Introduction

INTRODUCTION

1.1- DEFINITION OF CORROSION

The most important electrodic process of vast practical significance is that resulting in the dissolution of a metal in a solution or in the formation of a film of conducting moisture adhering to a metal surface. The process is termed “corrosion”. It is the rate of corrosion which determines the significance of corrosion. It is now generally accepted that corrosion is a reversion or a partial reversion from the metastable condition of the metal to a stable condition of the mineral accompanied by a reduction in the free energy of the system. Common examples of material's corrosion are rusting of iron and the tarnishing of silver, copper etc. The rate of the metal dissolution is governed by materials characteristics and the environment.

1.2- COST OF CORROSION

In recent years corrosion by chemical and electrochemical reactions has assumed great economic importance throughout the world. The estimated annual loss due to corrosion is enormously large. Studies worldwide have shown that the overall cost of corrosion amounts to at least 2-3% of the Gross National Product and that 20-25% of the cost could be avoided by using appropriate corrosion control technology [1]. In USA the cost of corrosion per year has been estimated to be over 126B (billion) dollars in 1982. The problem of preventing of metallic corrosion is extremely complex but it is of great technological and economical importance. Corrosion of metals can be controlled by taking suitable preventive measures such as painting, plating, use of expensive alloys, use of inhibitors etc. Corrosion of engineering components many times leads to the loss of production and sometimes it may be hazardous too.

1.3- CLASSIFICATION OF CORROSION

All the metallic materials consist of atoms having valency electrons which can be donated or shared. In a corrosive environment the components of the alloy get ionized and the movement of the electrons sets up a galvanic or electrochemical cell which causes oxidation, reduction, dissolution or simple diffusion of the elements.

The metallurgical approach of corrosion of metals is in terms of the nature of the alloying characteristics, the phases existing and their inter-diffusion under different environmental conditions. In fact, the process of corrosion is a complex phenomenon and it is difficult to predict the exclusive effect or the individual role involved by any one of the above mentioned processes.

Based on the above processes, corrosion can be classified in many ways as low temperature and high temperature corrosion, direct oxidation and electrochemical corrosion, etc. The preferred classification is:

(i) dry or chemical corrosion, and

(ii) wet or electrochemical corrosion.

Dry corrosion occurs in the absence of a liquid phase or above the dew point of the environment. Vapours and gases are usually coordinates, it is often associated with high temperature. An example is the attack of steel by furnace gases.

Wet corrosion occurs when a liquid is present in contact with the metal. This occurs in aqueous solutions or electrolytes. A common example is corrosion of steel by water.

The nature and extent of corrosion depend on the metal and the environment. The important factors which may influence the corrosion process are:

(i) nature of the metal.

(ii) nature of the environment.

(iii) electrode potential.

(iv) temperature.

(v) solution concentration.

(vi) aeration.

(vii) agitation.

(viii) pH of the solution and

(ix) nature of the corrosion products.

1.3.1- Various forms of corrosion [2]

Corrosion can manifest itself in the following main forms:

1.3.1.1- General corrosion or uniform attack

This is the most common type in which the corrosion is uniform over the entire exposed surface. an example of this is water tank exposed to the atmosphere.

1.3.1.2- Pitting or localized attack

It is one of the most destructive and insidious forms of corrosion. It is a highly localized corrosion, the attack is being limited to extremely small areas. An example is the corrosion of stainless steels in chloride solutions.

1.3.1.3- Galvanic corrosion

It is an accelerated electrochemical action due to two different metals being in electrical contact and exposed to an electrolyte. Heat exchanger failure in which aluminium tubes are supported by a perforated steel sheet is an example of this type of corrosion.

1.3.1.4- Crevice corrosion

This type of corrosion takes place when only one metal is in contact with different concentrations of the environment. Rectangular metal containers and reverted lap joints offer the possibility for this type of corrosion.

1.3.1.5- Stress corrosion

It is the spontaneous cracking resulting from the combined effect of prolonged stress and corrosive attack. Caustic embrittlement of boilers provides an example for this type of corrosion.

