques.

The most common and easiest way of preventing corrosion is through the judicious selection of material once the corrosion environment has been characterized and by the use of chemical inhibitors is the most practical and cost effective means of controlling corrosion of metals in acid solutions. However, a number of inhibitors of acid corrosion of aluminum are toxic, non-biodegradable and expensive.

**1.3 AIM**

The aim of this study is to investigate the inhibitive effect of alanine on corrosion of aluminium in 0.5 M HCl solution using the weight loss technique.

**1.4 SCOPE OF STUDY**

This study is limited to the study of use of organic inhibitors to reduce the failure of aluminum due to acidic corrosion. This is achieved by determining the inhibition efficiency of alanine by testing different concentration of alanine on aluminum in an acidic solution.

CHAPTER TWO

REVIEW OF RELATED LITERATURE

## 2.0 CONCEPT OF CORROSION

 Modern science and technology has at its disposal a wide range of constructional materials – metals and alloys, plastics, rubber, ceramics, composites, wood etc and the choice of an appropriate material for a given application is the responsibility of the design engineer (Shreir *et al*, 2000). There are no general rules governing the selection of a particular material for a specific purpose, and logical decision involves a consideration of the relevant properties – availability, ease of fabrication, relative cost, etc of different materials. The decision is most often determined by economic factor rather than properties, and ideally the material selected should be the cheapest possible that has adequate properties to fulfill the specific function.

For metals, mechanical, physical and chemical properties must be considered. According to Shreir *et al* (2000), the mechanical and physical properties may be expressed in terms of constants, while the chemical properties of a given metal are dependent entirely on the environmental conditions prevailing during service. While a metal or an alloy may be chosen largely on the basis of its mechanical and physical properties, the fact still remains that there are very few applications involving the effect of the interaction of a metal with its environment that can be completely ignored. The importance of this interaction is of varying significance depending on the circumstance. For instance, the slow uniform wastage of steel of massive cross section (as in railway lines or sleepers) is not far less important than the rapid perforation of buried steel pipe or the sudden component in sodium hydroxide solution.

Corrosion may be considered as an oxidation process in which an oxide coating is formed on the surface of the metal undergoing the process (Onen, 2000). In the case of non-metallic materials, the term corrosion invariably refers to their deterioration from chemical causes. Many authors (Potter, 1956; Vernon, 1957 and Hoar, 1961) consider metallic corrosion as interaction of a metal or alloy (solid or liquid) with its environment. Corrosion has also been defined by Fontana and Greene (1967) and Uhlig (1971) as the undesirable “deterioration” of a metal or alloy – an interaction of the metal with its environment that adversely affects those properties of the metal that are to be preserved. This definition is also applicable to non-metallic materials like glass, concrete etc.

When exposed to an industrial atmosphere, steel reacts to form „rust‟ of an approximate composition, Fe2O3.H2O, and being loosely adherent , this does not form a protective barrier to isolate the metal/alloy from the environment; thus the reaction proceeds at an approximately linear rate until the metal/alloy is completely consumed. The rapid dissolution of a vessel constructed of titanium in hot 40% H2SO4 with the formation of Ti4+ aquo cations conforms with both the „‟transformation‟‟ and

„‟deterioration‟‟ definitions of corrosion. If the potential of the metal is raised (anodic protection), a thin adherent protective film of Titanium (IV) oxide(which isolates the metal from the acid) is formed.

Fontana and Staehle (1990) have stated that corrosion includes the reaction of metals, glasses, ionic solids, polymeric solids and composites with environments that embrace liquid metals, gases, non-aqueous electrolytes and other non-aqueous solutions. Corrosion may also be considered as a branch of chemical thermodynamics, or kinetics, as the outcome of electron affinities of metals and non-metals, as short-circuited electrochemical cells, or as the demolition of the crystal structure of a metal (Evans, 2000).

Corrosion in the context of corrosion science may therefore be defined as the reaction of a solid with its environment while in the context of corrosion engineering, it may be considered as the reaction of an engineering constructional material (metals or non-metals) with their environments with consequent deterioration in properties of the materials.

## 2.1 CORROSION AS A REACTION AT A METAL/ENVIRONMENT INTERFACE

Most metallic corrosion result from electrochemical effects. When this occurs, corrosion is initiated by the flow of electrons between the electrode sites of different potentials in contact with an aqueous electrolytic solution (e.g. salt solution). The metals dissolve at the anodic site on the surface of the metal where the electrons are released as represented by equation (1) (Hamsson *et al*, 1987).

 M(s) M2+(aq) + 2e-(2.1)

It has been established that metals corrode when exposed to the atmosphere as well as in halide solutions (Seinko and Plane, 1974; Bajah and Godman, 1984 and Fontana and Staehle, 1990). According to these authors, corrosion involves the transfer of electrons along the surface of the metal under the influence of a potential difference. It has equally been observed by different workers (Seinko and Plane, 1974; Akhmetov *et al*, 1989 and Sharma and Sharma, 1999) that metals /alloys do not corrode in dry air or in water completely free of air. Corrosion therefore, requires oxygen and water to occur.

Corrosion is accelerated by acids or by contact with less active metals such as tin or copper. Certain salt solutions also hasten corrosion, not only because they are acidic by hydrolysis, but also because of specific catalytic effects or reactions of the anion. Corrosion, according to Shreir *et al* (2000) may be regarded as a heterogeneous redox reaction at a metal/nonmetal interface in which the metal is oxidized and the nonmetal reduced. It can be expressed by the simple chemical reaction:

 aA + bB cC + dD (2.2)

where A is the metal, B, the non-metal (environment) reactant(s), C and D are the reaction products. C is the oxidized form of the metal (corrosion product) and D is the reduced form of the non-metal (another corrosion product). In its simplest form, reaction

(2) becomes

 aA + bB cC (2.3)

 e.g. 4Fe + 3O2 2Fe2O3.

Reactions of this type which do not involve water or aqueous solutions are referred to as

„‟dry corrosion reactions‟‟. The corresponding reaction(s) in aqueous solutions are called

„‟wet corrosion reactions‟‟, and the overall reaction(s) can be expressed as

 4Fe + 2H2O + 3O2  2Fe2O3.H2O (2.4)

Thus in all corrosion reactions, one (or more) of the products will be an oxidized form of

the metal, aqueous cations (e.g. Fe2+(aq), Fe3+(aq)), aqueous anions (e.g. HFeO2-(aq), FeO42-(aq) or solid compounds (e.g. Fe (OH)2, Fe3O4, Fe3O4.H2O, Fe2O3.H2O), while the other reaction product(s) will be reduced form of the non-metal. In the interaction of a metal with a specific non-metal(s) under specific environmental conditions, the chemical nature of the non-metal, the chemical and physical properties of the reaction products as well as the environmental conditions (temperature, pressure, velocity, viscosity etc) will be important in determining the form extent and rate of the corrosion reaction.

### 2.1.1 Environments in Corrosion Process

Corrosion only takes place in specific environment(s) which may be „damp‟, „wet‟ or „dry‟. Environments in corrosion studies include: concentration, pH, velocity, temperature, atmosphere, natural waters, sea water, chemicals, fused salts, liquid metal(s), flue gas, bacteria e.t.c. During corrosion, the kinetics of the cathodic and anodic partial reactions controls the rate of overall corrosion reaction.

Shreir *et al* (2000) considered environmental factors such as concentration, velocity and temperature on the assumption that either the anodic or cathodic reaction is rate controlling. Thus, if a metal is corroding under cathodic control, it is apparent that velocity of the solution will be more significant when diffusion of the cathodic reactant is rate controlling, though temperature may have an effect. If on the other hand, the cathodic process requires high activation energy, temperature will have the most significant effect.

These workers assert that effects of concentration, velocity and temperature are complex and it will become evident that these factors can frequently outweigh the kinetic and thermodynamic considerations. An increase in hydrogen ion concentration will raise the redox potential of the aqueous solution with a consequent increase in corrosion rate. If however, there is an increase in the rate of the cathodic process, there will be a decrease in corrosion rate when the metal exhibits an active/passive transition. When metals are subjected to high velocity and temperature, these complex environmental conditions may not necessarily apply.

Numerous metals and alloys used in practice show a wide variation in response to various anions in acid and alkaline solutions that common features are difficult to discern and a basis for predicting corrosion behaviour is not very apparent. Although pourbaix (potential-pH) diagrams have led to greater understanding of the changes in the corrosion behaviour of a metal due to change in pH, they are less instructive about the behaviour of alloys and the maxima in the corrosion rate that occurs frequently with increasing acid concentration. For instance, Fe-18Cr-8Ni stainless steel has a low rate of corrosion in dilute H2SO4 but increases with increase in concentration to a maximum, followed by decreasing rate on further increase in concentration (Figure 1).



**Corrosion rate (mgd**

**m**

**-**

**1**

**d**

**-**

**1**

**)**

**H**

**2**

**SO**

**4**

**(**

**%**

**)**

## Figure 1: Corrosion Rate Fe- 18Cr-8Ni as a Function of H2SO4 Concentration at 20oC

 Thermochemical data available show that potential- pH diagrams can be calculated for anions like SO42-, Cl-, citrate, S2- e.t.c (Wickstrom, 1966; Peckner and Bernstein,

1977). However, there is no available method for calculating the relationships for alloys. For simple alloy systems, this may be possible since dissolution of each phase appears to be a simple additive mechanism (Truman, 1978).

 Metals are more frequently exposed to the atmosphere than any other corrosive environment. Atmospheric corrosion is also the oldest corrosion problem known to man yet not fully understood. The main reason for this paradox lies in the complexity of the variables which determine the kinetics of the corrosion reactions. Thus, corrosion rates vary from place to place, hour to hour and from season to season. This complexity sometimes makes meaningful results from laboratory experiments very difficult to obtain. In atmospheric corrosion, emphasis is often placed on metals (like iron and steel, zinc, copper, lead, aluminium and chromium) whose corrosion is of economic importance.

Atmospheric corrosion is classified as dry oxidation, damp corrosion and wet corrosion (Shreir *et al*, 2000).

 Dry oxidation takes place in the atmosphere with metals that have negative free energy of oxide formation. Damp and wet atmospheric corrosion are characterized by the presence of a thin, invisible film of electrolyte solution on the metal surface (damp type) or by visible deposits of dew, rain, sea-spray e.t.c (wet type). The corrosion products may be soluble or insoluble. Insoluble products usually reduce the rate of corrosion by isolating the substrate from the corrosive environment. Soluble corrosion products may increase corrosion rate either by increasing the conductivity of the electrolyte solution thereby decreasing the „‟internal resistance‟‟ of the corrosion cells or by acting hygroscopically to form solutions at humidities above or at that in equilibrium with saturated solution (Peckner and Bernstein, 1977). However, whether the corrosion products are soluble or insoluble, protective or non-protective, the corrosive atmosphere experienced by the substrate (micro-environment) is modified from the macroenvironment experienced by a bare substance.

 At ordinary temperatures, most engineering metals are protected by very thin oxide films, (3 to 10 nm or 10m-9 thick) (Talbot and Talbot, 1998). These films form very rapidly in contact with atmospheric oxygen but subsequent growth in uncontaminated air with low humidity is imperceptible. It is for this reason that aluminium, chromium, zinc, nickel and some other common metals remain bright in unpolluted indoor atmosphere. Unprotected active metals exposed to water or rains are vulnerable but corrosion can be delayed or even prevented by natural or artificially contrived conditions in the environment.

It is a remarkable and important fact that, except where there is gross dilution or contamination, the relative proportions of the major constituents of sea water are practically constant all over the World. The major constituents of sea water (parts per thousand, ppt) are given in Table 1 below.

**Table 1: Major Constituents of Sea Water (parts per thousand, ppt).**

##  (Chlorinity = 190/00, Density at 20oC = 1.0243)

 Chloride (Cl-) 18.979 9

 Sulphate (SO42-) 2.648 6

 Bicarbonate (HCO3-) 0.139 7

 Bromide (Br-) 0.064 6

 Fluoride F-) 0.001 3

 Boric acid (H3BO3) 0.026 0

 Sodium (Na+) 10.556 1

 Magnesium (Mg2+) 1.272 0

 Calcium (Ca2+) 0.400 1

 Potassium (K+) 0.380 0

 Strontium (Sr2+) 0.013 3

 Source: Sverdrup et al (1942)

 Minor constituents of sea water include organic and inorganic molecules, some of which form metallic complexes whose trace amounts can significantly affect the corrosion mechanism. Trace metallic complexes also play an important role in determining the physiology of biological organisms whose presence in sea water can exert considerable control over corrosion reactions. The presence of such complexing agents in sea water could explain the difficulty of stimulating the natural products for common research investigations in the laboratory (Rowlands, 2000).

Ferrous metals, of which steel is technically the most important, have a remarkably steady rate of corrosion when fully immersed in sea water. The corrosion of mild steel is initially very rapid but falls gradually over several months to a fairly steady rate as shown in Table 2.

## Table 2: Effect of Exposure Period on Corrosion Rate of Mild Steel, Copper and Aluminium at 30oC and Pressure of 760mmHg

 Exposure Time Average corrosion rate for the period (mm/y)

 (Months) Mild steel Copper Aluminium

1. 0.33 - -
2. 0.25 - -
3. 0.19 - -

 6 0.15 - -

 12 0.13 0.034 0.0043

 24 0.11 0.019 0.0021

 48 0.11 0.018 0.0017

 Source: (Southwell *et al*, 1965, Southwell *et al*, 1968 and Rowlands, 2000)

It is generally agreed that steel composition within the practical range for ship plate has little influence on the corrosion rate in sea water (Hudson, 1950; Forgeson *et al*, 1965 and Evans and Rance, 1963). Owing to the laborious task of obtaining corrosion rates from gravimetric measurements, data for the effect of exposure time on corrosion rates have been very limited.

Many common non-ferrous metals corrode relatively slowly in still or slow-moving sea water. The effect of exposure time on the corrosion of copper and aluminium is illustrated in Table 2. The results quoted by Southwell *et al* (1965) and Southwell *et al* (1968) for corrosion rates of copper and aluminium in tropical salt waters suggest that corrosion rate increases by a factor of 2 for every 10oC rise in temperature.

There are many instances where two or more chemicals exert a marked synergistic action such that low dissolution rates obtained in either environment become greater in the presence of both. Furthermore, the corrosiveness of a chemical will be affected by the presence of certain impurities, which may act as either accelerators or inhibitors. The majority of metals and alloys available depend for their resistance to corrosion on the properties of an oxide film or corrosion product which is initially formed by the corrosion process (Boden, 2000).

### 2.1.2 Metals

Heterogeneities associated with a metal have been classified by Ehrlich and Turnbull (1959) as atomic, microscopic (visible under an optical microscope) and macroscopic as summarized in Table 3. It is relevant to observe, however, that detailed mechanism of all aspects of corrosion, e.g. the passage of a metallic cation from the lattice to the solution, specific effects of ions and species in solution in accelerating or inhibiting corrosion or causing stress corrosion cracking e.t.c must involve a consideration of the detailed atomic structure of the metal or alloy.

## Table 3: Heterogeneities in Metals

### 1. Atomic

1. Sites within a given specific layer („normal‟ sites); these vary according to the particular crystal plane
2. Sites at edges of partially complete layers.
3. Point defects in the surface layer; vacancies (molecules missing in surface layer), kink sites (molecules missing at edge of a layer), molecules adsorbed on top of a complete layer.
4. Disordered molecules at point of emergence of dislocations (screw or edge) in a metal surface.

### 2. Microscopic

(a) Grain boundaries – usually, but not invariably, more reactive than grain interior. (b) Phases – metallic (single metal, solid solutions, intermetallic compounds), non-metallic, metal compounds, impurities e.t.c – heterogeneities due to thermal or mechanical causes.

### 3. Macroscopic

1. Grain boundaries.
2. Discontinuities on metal surface – cut edges, scratches, discontinuities in oxide films (or other chemical films) or in applied metallic or non-metallic coatings.
3. Bimetallic couples of dissimilar metals.
4. Geometrical factors- general design, crevices, contact with non-metallic materials. e.t.c.

Source**:** Ehrlich and Turnbull (1959) The corrosion behaviour of different constituents of an alloy, according to these authors, is well known, since the etching techniques used in metallography are essentially corrosion processes which take advantage of the different corrosion rates of phases as a means of identification. For instance, the grain boundaries are usually etched more rapidly than the rest of the grain due to the greater reactivity of the disarrayed metal. Macroscopic heterogeneities, e.g. crevices, discontinuities in surface films, bimetallic contacts e.t.c, will have a pronounced effect on the location and the kinetics of the corrosion process (Shreir *et al*, 2000). Aluminum and mild steel are used for this study. Aluminium and its alloys have many engineering applications because of their combination of lightness with strength, their high corrosion resistance, their thermal and electrical conductivity, their heat and light reflectivity as well as their hygienic and nontoxic qualities. The variety of forms in which they are available also enhances their utility (Bailer *et al*, 2000). Pure aluminium has good working and forming properties- low mechanical strength and high ductility. Although the principle of aluminium cladding was originally applied to high strength aircraft alloys, it is now utilized in several important industrial applications. With an atomic mass of 26.97gmol-1, aluminium has a density of 2700 kgm-3 at 293K, inter atomic distance of 2.863A and a crystal structure that is face-centred cubic (Scammons, 1981).

 Aluminum is a very reactive metal with a high affinity for oxygen. The metal is nevertheless highly resistant to atmospheres and to a great variety of chemical agents. This resistance, according to Bailer *et al*, (2000), is due to the inert and protective character of the aluminium oxide film which forms on the metal surface. In most environments, therefore, the rate of corrosion of aluminium decreases rapidly with time.

A corrosion rate increasing with time s rarely encountered with aluminium, except in aqueous solutions at high temperatures and pressures.

 The oxidation of aluminium at room temperature is reported to conform to an inverse logarithmic equation for growth periods up to 5 years duration (Godard, 1967). At elevated temperatures, oxidation studies over shorter periods illustrate conformity to parabolic, linear and logarithmic relationships according to time and temperature. The kinetic variations are attributed to different mechanisms of film formation (Ayimore *et al*, 1960 and Bartlett, 1964). General dissolution of aluminium occurs in strongly acidic or alkaline solutions with some specific exceptions. Thus, in concentrated HNO3, the metal is passive and the kinetics of the process is controlled by ionic transport through the oxide film, while inhibitors like silicates permit the use of some alkaline solutions up to pH of 11.5 with aluminium. Even where corrosion may occur to a limited extent, aluminium is often preferred to other metals because its corrosion products are colourless.