1.3.1.6- Erosion – corrosion

It is the acceleration in the rate of attack of a metal because of the relative movement between a corrosive fluid and the metal surface. Heat exchanger tubes with water movement undergoes this type of corrosion.

1.3.1.7- Fretting corrosion

It is a case of deterioration resulting form repetitive rumbling at the interface between two surfaces in a corrosive environment. It is found in aircraft engine parts.

1.3.1.8- Filiform corrosion

It is a special type of rusting which occurs on certain metals under protective films like paints and is characterized by a thread like growth. Filiform corrosion may be found on tools coated with oil films, refrigerator doors etc.

1.4- ELECTROCHEMICAL THEORY OF CORROSION

An atom has a massive positively charged central nucleus surrounded by a cloud of negatively charged electrons. This cloud of electrons is accommodated in a series of shells. The outermost shell should have eight electrons in the most stable state of an element. If the electrons are insufficient to fill the outer most shell, the atom tends to obtain a cloud of complete shells by gaining or losing electrons to give rise to modified atoms called 'ions'.

Evans [3] has explained the role of these ions in the corrosion and dissolution of metals and alloys under the influence of the exchange of ionic charges. This has laid down the basis of the electrochemical theory of corrosion. When a metallic object is immersed in a corrosive medium the metallic surface gets divided into areas having different potentials under the influence of various metallic phases, grain boundaries stress and strain, impurities etc. In an electrolyte the metal undergoes disintegration due to the displacement of a hydrogen ions in the electrolyte by those of the anode metal, resulting in the formation of a galvanic cell.

The corrosion generally involves the formation of hydrogen gas at the cathode in an acidic medium.

The anodic reaction is

$$M \rightarrow M^{++} + 2e^{-} \qquad (1.1)$$

This represents oxidation of the metal. The cathodic reaction is

$$2H^{+} + 2e^{-} \rightarrow H_2\uparrow \qquad (1.2)$$

The other possible cathode reaction is the reduction of oxygen in acidic solutions

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \qquad (1.3)$$

In neutral and alkaline solutions, however, the accumulation of electorns on the cathode is prevented (except for a very active metal) only by the intervention of oxygen which is reduced according to the equation

$$2H_2O + O_2 + 4e^{-} \rightarrow 4OH^{-} \qquad (1.4)$$

The essential concept of the electrochemical mechanism is that the corrosion of a metal is a redox reaction, occurring at a metal/solution interface with consequent transfer of electrons through the metal and ions through the solution. The tendency of a metal to corrode may be expressed by the amount of energy liberated in the changes from the metallic state to the oxidized state or in electrochemical terms by the standard electrode potential of the metal. The metals are arranged in order of their electrode potential, the noble metals appearing at the passive end and the more reactive metals appearing at the active end of the series. Although brass has fairly a good corrosion resistance, owing to the presence of zinc (electronegative) the corrosion behaviour of brass is shifted towards higher electronegativity.

1.4.1- Polarization

An electrode is no longer in equilibrium when a net current is continuously flowing to or away from its surface. The extent of charge at the measured potential of such an electrode depends on the magnitude of the external current and its direction. The potential always changes in a direction so as to oppose the shift from the equilibrium and hence to oppose the flow of current. Whether the current is impressed externally or developed internally due to a galvanic cell, the anode always becomes more anodic decreasing the potential difference. Thus the extent of potential change caused by the flow of current from an electrode is called 'polarization'. There are three types of polarization which can be described as follows.

1.4.1.1- Concentration polarization

According to the Nernst equation the potential of an electrode depends upon the concentration of ions in the electrolyte in its immediate vicinity. For example, consider the reduction of M^{+n} in a solution in which its activity is given by $a_{M^{+n}}$. In the absence of an external current the potential E is given by the Nernst equation,

$$E_1 = E_1^o + \frac{0.0592}{n} \log (a_{M^{+n}}) \tag{1.5}$$

If an external current is made to flow so as to accelerate the reduction rate, then concentration of the M^{+n} ions in the solution near the electrode decreases. This decrease in concentration is usually made up by fresh M^{+n} ions brought to electrode by (i) ionic migration (ii) diffusion and (iii) convection.