 The corrosion resistance of aluminium in a variety of media has been reported. It has been observed that mono-chloroacetic acid has no corrosive effect and di-chloroacetic acid has negligible effects up to 5M but tri-chloroacetic acid produces a vigorous reaction (Bailer *et al*, 2000). The corrosion rate of aluminium conductors in integrated circuits has been reported by Lerner and Eldridge (1982). Kunze (1976) has reported on the corrosivity of various foodstuffs to aluminium packaging materials while Singh (1981) showed that surface roughness has an important effect on the well water staining of aluminium and its alloys.

## 2.2 TYPES OF CORROSION

Corrosion can affect the metal in a variety of ways depending on its nature and the precise environmental conditions prevailing, and a broad classification of the various forms of corrosion. Five major types have been identified by Shreir (2000) and Uppal and Bhatia (2001) as uniform, localized, pitting, selective dissolution and conjoint action of corrosion and a mechanical factor. Thus, a 18Cr-8Ni stainless steel will corrode locally during intergranular attack, crevice corrosion or pitting. Shreir (2000) observed that in certain circumstances selective attack along an „‟active path‟‟ in conjunction with a tensile stress may lead to transgranular fracture. The different types, characteristics and examples of corrosion are summarized in Table 4 below.

## Table 4: Types, Characteristics and Examples of Corrosion

Type Characteristic Examples

2.2.1 Uniform All areas of the Oxidation and tarnishing; (or almost uniform) metal corrode at active dissolution in acids; the same (or similar) anodic oxidation and passivity; rate chemical and electrochemical polishing; atmospheric and immersed corrosion in certain cases.

2.2.2 Localized Certain areas of the metal Crevice corrosion; fill form surfaces corrode at higher corrosion; deposit attack; rates than others due to bimetallic corrosion; „‟heterogeneities‟‟ in the intergranular corrosion and metal, the environment or weld decay. in the geometry of the structure as a whole. Attack ranges from slightly localized to pitting.

2.2.3 Pitting Highly localized attack at Pitting of passive metals specific areas resulting in small such as the stainless pits that penetrate into the metal steels, aluminium alloys and may lead to perforation. e.t.c in the presence of specific ions e.g. Cl- ions

2.2.4 Selective one component of an alloy Dezincification, dissolution (usually the most active) is dealuminification, selectively removed from the graphitization.

alloy.

2.2.5 Conjoint action Localized attack or fracture Erosion-corrosion, of corrosion and due to the synergistic action fretting corrosion,

mechanical factor of a mechanical factor and impingement attack, corrosion. cavitation damage; stress corrosion, cracking (SCC), hydrogen cracking and corrosion fatigue.

Source: (Shreir, 2000)

Ideally, the metal selected, or the protective system applied to the metal, should be such that no corrosion takes place at all, but this is seldom technologically or economically feasible. It is therefore, necessary to tolerate a rate and form of corrosion that will not significantly detrimental to the properties of the metal during its anticipated life span. Thus, provided the corrosion rate is known, the slow uniform corrosion of a metal can frequently be allowed in the design of the structure. For instance, in the case of a metal that shows an active/passive transition, the rate of corrosion in the passive region is usually acceptable whereas the rate in the active region is not. It follows then that certain forms of corrosion are tolerable and that corrosion control/inhibition is possible, provided that the rate and form of the corrosion reaction are predictable.

 Shreir (2000), Uppal and Bhatia (2001), reported that pitting is one of the most destructive and insidious form of corrosion as the attack is extremely localized. It frequently leads to perforation and consequent corrosion failure. In other cases, pitting may result in loss of appearance, which is of major importance when the metal/alloy concerned is used for decorative architectural purposes. Aluminium saucepans in use become pitted with time. These pans, however, remain functional as the pits seldom penetrate them.

## 2.3 EFFECTS OF CORROSION ON MATERIALS (METALS/NON METALS)

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment and structures are often more serious than the simple loss of mass of a metal. Failures of various kinds and the need for expensive replacements may occur even though amount of metal destroyed may be quite small. Some of the harmful effects of corrosion are as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localized zones so as to give a crack-like structure, very considerable weakening may result from quite a small amount of metal loss.
2. Hazards or injuries to people arising from structural failure (e.g. bridges, cars, aircrafts).
3. Loss of time in availability of profile-making industrial equipment.
4. Reduced value of goods due to deterioration of appearance.
5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).
6. Perforation of vessels and pipes, thus allowing escape of their contents and possible harm to the surroundings. For instance, a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tube perforates.
7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface. 8. Mechanical damage to valves, pumps, e.t.c, or blockage of pipes by solid corrosion products

Added complexity and expense of equipment needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

 The effects of corrosion on different metals /alloys were discussed by Fontana and

Staehle (1975), Fontana and Greene (1978) and Hamsson *et al* (1987) under metallurgical, environmental and field effects. Metallurgical effects according to these workers are primary determining factors in corrosion behaviour of metals and alloys. Environmental factors like oxygen concentration in water or the atmosphere, the pH of the electrolyte, the temperature, the concentration of various salts solutions e.t.c in contact with the metal play a significant role in the rate of corrosion of metals even if the metals are completely pure or homogeneous.

 Halide ions are adsorbed on the metal surface or on the thin oxide layer to produce strong electric fields that draw in ions from the metal in order to determine its corrosion. The halide form surface complexes with the metal ions. The stability of the halide in the surface complex determines the effect of corrosion kinetics of the metal/alloy. According to Bailer *et al* (1978), a miniature cell is set up by couple action, metal (M) corroding to M2+ ions at the anode and water being reduced to hydroxyl ions and hydrogen at the cathode. The hydroxyl is readily oxidized by air to a hydrated compound.

 Metallurgically, crystal defects might affect the corrosion behaviour of metals which owe their corrosion resistance to the presence thin passive or thick protective films on their surface. The crystal defects and structural features might invariably affect the thickness, strength, adhesion, porosity, composition solubility e.t.c of these surface films, and hence in turn, the corrosion behaviour of the formed metal surfaces (Procter, 2000). According to Procter (2000), the attack proceeds along a number of narrow planar paths (usually but not necessarily intergranular).

 Aqueous environments range from very thin condensed films of moisture to bulk solutions. These include natural environments such as the atmosphere, natural waters, soils, body fluids e.t.c, as well as chemicals and food products (Shreir, 2000).

All corrosion reactions, according to Shreir (2000), are characterized by the following features:

1. The electrified interface between the metal and the electrolyte solution (the metal surface may be film-free or partially or completely covered with films or corrosion products).
2. Transfer of positive charge from the metal to the solution with consequent oxidation of the metal to a higher valence state.
3. Transfer of positive charge from the solution to the metal with consequent reduction of a species in solution (an electron acceptor) to a lower valence state.
4. Transfer of charge through the solution and corroding metal.

 It follows that corrosion is an electrochemical reaction in which the metal itself is a reactant and is oxidized (loss of electrons) to a higher state, while another reactant, an electron acceptor, in solution is reduced (gain of electrons) to a lower oxidation state. Since corrosion is essentially a reaction between a metal and its environment, the very significant effect of crystal defects and metallurgical structure on certain corrosion phenomena is to be expected. It is not possible to neglect the metallurgical aspects of a corrosion problem than it is to overlook the environmental and electrochemical factors

(Procter, 2000).

## 2.4 CORROSION INHIBITION/PROTECTION

 Corrosion control/inhibition may be regarded as the regulation of the corrosion reaction such that the physical and mechanical properties of the metal are preserved during the anticipated life of the structure/component. Several techniques for inhibiting or preventing corrosion are available. Coating the surface with some impermeable layer, such as paint, may prevent the access of damp air. Unfortunately, the protection fails disastrously if defects in the paint surface allow access of moist air (Atkins, 1978). Corrosion then takes place beneath the paint work, and extent of damage may be much greater than casual inspection. Surface coating is also provided by galvanizing.

 Traditional methods of corrosion prevention involve keeping air and moisture away from the metal/alloy (by a protective layer of paint, grease, or some other metal); lowering the reactivity by alloying or making the metal to be protected, cathode of a cell (Bailer et al, 1978). When connected to piece of more active metal, the metal to be protected becomes the cathode. Zinc, magnesium and aluminium are often employed.

The active metal is rapidly corroded and it is sometimes referred to as the „‟sacrificial anode‟‟.

 Generally, strategies for corrosion control should include: passivity, conditions in the environment, cathodic protection, protective coatings corrosion costs, criteria for corrosion failure, material selection and geometric factors (Talbot and Talbot, 1998). Passivity is a state of low corrosion rate brought about under a high anodic driving force, or potential, by the presence of an interfacial solid film, usually an oxide. Passive metals are thermodynamically unstable; they possess kinetic stability, which is engendered by solid interfacial film, and without which corrosion would occur (Burstein, 2000). From engineering point of view, the phenomenon of passivity is a remarkable one because of the extremely thin film required to produce passivity. Passivity of a metal according to Burstein (2000), lies in contrast to its activity, in which the metal corrodes freely under an anodic driving force. Aluminium is a typical example of a metal endowed with the ability to establish a naturally passive surface in appropriate environments. Some metals passivate spontaneously in water if the pH is within ranges corresponding to the potential-independent domains of stability for oxide or hydroxides (Talbot and Talbot, 1998).

 Unprotected active metals exposed to water or rains are vulnerable but corrosion can be delayed or even prevented by natural or artificially contrived conditions in the environment. Steels corrode actively in moist air and water containing dissolved air but the rate of dissolution can be restrained by the slow re-supply of oxygen and by deposition of chalky or other deposits on the metal surface from natural waters. For thick steel sections, (such as rail road track), no further protection may be require (Talbot and Talbot, 1998).

 Cathodic protection provides a method of protecting active metals in continuous contact with water as in ships and pipelines. It depends on the metal dissolution reaction with an electrical potential applied by impressing a cathodic current from a DC generator across the metal/environment interface. The protection is obtained at the expense of the second metal, which is sacrificed.

 When other protective strategies are inappropriate or uneconomic, active metals must be protected by applied coatings. The most familiar coatings are paints or a term covering various organic media, usually based on alkyl and epoxy resins, applied as liquids which subsequently polymerize to hard coatings. Alternatively, a vulnerable but inexpensive resistant metal, usually applied by electrodeposition. An important special use of a protective metal coating is the layer of pure aluminium mechanically bonded to aluminium aircraft alloys, which are strong but vulnerable to corrosion.

 Estimates of the costs of corrosion are useful in drawing attention to wasteful depletion of resources. Such costs include the prices of resistant metals and costs of protection, maintenance and planned amortization. An essential objective in design is to produce structures or manufacture products which fulfill their purposes with maximum economy in the overall use of resources interpreted in monetary terms.

 The economic use of resources is based on planned life expectances for significant metal structures or products. The limiting factor may be corrosion or some other factors, such as: wear of moving parts, fatigue failure of loaded components, failure associated with accessories, obsolete technology or stock replenishment cycles. The criterion for corrosion failure is therefore premature termination of the useful function of the metal by interaction with its environment, before the planned life has elapsed.

 It is natural to consider using an inexpensive, easily fabricated metal, such as plain carbon steel. On reflection, it may be clear that unprotected inexpensive materials may not resist the prevailing environment and it is required that protection be applied, the environment be controlled or a more expensive metal be chosen. The choice is influenced by prevailing metal/material prices. The prices of metals vary according to purity and form, because they include refining and fabricating costs. This is shown in Table 5 below.

## Table 5: A Selection of Metals/Alloys and their Prices

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  Metal  |     | Form   |   |   Price/Tonne  US$ N  |
| **Pure metals:** Aluminium, Copper Lead Nickel Tin Zinc **Steels+** Mild steel   **Stainless steels**AISI 409 AISI304  AISI 316    | Primary metal ingot Primary metal ingot Primary metal ingot Primary metal ingot Primary metal ingot Primary metal ingot  Continuously cast slab 6mm thick hot-rolled plate, 1m wide coil 2mm thick cold-rolled plate, 1m wide coil 0.20mm electrolytic tin-plate, 1m wide coil   2mm sheet 6mm thick hot-rolled plate, 1m wide coil 2mm thick cold-rolled steel, 1m wide coil 6mm thick hot-rolled plate, 1m wide coil 2mm thick cold-rolled steel, 1m wide coil  | 1486 2323  662 6755 5845 1021   215 625 752 1520   2383 2937 3333 3663 4059  | 208040 325220  92680 945700 818300 142940  30100  87500  105280  212800  333620  411180  466620  512820  568260  |

 Source: (Talbot and Talbot (1998)

 When the philosophy of a design is settled and suitable materials selected, the proposed physical form of the artifact must be scrutinized for corrosion traps. Protected or not, the less time a metal /alloy spends in contact with water, the less is the chance of corrosion. All that is required are precautions, such as angle sections disposed apex upwards, box sections closed off or fitted, with drainage holes, tank bottom raised clear of the floor, and drainage taps fitted at the lowest points of systems containing fluids.

 In recent years, scientists are more concerned with the use of certain compounds as corrosion inhibitors in metal-corrodent systems (Ita and Offiong, 1997). Imidazoline surfactants have been reported by Wang *et al* (2005) to be well utilized in the field of oil wells and oil/gas pipelines protection. According to these workers, the primary action of corrosion inhibition is determined by the adsorption of the surfactant‟s concentration, functional group, alkyl hydrophobic chain lengths and the environment. The inhibitive efficiency of some mono ionic, amphoteric, cationic and anionic surface agents in dissolution of copper in 4.5MHNO3 has been reported (Muayta *et al*, 2001). It is suggested by these researchers that the increase in inhibition efficiency may be due to the formation of a monolayer on the surface of the metal.

 It has been accepted that corrosion inhibition process results from the formation of organic inhibitor films on the metal surface (Ait Chikh *et al*, 2005). The inhibitor films can be classified as a chemisorbed film, donating a lone pair of electrons attached to the central adsorption atom in a functional group as an electrostatic adsorption film and as a precipitation and / or a complex film reacting with dissolved metal ion and organic inhibitor molecule (Hammer and Nathan, 1993). Corrosion inhibition has also been reported by several investigators (Ekpe *et al*, 1994; Ekpe *et al*, 1997; Ebenso *et al*, 1999; Ekpe *et al*, 2001; Ebenso *et al*, 2004 and Onen, 2004) to be via physical adsorption. Reporting on the effect of piperidones on hydrogen permeation and corrosion inhibition of mild steel in acidic solutions, Kiyer *et al*, (2000) stated that these compounds behave predominantly as cathodic inhibitors. These workers further observed that corrosion of mild steel is mainly controlled by a charge transfer process. The corrosion performance of various stainless steels, nickel alloys and refractory metals has been evaluated in hot methane sulphonic acid by Gaur and Srinivasan (1999) using weight loss and polarization techniques. The corrosion inhibition effect of some inorganic inhibitors was also explored. The result of this study showed that most of the stainless steels, nickel alloys and titanium corrode to a considerable extent while zirconium and tantalum withstood the environment. The results also reveal that the addition of ferric (Fe3+) and nitrate (NO3-) produced an inhibiting effect.

 After evaluating the inhibition characteristics of five vapour phase corrosion inhibitors (dicyclohexyl ammonium nitrate, cyclohexyl ammonium-N-cyclohexyl carbonate, ammonium benzoate, ammonium sorbate and diethyl ammonium caprylate) on four commercial metals (iron, copper, aluminium and zinc), Skinner *et al* (1999), asserted that diethyl ammonium caprylate performed the best. Inhibition of corrosion of mild steel in HCl solution by (4-amino-2-2methyl-5-pyrimidyl methylthio) acetic acid and its precursors has also been reported by Abiola and Oforka (2002). Inhibition efficiency of theses compounds were found to increase with increase in inhibitor concentration but decreased with increase in temperature.

##  2.5 CORROSION INHIBITORS

 Corrosion inhibitors are compounds/substances that restrict or prevent corrosion process from taking place. They intervene with corrosion kinetics and thereby protect metals from corrosion. Inhibitors find applications in pickling, cleaning, acid descaling

e.t.c. Some occur naturally and others are introduced artificially as a strategy for corrosion control. The types of corrosion for which these inhibitors are used are diverse (Mernari *et al*, 2001). It has been reported by several workers (Ebenso *et al*, 1999; Ekpe *et al*, 2001; Mernari *et al*, 2001 and Onen, 2004) that compounds whose structures contain oxygen, nitrogen and sulphur inhibit corrosion effectively with percent inhibition efficiency following the order: O < N < S. Natural products/organic compounds, inorganic complexes and their derivatives and dyes have successfully been used as corrosion inhibitors of aluminium mild steel in acid corrodent.

###  2.5.1 Inhibitors of Plant Origin

 Natural plant and animal products have continued to receive attention as sources of environmentally friendly, non-toxic and inexpensive corrosion inhibitors for acid cleaning (Hosary and Salem, 1984; Ekpe *et al*, 1994; Onen, 2004; Orubite and Oforka, 2004; Orubite and Hamilton, 2004 and Onen, 2005). Most of theses plants contain various organic compounds such as amino acids, alkaloids, phenolics, pigments, tannins e.t.c.

 In 2004, *Nypa fruiticans wurmb* leaves extract was effectively used by Orubite and Oforka to inhibit corrosion of mild steel in HCl. A similar study using *Nypa fruiticans wurmb* fruits and leaves extracts was also carried out by Orubite and Hamilton (2004).

It was found by these workers that the fruits inhibited corrosion of mild steel slightly better than the leaves of the same plant with corrosion inhibition efficiency in the order: 68% > 67% at a maximum inhibitor concentration of 0.32gdm-3. The inhibitory effect of these extracts was attributed to the presence of nitrogenous compounds which may have unshared pair of electrons on nitrogen or other atoms.

 Ekpe *et al* (1997) studied and consequently reported on the corrosion inhibition of aluminium-magnesium alloy in alkaline medium using *carica papaya* leaves extract. *Carica papaya* leaves extract was found to be an effective inhibitor for aluminiummagnesium alloy corrosion by these authors. The effect of molasses on the corrosion of mild steel, aluminium and copper in acids has also been investigated by Hosary and Salem (1984). From their investigation, these researchers found molasses (naturally occurring substances) to be good corrosion inhibitors of mild steel, aluminium and copper in acidic media.

 Mescaline, an alkaloid in *opuntia spp* (cactus milk), has been identified as the main component in the plant that inhibits corrosion of mild steel in acid medium

(Onen, 2004). This was found to be due to the presence of –C=O and –N=N- in mescaline. *Calotropis procera (timpapiya)* milk extract has also been studied as a possible corrosion inhibitor by Onen (2005). The study revealed that mild steel corrosion in HCl can effectively be inhibited using *timpapiya* milk extract. From the phytochemical analysis of this plant‟s extract, tannins, phenolics and alkaloids were detected. The action of timpapiya milk extract as a corrosion inhibitor was therefore attributed to the presence of these compounds. In 1994, Ekpe *et al*, reported on the inhibitory action of *azadirachta* leaves extract on corrosion of mild steel in tetraoxosulphate (VI) acid.