The first two of these ionic modes of transfer inevitably occurs, while the last can be controlled. At low reduction rates the migration of ions is sufficient to keep the concentration near the electrodes to the desired level. At higher currents, on the other hand, concentration of these ions changes to say M_s^{+n}. The potential of the electrode E_2 in this condition is given by

$$E_2 = E_2^o + \frac{0.0592}{n} \log (a_{M_s^{+n}}) \tag{1.6}$$

The difference in potential $E_2 - E_1$ is known as concentration polarization and is given by, η_C

$$\eta_C = E_1 - E_2 = \frac{0.0592}{n} \log \frac{a_{M^{+n}}}{a_{M_s^{+n}}} \tag{1.7}$$

1.4.1.2- Activation polarization

Activation polarization is caused by a slow electrode reaction. In this case some activation energy is required for the reaction to start on the electrode surface. An example is the reduction of hydrogen ions on the cathode surface.

$$2H^+ + 2e^- \rightarrow H_2\uparrow \tag{1.8}$$

1.4.1.3- Resistance polarization

During the measurement of polarization there is also an ohmic drop (i_R) through either a portion of the electrolyte surrounding the electrode or through a metal reaction product film on the surface or both. This contribution to polarization is equal to i_R where 'i' is the current density and 'R' represents the value of the path resistance in ohms.

1.5- Cu-Zn BINARY PHASE DIAGRAM

Copper and zinc having atomic size 1.27 Å and 1.37 Å and face centered cubic (FCC) structure and hexagonal close packed (HCP) structure, respectively, combine to form a series of solid solutions and intermetallic compounds [4]. The copper-rich side of the binary phase diagram is shown in Fig. (1.1). Three important phases occurring on the copper rich side of the phase diagram are α, β and γ. Alloys having composition between A & B solidify as the α-solid solution having maximum solubility of 39 (wt) % Zn at 454°C. It has a face centered cubic (FCC) structure and having a short range order. In alloys of composition between B and C, the first crystal to form is of the α-solid solution, but at 902°C, an intermetallic β phase is precipitated. It has a body centered cubic (BCC) structure and it extends form 46.6 to 50.6 (wt) % at room temperature. The β phase itself undergoes allotropic transformation on cooling and below 486°C the β phase transforms into the β' phase. On further increase in the zinc content another intermediate phase known as γ phase is formed which has a complex body centered cubic type of (BCC) structure. It extends from 59.1 to 67.2 (wt)% zinc and this phase is very brittle. In brasses of intermediate composition either α or a mixture of α + β or α + β + γ phase are present in the alloy. The properties of the alloy can be altered by changing the phase distribution.

1.6-PHYSICAL AND MECHANICAL PROPERTIES OF COPPER AND BRASSES

Copper and copper alloys are widely used in many environments and applications because of their excellent corrosion resistance. they are having combinations of other properties such as superior, electrical and thermal conductivity, ease of fabrication and having a wide range of mechanical properties such as elongation and tensile strength. The elongation and tensile strength of brasses increase with an increase in the zinc content. The elongation rises rapidly in the α-range, showing maximum at 30% zinc. When the β-phase appears, the ductility decreases. The tensile strength in the β-phase range decreases with an increase in the zinc content and with the appearance of the γ-phase, the alloy becomes very brittle. In general, the α phase of a brass may be described as ductile, the β phase as tough and the γ as a brittle phase. Generally, commercial brasses are restricted upto 40% zinc, because with a further increase in zinc content γ phase forms and makes the alloy very brittle.

1.7- APPLICATIONS OF COPPER AND COPPER ALLOYS

Copper and copper alloys provide superior properties in many of the applications. They are widely used in the construction of heat exchangers, condensers, and valve systems. They are mostly used in architectural items, building fronts, rails, lock bodies, door knobs etc.