The report revealed that *azadirachta* leaves extract can be utilized for effective inhibition of mild steel corrosion in H2SO4.

###  2.5.2 Organic Inhibitors

Organic inhibitors are applied extensively to protect metals from corrosion in many aggressive acidic media (El-Naggar, 2007). In general, organic compounds such as amines, acetylenic alcohols, heterocyclic compounds have been in use as inhibitors in industrial applications (Mernari *et al*, 2001). According to Mernari *et al* (2001), oxadiazole has special affinity towards metal surfaces, displacing water molecules on the surface. In addition, oxadiazole possesses abundance of -electrons and unshared electron pairs on the nitrogen, sulphur and oxygen atoms which can interact with dorbital of iron to provide a protective film.

 Piperidones have been studied as possible corrosion inhibitors of mild steel in acidic solutions by Kiyer *et al* (2000). The study showed that the combined influence of -CO and –NH groups in piperidones enhanced their performance as corrosion inhibitors. Inhibition of acid corrosion of aluminium by thiophene and its derivatives has been investigated by Samarkandy *et al* (2001). From their findings, these investigators concluded that the corrosion rate decreases linearly with increasing value of Hammet constants. They attributed the inhibition ability of the compounds to the number of adsorption sites (S and O). That, thiophene and 2-chlorothiophene has only one adsorption site(S) while 2-thiophene carboxylic acid, 2-acethyl thiophene and

2-thiophene carboxyldehyde have an additional adsorption site i.e. the oxygen atom of carbonyl group.

 The effect of some phenols (phenol, resorcinol and pyrogallol) on the corrosion of

Al, Cu, and Al-Cu alloys in NaOH solutions has been examined by El-Shayeb *et al* (1999) using potential-time polarization and weight loss techniques. The results of this examination showed that the additives had only a very slight effect on the passivation of

such metals and alloys in 10-5 MNaOH, but a significant effect in 0.1MNaOH. The inhibition efficiency in general increased with increasing additive concentration except for Cu in pyrogallol. The inhibition of corrosion by these compounds was attributed to their adsorption on the electrode surface. The inhibitive efficiencies of pyridine and some of its derivatives have been studied in relation to the corrosion of Al (grade 1100) in 1% HCl at 25,35,45,55C. The efficiencies increase in the order: pyridine, aniline, 2-picoline, 4-picoline, and 2: 4-lutidine (Yadav, 1999). This researcher also found that the inhibitors act predominantly on cathodic sites and only partially effective on anodic sites.

 Sulfa drugs compounds (e.g. sulfaguanidine, sulfamethazine, sulfamethoxazole and sulfadiazine) have been used to evaluate corrosion inhibition of mild steel in acidic medium by El-Naggar (2007). The result showed good inhibition efficiency in the order: sulfadiazine > sulfamethoxazole > sulfamethazine > sulfaguanidine. The experimental result revealed also that the inhibition mechanism for the sulfa drugs compounds is mainly due to adsorption. More so, these compounds reduce corrosion of mild steel more effectively in HCl than in H2SO4 solutions.

Similarly, the inhibition of mild steel in HCl solution by

 P-aminobenzenesulphanilamide, PABSA and its derivatives (N‟-2-

pyrimidylsulphanilamide, N-2-PSA and N‟-2-thiazolysulphanilamide, N-2-TSA) has been investigated by Onen (2007). The investigation revealed that the inhibition efficiency and surface coverage increase with increasing concentration but decrease with increasing temperature in the order: PABSA< N-2-PSA < N-2- TSA. The inhibition characteristics of the compounds (sulpha drugs) studied conformed to the Langmuir adsorption isotherm. The results also indicate that inhibitors act effectively on the cathodic than on anodic sites. Corrosion inhibition of mild steel in 0.1MHCl by

4-Formylmopholine hydrazone (FMH) and 4-Formylmorpholine (FM) was assessed by Ita (2004). His findings showed that these new inhibitors appreciably inhibit corrosion of mild steel in 0.1MHCl particularly at higher temperatures in the order: FMH > FM.

 Inhibition efficiencies have been investigated for two azoles –

2-mercaptobenzoazole (CBA) and 2-methylbenzoazole (MBA), containing nitrogen, sulphur, or selenium atoms, on the corrosion of type 304 stainless steel in 2MH2SO4 and

3MHCl using weight loss, gasometry and polarization methods (Ai-Mayouf et al, 2001). It was shown that some of these compounds provide 90% inhibition efficiency at a concentration of 5 x 10-4M and that the efficiency depends on the heteroatom and decreases in the order: Se > S > N > O. These inhibitors were more efficient in H2SO4 than in HCl whereas the opposite is true for inhibitors with nitrogen alone. Inhibitive action of triazoles on corrosion inhibition of mild steel has also been studied through weight loss and various electrochemical techniques (Bentiss *et al*, 2000). Results obtained showed that these organic compounds are good inhibitors. Triazoles are able to reduce the corrosion of steel more effectively in IM HCl than in 0.5M H2SO4. The adsorption of these inhibitors on mild steel surface in both acids obeys the Langmuir adsorption isotherm. The comparative study of corrosion inhibition of triazoles derivatives indicates that efficiency of the 4-aminotriazole is greater than that of the 4Htriazole.

 Corrosion inhibition of zinc pigment in aqueous alkaline media by different high and low molecular weight organic inhibitors has been examined (M‟‟ller, 2000) and compared with that given by potassium dichromate (K2Cr2O7) inhibits this corrosion reaction moderately. It was also noticed by these workers that heterocyclic compounds are very poor corrosion inhibitors and less effective than K2Cr2O7. Certain polymers with low acid numbers and low molecular masses and an epoxy ester rein are more effective inhibitors than K2Cr2O7. Thus, some non-toxic polymers or paint resins can be considered

as possible substitutes for toxic K2Cr2O7.

### 2.5.3 Inorganic Complexes as Inhibitors

 There has been growing interest in the use of inorganic compounds and their derivatives as inhibitors for aqueous corrosion of metals/alloys. Various inorganic complexes, and their derivatives –aromatic thiosemicarbazones, methyl and phenyl thiosemicarbazones, pyridoxal, 4-ethyl semithiocarbazide, pyridoxal-(4-methyl semicarbazone) and its zinc (II) complex, acetamide and thiourea, 2- acetyl pyridine-(4phenylthiosemicarbazone), 2-acetyl pyridine-(4-phenyl-iso-methylthiosemicarbazones) and 2-acetyl pyridine –(4-phenyl-iso-ethylthiosemicarbazone) have been investigated and reported as corrosion inhibitors by different researchers (Ibok *et al*, 1993; Ekpe *et al*, 1995; Ita and Offiong, 1997; Ebenso, 1998 and Ekpe *et al*, 2004).

 Reporting on the effect of molecular structure on the efficiency of amides and thiosemicarbazones, used for corrosion inhibition of mild steel in HCl, Ebenso et al

(1999) stated that all molecules containing thiocarbonyl groups (e.g.thiourea, thioacetamide and thiosemicarbazide) have higher inhibition efficiencies than corresponding compounds (urea, acetamide and semicarbazide) which do not contain them. The report also reveals that some of the heterocyclic thiosemicarbazones used for the study obey the mechanism of chemical adsorption, with the inhibition efficiency (I %) increasing with increase in temperature. Ekpe *et al*, in 2001, also investigated the mutual effects of thiosemicarbazones derivatives on the acidic corrosion of aluminium. The workers concluded from their investigation that the combined compound used inhibited the corrosion of aluminium to a reasonable extent. The inhibition efficiency, according to these authors, increases with increase in iso group in the mixture and this was attributed to the shielding/exposure of the adsorption sites of the molecules.

 A similar study – „‟Inhibition of acid corrosion of aluminium by some derivatives of thiosemicarbazone‟‟ was equally conducted by Ekpe *et al* (2004). From the findings of their study, these workers reported that the compounds used as inhibitors [2-acetylpridine-(4-phenylthiosemicarbazone), 2-acetylpyridine-(4-phenyl-isomethylthiosemicarbazone) and 2-acetyl pyridine-(4-phenyl-iso-ethylthiosemicarbazone)], retard the acid corrosion of aluminium to a remarkable degree at high inhibitor concentrations, but become accelerators at very low concentrations. This, they attributed to very weak films of the compounds (or adsorbates) on the aluminium surface which can easily be washed off by the corrosion medium.

 Phosphates, polyphosphates and/or chromates have been used as corrosion inhibitors. When used as inhibitors in aqueous solutions, chromate ions passivate by maintaining a coherent oxide film on the metal surface. Passivation is maintained even in a boiling concentrated chromic acid solution in which many of the oxides are soluble (Short and Cole, 2000). The use of chromates as inhibitors has however, been restricted by environmental regulation due to its toxicity.

 The use of phosphate coatings for protecting steel surfaces has been known for over 60 years and during this period, commercial utilization has steadily increased until today where the greater part of the World‟s production of motor cars, bicycles, refrigerators, washing machines, office furniture e.t.c is treated in this way. According to Richardson and Shaw (2000), the greatest use of phosphate coatings is as a base for paints, although other important applications are in conjunction with oil, grease, wax and spirit stains to provide corrosion resistant finish. Mild steel is the material most frequently subjected to phosphate treatment, but a variety of other ferrous surfaces are also processed. Phosphate treatments designed for steel can also be used for simultaneous treatment of zinc die casting, hot-dipped zinc, zinc plated and cadmium-plated articles, but if there is a large quantity of these non-ferrous articles it is more economical to phosphate them without the steel.

 Commonly used phosphates are hydroxylethyldiaminediphosphonic acid (HEAP) and aminotrimethyldienephosphonic acid (ATMP) (Uppal and Bhatia, 2001). These compounds possess anticorrosion and antiscaling properties. It has also been found that in the range of 600ppm and in the absence of scale forming salt, ammonia works as a perfect corrosion inhibitor. According to Uppal and Bhatia (2001), multi components inhibitors (e.g. zinc phonic acid) are very efficient as inhibitors for corrosion of carbon/mild steel.

 The use of vitreous enamel coatings (coating of glassy substances which have been fused on to metals to give a tightly adherent hard finish resistant to many abrasive and corrosive materials) has been reported as corrosion inhibitors. Reviewing the effectiveness of vitreous enamel coatings, Millar and Wilson (2000), stated that the purpose of this class of coatings is two fold, i.e. to confer corrosion protection to the metal substrate and at the same time, to provide permanent colour, gloss and other aesthetic values. An enamel is usually formulated to withstand one of the corrosive agents (acids, alkalis, detergents, water e.t.c) more specifically than another, but vitreous enamel as a general finish, has good „‟all round‟‟ resistance, with a few exceptions such as HF and concentrated or fused NaOH or KOH.

### 2.5.4 Use of Dyes as Inhibitors

Organic compounds with functional group containing hetero-atoms are of particular interest as corrosion inhibitors. Dyes are coloured organic compounds containing different functional groups depending on the type of dye (Finar, 2002). Different types of dyes are known: azo dyes (e.g. Methyl orange, Congo red, Methyl orange), heterocyclic dyes (e.g. Safranine T, Methylene blue), xanthene dyes (e.g. Eosin, Thymol blue, Phenolphthalein, Phenol red, Rhodamine B), cyanine dyes and anthraquinoid dyes (e.g. Alizarin red S, Alizarin yellow). About half of the dyes in industrial use today are azo dyes due to their strong colouration and are mostly prepared from diazonium salts (Roberts and Casserio, 1979). The structural features that impart colour are >C=C<, >N=O, -N=N-, >C=O, aromatic rings and NO2. Multi-colour effects have been given to anodized aluminium samples by the use of dyes (Talati and Gandhi, 1984; Talati and Daraji, 1988).

 Several workers have shown that some dyes inhibit corrosion of aluminium and mild steel in hydrochloric acid corrodent (Talati and Patel, 1974; Talati and Joshi, 1980).

Cyanine dyes have also been found to be efficient corrosion inhibitors on metal-corrodent systems (Maklouf *et al*, 1995) while green S and erythrosine have been reported by Ita and Edem (2000) as potential inhibitors for mild steel corrosion in HCl solutions. Corrosion inhibition of mild steel in H2SO4 solutions by Congo red dye has also been investigated at different temperatures using gravimetric techniques by Oguzie et al (2004). The investigation showed that Congo red inhibits corrosion of mild steel in acidic environment with the inhibition efficiency increasing with concentration but decreases with rise in temperature. This, according to the authors, suggests that the inhibitor molecules were physically adsorbed on the metal surface.

 The corrosion inhibition of aluminium and mild steel in H2SO4 in the presence of methylene blue at 30-40oC was studied by Ebenso *et al* (2004). Methylene blue was found to inhibit the acid corrosion of both aluminium and mild steel. The inhibitory action of methylene blue was ascribed to the presence of N and S in the central ring of the compound. These, according to these workers, give out positively charged ions and may, therefore get adsorbed to negatively charged sites on the metal surface. They concluded that methylene blue has a strong tendency to displace the adsorbed OH- ions and get attached to the anodic sites of the corroding metal through the lone pair of unshared electrons of the N-atom. In a separate study, corrosion inhibition of mild steel in HCl solutions was carried out using methylene blue dye by Oguzie *et al* (2004).

Like Ebenso *et al* (2004), these researchers concluded that the dissolution process was probably inhibited by physical adsorption of methylene blue molecules on the metal surface, thereby blocking the active corrosion sites.

 Alizarin red, an anthraquinoid, mordant dye, has been reported as an efficient inhibitor of aluminium corrosion in H2SO4 by Onen (2006). The percent inhibition efficiency (I %) and surface coverage () of alizarin red increased with increase in inhibitor concentration but decreased with increase in temperature. A negative value of average free energy of adsorption, Gads, was also reported by the author suggesting that the inhibitor is strongly adsorbed on the metal surface. The negative value equally indicates that the adsorption of the inhibitor is spontaneous, which is a characteristic of strong adsorption with the metal surface, thus, supporting physical adsorption. Bis-and mono-azo dyes have been used as corrosion inhibitors for aluminium in HCl and NaOH solutions (Madkour *et al*, 1999).

 Similarly, the adsorption and corrosion inhibition of bismark brown (BB) on aluminium (AA1060) in 0.1M NaOH solutions was studied at 25 and 70oC using gravimetric technique by Oguzie *et al* (2006). The results indicate that BB acts as an inhibitor in the alkaline environment by adsorption on the metal surface and the inhibition efficiency was found to increase with dye concentration.

##  2.6 EFFECT OF HALIDES ON CORROSION INHIBITION

 Molten halides are largely used for electro winning of metals, alloys and gases and in high-temperature batteries (Feng and Melendres, 1982).Addition of halide salts to acid solutions (HCl, H2SO4, e.t.c.) with any organic compound results in a co-operative effect which inhibits metallic (Fe, Al, e.t.c.) corrosion (Ebenso, 2003). In acid medium, halides are known to stimulate and inhibit corrosion of metals/alloys. The protective properties of an inhibitor in HCl/H2SO4 can also be improved by the addition of certain anions particularly halide ions (Cl-, Br- and I-) to the solution (Bhajiwala and Vashi, 2001 and Ebenso, 2003).Ebenso(2003), reported a synergistic effect when inhibition of aluminium corrosion in H2SO4 using 2-actylphenthiazine (2APTZ) and on the addition of halide ions. Chemical adsorption was proposed for the inhibition.

 Most often, a synergistic effect in the corrosion inhibition process is observed as a result of these ions being added to the inhibitor-H2SO4 mixture. Antagonism (passivity) has also been reported (Ebenso *et al*, 2004 and Oguzie *et al*, 2004) in the study of joint effects of halide ions and methylene blue on corrosion inhibition of aluminium and mild steel in acid corrodent. Passivity, according to these researchers, accounted for the observed inhibition of aluminium corrosion, with the addition of the halide ions. It has equally been found by these workers that ionic radii and electronegativity of halide play significant role in the adsorption process. A similar assertion was made by Onen (2006), when the influence of halide ions on corrosion inhibition of aluminium in H2SO4 was investigated using alizarin red as an inhibitor. The inhibition efficiency (I %) and the degree of surface coverage () obtained from the study increase in the order:

I- > Br- > Cl- supporting the fact that the ionic radii and electronegativity of the halide ions play an important role in the adsorption mechanism.

 The corrosion inhibition of aluminium in H2SO4 in the presence of polyvinyl alcohol (PVA) and polyethylene glycol (PEG) and the effect of addition of halides (KCl, KBr and KI) was studied by Ebenso *et al* (2006) using the hydrogen evolution technique at 30 and 40oC. Inhibition efficiency (I %) increased with concentration of PVA and PEG – but with PEG having higher I %. The synergism parameters (SI) obtained were found by the authors to be greater than unity for both PVA and PEG, which indicates that the enhanced inhibition efficiency caused by the addition of the halides is only due to synergism. Competitive adsorption of halide and corrosion inhibitors and of mixtures of inhibitors has been observed after a comparative study of the efficiency of some organic inhibitors (benzimidazole, 1-hydroxybenzotiazole, benzotriazole and 2-mercaptobezoxazole) for the corrosion inhibition of copper in aqueous chloride media by Fleischmann *et al* (2005).

The correlation between inhibition efficiency and molecular structure of alkyl quaternary ammonium halide (AQAH) has been investigated and reported. The results, according to LinNiu *et al* (2005), show that besides the concentration, structure of alkyl groups and the type of halide ions of these AQAH inhibitors greatly influenced the inhibition efficiency. Effect of iodide ions on corrosion inhibition of mild steel in 0.5M H2SO4 by poly (4-vinylpyridine), P4VP, was studied by Larabi and Harek (2004).

From the study, it was revealed also that the phenomenon of synergism exists between P4VP and the iodide ions. This according to the authors enhanced the inhibition efficiency.

**CHAPTER THREE**

**RESEARCH MEHTODOLOGY**

**Specimens and Surface Pretreatment**

A commercial specimen of Al with chemical composition in table 1 was used.

Having dimension R =1.37 L=5.38 cm with exposed area of 26.090417 cm². Before all measurements, the specimen was mechanically polished. This was achieved by using a series of emery papers with different grade (320-600-1200), starting with a coarse one and proceeding in steps to fine grades. After this process the specimen was washed with double-distilled water, degreased with alanine and finally , dried with a stream of air .The specimen was then weighed and immersed in the test solution.