Heat exchangers and condensers are used in marine device, steam power plants and chemical process applications. They are widely used in electrical wiring, hardware, connectors, printed circuit boards and electronic applications that required combinations of electrical, thermal and mechanical properties.

1.8- CORROSION OF COPPER AND COPEPR ALLOYS [5]

Copper and its alloys are unique among the corrosion resistance alloys, in that they do not form a truly passive corrosion product film. In aqueous environments at ambient temperatures the corrosion product predominantly responsible for protection is cuprous oxide (Cu_2O). This Cu_2O film is adherent and follows a parabolic growth kinetics. Cuprous oxide is a p-type semiconductor formed by electrochemical processes.

$$4\,Cu + 2\,H_2O \rightarrow 2\,Cu_2O + 4H^+ + 4e^- \qquad (1.9)$$

and

$$O_2 + 2\,H_2O + 4e^- \rightarrow 4\,OH^- \qquad (1.10)$$

with the net reaction

$$4Cu + O_2 \rightarrow 2Cu_2O \qquad (1.11)$$

For the corrosion reaction to proceed, copper ions and electrons must migrate through the Cu_2O film. Consequently reducing the ionic or electronic conductivity of the film by doping with divalent or trivalent cations should improve corrosion resistance. In practice alloying additions of Al, Zn, Sn, Fe, and Ni are used to dope the corrosion product films and they generally reduce corrosion rates significantly.

1.9- COPPER AND HIGH COPPER ALLOYS

They have excellent resistance to corrosion in sea water but are susceptible to corrosion at high water velocities. They are used in applications that require enhanced mechanical performance, often at slightly elevated temperatures.

1.9.1- Brasses

Brasses are basically Cu-Zn alloys and are the most widely used groups of copper alloys. The resistance of brasses to corrosion by aqueous solution does not change markedly as long as the zinc content does not exceed about 15%. Above 15% zinc, dezincification may occur. Quiescent or slowly moving saline solution, brackish waters, and mildly acidic solution are environments that often lead to the dezincification of unmodified brasses. Susceptibility to stress-corrosion cracking (SCC) is significantly affected by zinc content. Alloys that contains more zinc are non susceptible to SCC. Elements such as Pb, Te, Be, Cr, P and Mn have little or no effect on the corrosion resistance of copper and binary copper-zinc alloys. These elements are added to improve mechanical properties such as machinability, strength and hardness.

1.9.2- Tin brasses

Tin addition significantly increases the corrosion resistance of some brasses, especially resistance to dezincification. Admiralty metal has a greater resistance to dealloying because of the addition of 1% tin to 70-30 brass. Similarly muntz metal is the alloy resulting from the addition of 0.75% tin to the basic 60-40 brass.

1.9.3- Aluminium brasses

An important constituent of the corrosion film on a brass that contains a few percent aluminium, in addition to copper and zinc is aluminium oxide (Al_2O_3), which markedly increases the resistance to impingement attack in turbulent high velocity saline water. The arsenical aluminium brass is frequently used for marine condensers and heat exchangers in which impingement attack is likely to pose a serious problem. Aluminium brasses are subjected to dezincification and it is inhibited, by adding 0.02 to 0.10% arsenic. The addition of phosphorus, arsenic or antimony (typically 0.02 to 0.1%) to admiralty brass, navel brass or aluminium brass effectively produces high resistance to dezincification.

1.9.4- Phosphor bronzes

Addition of tin and phosphorous to copper produces good resistance to corrosion in flowing sea water and in most non-oxidizing acids except HCl. Alloys containing 8-10% tin have high resistance to impingement attack. Phosphor bronzes are much less susceptible to SCC than brasses, and are similar to copper in its resistance to sulphur attack. Tin bronzes (alloy of Cu-Sn) are found to be used primarily in the case form in which they are modified by further alloy additions of Pb-Zn and Ni. Tin bronzes are used in pumps, valves, gears and brushings. Wrought tin bronzes are known as phosphor bronzes and they find use in high strength wire applications such as wire rope. This group of alloys has a fair resistance to impingement and good resistance to biofouling.