**Preparation of extract (inhibitor) and Test Solution**

The aggressive of 0.5 M HCl was prepared by dilution of AR grade(%) HCl with distilled water. Six different concentrations (0.0025g/dm3,0.0050 g/dm3,0.0075g/dm3, 0.0100g/ dm3, 0.0125g/dm3 and 0.0250g/dm3) of the extract were prepared with 0.5 M hydrochloric acid solution and were used for all measurement .

**Methods**

The corrosion rate of Al in 0.5 M HCl followed by using chemical methods . This method is done in, weight loss method (WL).

**Weight loss study using alanine**

Experiments were conducted for the immersion times 30,60,90,120,150,180,210 mins. Preweighted aluminium specimens were suspended for different immersion periods in 0.5 HCl with and without the inhibitor in different concentrations ranging from concentrations (0.0025, 0.0050, 0.0075, 0.0100, 0.0125 and 0.0250 g/dm3) of the extract into seven separate beakers maintained at 303, 313and 323K. .After the specified time the coupons were removed from test solution, thoroughly washed with double distilled water, dried well and then weighted. The percentage of inhibitor efficiency (IE%) for various concentrations of inhibitor were calculated as

%IE = [ (Mu-Mi) / Mu] x 100 ...(1)

Where Mu is mass loss without inhibitor and ” Mi is mass loss with inhibitor.

# CHAPTER FOUR

# RESULTS AND DISCUSSION

Effect of Reaction Conditions on Corrosion Rate and Inhibition Efficiency of Alanine

**Effect of inhibitor Concentration (Gravimetric results**)

The weight losses (gravimetric measurements) for the Aluminium in 0.5 M HCL containing different concentrations of the Alanine as a function of time are presented in Figures. 1,2,3. The results show that weight losses increase with increase in time but decrease with increase in concentration of Alanine.

As shown in Figures 1,2,3, the inhibition efficiency of the extracts on the mild steel increases with increasing concentration of the plant extracts. This is expected because as the concentration of the plant extracts increases, the fraction of the surface covered by the adsorbed molecule also increases which results into an increase in the inhibition efficiency. The inhibition efficiency increases progressively as the concentration of the extracts increases However, the inhibition efficiency decreases with increase in the temperature of the reaction medium.

At 313 K, as the concentration of Alanine increases from 0.0025 to 0.0250 g/dm3, the weight losses of the aluminium coupons reduce as shown in Figure 2.This shows us that Alanine is still effective in inhibiting the corrosion of aluminium at 313 K. The weight loss of the aluminium coupons still reduced with increasing extract concentration as seen in Fig. 3. This depicts that, even at 323K, Alanine inhibits the corrosion of aluminium in hydrochloric acid solution.

The decrease is due to the inhibitive effects of Alanine and these effects increase with increase in Alanine concentration. This behavior indicates that the Alanine is strongly inhibit the corrosion of the aluminium and the degree of inhibition is concentration dependent. There is a progressive increase in weight loss as the temperature is increased from 303K to 323K (Figures 1,2,3). This signifies that the dissolution of the metals increased at higher temperatures. This observation is attributed to the general rule guiding the rate of chemical reaction, which says that chemical reaction increases with increasing temperatures. Also an increased temperature favors the formation of activated molecules, which may be doubled in number, with 10oC rise in temperature,thereby increasing the reaction rate. This is because the reactant molecules gain more energy and are able to overcome the energy barrier more rapidly24. An increase in temperature may also increase the solubility of the protective films on the metals, thus increasing the susceptibility of the

**Table 1: Percentage composition of the studied specimen**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Si | Fe | Cu | Mn | Mg | Cr | Zn | Ti | Al |
| 0.95 | 0.25 | 0.05 | 0.40 | 0.66 | 0.04 | 0.04 | 0.03 | Remainder |

**Table 2:** Activation Energy values with the various concentrations of the extract

|  |  |  |
| --- | --- | --- |
| **Concentration** | **Activation energy** | **Average Activation** |
|  **of Extract** | **KJ mol-1** |  | **energyKJ mol-1** |
| **(g.dm3)** | **303K-313K** | **313K-323K** | **303K-313K** | **313K-323K** |
| Blank | 46.33 | 35.11 | 50.45 | 38.57 |
| 0.0025 | 47.69 | 36.68 |  |  |
| 0.0050 | 49.03 | 37.57 |  |  |
| 0.0075 | 49.73 | 37.61 |  |  |
| 0.0100 | 49.78 | 37.71 |  |  |
| 0.0125 | 54.89 | 37.96 |  |  |
| 0.0250 | 55.73 | 47.38 |  |  |

**Table 3: Adsorption Equilibrum constant (Kads) at different Temperatures**

|  |  |  |
| --- | --- | --- |
| **Temperature (K)** | **K ads.** | **R2** |
| 303 | 0.422 | 0.9964 |
| 313 | 0.256 | 0.9944 |
| 322 | 0.237 | 0.9977 |

# Table 4: Enthalpy and Entropy values of the reaction with various concentrations of the extracts Concentration of Extract (g.dm3) H (KJ mol-1) S (J mol-1K-1)

|  |  |  |
| --- | --- | --- |
| **Concentration of** | **-****H0** | **-****S0** |
| **extract (g.dm3)** | **(kJ mol-1)** | **( J .mol-1.K-1)** |
| Blank | 47.15 | 232.60 |
| 0.0025 | 36.77 | 205.19 |
| 0.0050 | 36.21 | 183.51 |
| 0.0075 | 27.11 | 174.36 |
| 0.0100 | 22.82 | 135.37 |
| 0.0125 | 16.48 | 132.00 |
| 0.0250 | 8.01 | 101.61 |

**Table 5: The Free energy of Adsorptions at various Temperatures**

|  |  |
| --- | --- |
| **Temperature(K)** | **-****G0(kJ mol-1** |
| 303 | 7.945 |
| 312 | 6.907 |
| 322 | 6.899 |

metal to corrosion 25. The solubility of oxygen gas decreases with increase in temperature.

Thus oxygen concentration is expected to be more at higher temperature which in this case is higher at 323K than at 313 and 303K. The presence of high concentration of oxygen thereby causes the metal to corrode faster. Also for solids, solubility generally increases with increasing temperature. This explains why the protective film which is solid becomes more soluble as the temperature is increased.

**Effect of Temperature on Inhibition Efficiency**

 The effect of temperature on the inhibition efficiency for aluminium in 0.5 M HCl solution in the absence and presence of different concentration of Alanine at temperature ranging from 303K to 323 K was obtained by weight loss measurements is displayed graphically in Figure 4.The inhibition efficiencies are found to decrease with increasing the solution temperature from 303 to 323 K.This behavior can be interpreted on the basic that relatively high temperature the increase in temperature results in the desorption of the inhibitor molecules from the surface of aluminium. Previous investigators showed that the corrosion rate increases with increase in temperature, which results into a decrease in the inhibition efficiency, Therefore, decreasing the reaction temperature favours the inhibition efficiency of acid extracts of Alanine on aluminium in hydrochloric acid.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Table 6: Kinetic data for aluminium in 2M HCl containing red onion skin extract from weight loss measurement****The Rate constant Half-Lifet1/2 Activation energy Average Activation energy studied K(min-1)X10-5 t (mins)x104 KJ mol-1 KJ mol-1****1****2****/**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **solution** | **303K** | **313K** | **323K** | **303K** | **313K** | **323K** | **303K** | **313K** | **303K 313K** |
|  |  |  |  |  |  |  | **-313K** | **-323K** | **-313K -323K** |
| Blank | 0.17 | 2.53 | 4.96 | 4.175 | 0.274 | 0.139 | 46.33 | 35.11 | 50.45 38.57 |
| 0.0025 | 0.16 | 2.23 | 4.53 | 4.331 | 0.311 | 0.15 | 47.69 | 36.68 |  |
| 0.0050 | 0.15 | 1.72 | 4.12 | 4.62 | 0.403 | 0.168 | 49.03 | 37.57 |  |
| 0.0075 | 0.14 | 1.49 | 3.83 | 4.95 | 0.465 | 0.181 | 49.73 | 37.61 |  |
| 0.0100 | 0.14 | 0.95 | 3.41 | 4.95 | 0.729 | 0.203 | 49.78 | 37.71 |  |
| 0.0125 | 0.13 | 0.90 | 3.06 | 5.33 | 0.77 | 0.226 | 54.89 | 37.96 |  |
| 0.0250 | 0.12 | 0.99 | 2.73 | 5.78 | 0.70 | 0.254 | 55.73 | 47.38 |  |

 |

Figure 4 also portrays an increase in inhibition efficiency of Alanine as the concentration of the extract increases in the acid solution.

However,aluminium corrosion rate in absence and presence of the Alanine obeys Arrhenius type reaction 28:lnrWL=lnA-Ea/RT ...(2)

where rWL is the corrosion rate obtained from WL measurements,Ea is the apparent activation energy,R is the molar gas constant,T is the absolute temperature and A is the frequency factor

In order to calculate the apparent activation energy of aluminium corrosion in the absence and presence of inhibitor,a plot of lnrWL vs.T-1was done as shown in Figure 5.The slope (Ea/RT) of the straight lines was used to calculate the apparent activation energy while the intercept(ln A) was used to calculate the frequency factor.Table 2 gives the calculated kinetic parameters.

**Adsorption Parameters**

Adsorption isotherms are very important in determining the mechanism of organoelectrochemical reaction. The inhibition of the corrosion of aluminum in 0.5M HCl medium

with addition of different concentrations of the extract can be explained by the adsorption of the components of the plant extract on the metal surface.

The principal step in the accomplishment of inhibitiors action in acid solution is usually established to be the adsorption on the metal surface.This leads to the assumption that the corrosion reactions are prohibited from occurring over the area(or active sites) of the metal surface enclosed by adsorbed inhibitior species,whereas these corrosion reactions take place on the inhibitorfree region30 .

The surface coverage() data are very useful on discussing the adsorption characteristics. When the fraction of surface covered is determined as a function of the concentraction at constant remperature,adsorption isotherm could be evaluated at equilibrium condition.Attemts were made to fit the ¸ values to various isotherm including Langmuir,Temkin,Frumkin,ElAwady,Freundlich and Flory-Huggins ect.The best fit was obtained with Langmuir isotherm as suggested by the plot between C/¸ and C (as shown in Figure 6) and the linear correlation coefficient of the fitted data was close to 1,indicating that the adsorption of the inhibitor molecules obey the Langmuir’s adsorption isotherm


# Fig. 1: Variation of Weight Loss with Time for Fig. 2: Variation of Weight Loss with Time for aluminium Coupons in 0.5 M HCl Solution aluminium Coupons in 0.5 M HCl Solution extract at 303K extract at 313 K

**Containing Different Concentrations of Alanine Containing Different Concentrations of Alanine**

**Fig. 3: Variation of Weight Loss with Time for Fig. 4. Variation of Inhibition Efficiency with aluminium Coupons in 0.5 M HCl Solution Inhibitor Concentration for aluminium Coupons**

**Containing Different Concentrations of Alanine in 0.5 M HCl Solution Containing Alanine**

 **extract at 323 K at Three Different Temperatures**

**Fig. 5. Arrhenius plots for aluminium corrosion in Fig. 6: Langmuir isotherm for Alanine**

**0.5 M HCl in absence and presence of different concentration of Alanine at 120 mint**

 **Fig. 7: Temkin isotherm for Alanine Fig. 8: Plot of logCR/T vs 1/T for Alanine**



**Fig. 9. Variation of Log (Wi - “W) with time (mins) for aluminium coupons in 0.5M HCl solution containing Alanine at 303K.** as expressed as :

 C¸-1=1/Kads.+Cinh. ...(3)

Where Cinh. is the inhibitor concentration and Kads.is the equilibrium constant for adsorption/ desorption process of the inhibitor molecules on the metal surface. Kads. Values were calculated from the intercept of the plot for adsorption process and related with the free energy change of adsorption G0ads,by the following equation:

 G0ads= -RT ln(kads.Cwater) ...(4)

The Langmuir adsorption parameters and the values of ,G0ads in thepresenceofAlanine are given in table 3.Inspection of Table 3 reveals that the negative values of, G0ads point to the strength of the adsorbed layer on the Aluminum surface and naturalness of the adsorption process with the formation of an adsorbed film on the Aluminium surface.

The plot of¸ vs log C was linear for Alanine (see Figute 7). The plots support the assertion that the mechanism of corrosion inhibition is due to the formation and maintenance of a protective film on the metalsurface and that the additive covers both the anodic and cathodic sites through uniform adsorption. The fit of the experimental data to these isotherms provide evidence for the role of adsorption in the observed inhibitive effect of the Alanine.

**Thermodynamic Study**

**Determination of Enthalpy and Entropy**

Thermodynamic parameters such as enthalpy (H) and entropy (S) of activation of corrosion process may be evaluated from the effect of temperature. The enthalpy and entropy of activation of corrosion process was calculated from the equation:

Log CR/T = log (R/nh ) + S/2.303R -H/2.303RT

...(5)

Where „CR is the corrosion rate, „T is the absolute temperature , „R is the molar gas constant, „n is Avogadro s constant, and „h is the Planck s constant. A plot of log CR/T vs 1/T is a straight line graph (see Figure 8) with a slope of (-”H/2.303R ) and an intercept of (log (log (R/nh ) + “S/2.303R ). From the slope and the intercept, ”*H* and ”S were calculated as reported by Abiola et al.

|  |
| --- |
| S-Allyl cysteine AlliinAllicin saponins**Fig. 10: The structure of some compounds present in Garlic plant** |

The results presented in Table 4 show that the enthalpy of activation values were all negative for Alanine which reflects the exothermic nature of the aluminum dissolution process. Also, the entropies of activation were negative indicating that the activation complex represents association steps and that the reaction was spontaneous and feasible. These results were in excellent agreement with the previous study.

**Free Energy of Adsorption**

The free energy of adsorption values, G°ads,were obtained by using equation (8) and the values obtained are presemted in Table 5.

 G°ads= -2.303RT log (55.5Kads) ...(6)

Results obtained indicate that the values of G°ads are negative in all cases, showing that the reaction is spontaneous 33 and that the Alanines are strongly adsorbed on the aluminum surface by physical adsorption. Previous investigators showed that the values of G°ads up to -20 kJmol-1 are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physisorption), while those more negative than -20 KJ mol-1 involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorption) . This observation also supports the earlier assertion that a physical adsorption is proposed as a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. The ”G values which are less than 10.5 kJ/ mol for various inhibitor concentrations (Table 5) revealed the decreased rate of corrosion reaction which is also substantiated by other studies.

**Kinetic Study**

**Determination of Rate Constant**

The corrosion reaction is a heterogeneous one, composed of anodic and cathodic reactions with the same or different rate. It is on this basis that kinetic analysis of the data is considered necessary. In this present study, the initial weight of aluminum coupon at time, t is designated Wi, the weight loss is “W and the weight change at time t, (Wi - “W). The plots of log (Wi - “W) against time (min) at 303 K and other temperatures studied, showed a linear variation which confirms a first order reaction kinetics with respect to the corrosion of aluminium corrosion in 0.5 M HCl solutions in the presence of the Alanine (Figure 9). The rate constant, halflife time and activation energy were calculated as shown in our earlier report 35. There is a general decrease in the rate constants from 303K - 323K with increasing concentrations of the red onion skin extract (Table 6).

**Determination of Half Life**

The values of half-life, t1/2, were calculated

using the equation:

 t1/2 =0.693/k ...(7)

The increase in half-life (t1/2) shown when the the Alanine is present further supports the inhibition of aluminium in 0.5 M HCl by the additives. The increase in half life indicates more protection of the metals by the the Alanine.

**On the basis of the experimentally**

Determined activation energy value (50.45 kJ mol-1 at 303 - 313 K), the additive is physically adsorbed on the coupons.Therefore, it is probable that a multilayer protective coverage on the entire aluminium surface was obtained 13.

**Phytochemical Constituents**

Garlic contains at least 33 sulfur compounds like aliin, allicin, ajoene, allylpropl, diallyl, trisulfide, sallylcysteine, vinyldithiines, Sallylmercaptocystein, and others. Besides sulfure compounds garlic contains 17 amino acids and their glycosides, arginine and others. Minerals such as selenium and enzymes like allinase, peroxidases, myrosinase, and others. Garlic contains a higher concentration of sulfur compounds than any other Allium species. The structure of the main representative compounds in Garlic are shown in Figure 10.

The above said phytochemical constituents present in Garlic having many active center such as sulfer,oxygen and nitrogen,which are regarded as centers of adsorption.Where the results of temperatures study have shown that mechanical adsorption takes place through physical adsorption,this effect of the extract cannot be ascribed to a definite component.It was found that aluminum surface in acid media have a positive charge36,which leads to electrostatic attraction of the negatively charge species(in this case Clions).In aqueous acidic solutions main constituents of Garlic exist either as neutral molecules or as protonated molecules(cations).So in view of the above the adsorption mechanism may occur as follows:

´ First,the acid’s anions(Cl-) adsorb physically on the positively charged metal surface,resulting surface charge modification significantly to negative charge.

´ Second,the protonated molecules are physically attracted to the anions layer which is formed on the metal surface.

The degree of protection increases with increase in extract concentration due to higher degree of surface coverage resulting from enhanced inhibitor adsorption.

From Figure 10 reveal of the chemical structures of these phytochemical constituents reveal that these compounds are easily hydrolysable and the compounds can be adsorbed on the metal surface via the lone pair of electrons present on their oxygen which make a barrier for charge and mass transfer leading to decrease the interaction of the metal with the corrosive environment. As a result, the corrosion rate of the metal was decreased. The formation of film layer essentially blocks the discharge of H+ and dissolution of the metal ions. Due to electrostatic interaction, the protonated constituent s molecules are adsorbed (physisorption) and high inhibition is expected.

**CHAPTER FIVE**

**CONCLUSION**

1. The acid extract of Garlic acts as good and efficient inhibitor for the corrosion of aluminum in hydrochloric acid medium.
2. Inhibition efficiency increases with the increase of extract concentration and decreases with rise in temperature .
3. The adsorption of different concentrations of the plant extract on the surface of the aluminum in 0.5 M HCl acid followed both Langmuir and Temkin adsorption isotherm.
4. The values of standard free energy of adsorption suggest that the adsorption of inhibitor on aluminium surface occurred by physisorption mechanism. the negative sign of the Free Energy of adsorption indicates that the adsorption of the inhibitors on the aluminum surface was a spontaneous process.
5. The negative values of enthalpy of adsorption (H) suggest that the chemical reaction involved in the adsorption of the inhibitors on the metal surface is an exothermic process, hence increase in the reaction temperature of the medium will decrease the inhibition efficiency.
6. The negative values of entropy of adsorption indicate that the reaction was spontaneous and feasible.

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