1.9.5- Copper-nickel

Of all the alloys of copper of commercial importance, copper-nickel alloy has the best general resistance to aqueous corrosion. These alloys are well suited to applications in chemical industry and are extensively used for condenser tubes and heat exchanger tubes in recirculating steam systems. They are superior to copper and to other copper alloys in resisting acid solutions and are highly resistant to SCC and impingement corrosion.

1.9.6- Copper-silicon alloys

These alloys generally have the same corrosion resistance as copper, but they have higher mechanical properties and superior weldability. These alloys appear to be much more resistant to SCC than the common brasses. Silicon bronzes are susceptible to embrittlement by high pressure steam.

1.9.7- Aluminium bronzes

Aluminium bronzes containing 5 to 12% aluminium have excellent resistance to impingement corrosion and high temperature oxidation. Aluminium bronzes are used for heater bars and for blades in wood pulp machine because of their ability to withstand mechanical abrasion and chemical attack by sulphite solution. Alloys up to 8% aluminium normally have completely FCC structures and good resistance to corrosion attack. Aluminium bronzes are generally suitable for service in non oxidizing mineral acids, alkaline and neutral solutions (phosphoric, sulphuric and hydrochloric acids and neutral saline solution such as NaCl, KCl).

Different forms of corrosion of copper and copper alloys in different environments are given in Table (1.1).

Table (1.1).

Form of attack	Characteristics	Preventive measures
General thinning	Uniform metal removal	Select proper alloy for environmental conditions based on weight loss data.
Galvanic corrosion	Corrosion preferentially near a more cathodic metal	Avoid electrically coupling dissimilar metals; maintain optimum ratio of anode to cathode area; maintain optimum concentration of oxidizing constituent in corroding medium
Pitting	Localized pits, tubercles; water line pitting; crevice corrosion: pitting under foreign objects or dirt.	Alloy selection; design to avoid crevices; keep metal clean.
Impingement Erosion-corrosion	Erosion attack from turbulent flow plus dissolved gases, generally as lines of pits	Design for streamlined flow, keep velocity low; remove gases from liquid phase; use erosion-resistant

Cavitation	in direction of fluid flow.	alloy.
Fretting surfaces	Chafing or galling, often occurring during shipment	Lubricate contacting interleave sheets of paper between sheets of metal; decrease load on bearing surfaces.
Intergranular corrosion	Corrosion along grain boundaries without visible signs of cracking	Select proper alloy for environmental conditions based on metallographic examination of corrosion specimens.
Dealloying	Prefernetial dissolution of zinc or nickel, resulting in a layer of sponge copper	Select proper alloy for environmental conditions based on metallographic examination of corrosion specimens.
Corrosion fatigue	Several transgranular cracks.	Select proper alloy based on fatigue tests in service environment; reduce mean or alternating stress.

SCC	Cracking, usually intergranular but sometimes transgranular, that is often fairly rapid	Select proper alloy based on stress-corrosion tests; reduce applied or residual stress; remove mercury compounds or NH_3 from environment.

1.10- CORROSION PREVENTION OF COPPER AND ITS ALLOYS

To minimize the losses due to corrosion various preventive methods have been developed. Many of the methods are based on the isolation of the metal from corrosive environments. This can be achieved either by the use of a foreign coating or by the formation of a protective film on the metal surface.

Alternatively the corrosive environment may be modified either by the removal of harmful constituents or by the addition of a substance which can be termed “inhibitor”. Some of the methods generally adopted to reduce the corrosion are:

1. Addition of alloying elements.
2. Coating on copper alloys and
3. Application of inhibitors

1.10.1- Addition of alloying elements

Addition of small amounts of alloying elements such as arsenic, aluminium, zinc, antimony, and phosphorous have been found to control the corrosion of brasses. Addition of 0.02-0.4% arsenic inhibits the dezincification of α-brass [6]. Small amount of arsenic in solid solution of α-brasses has effectively prevented dezincification even in most aggressive media but a further increase in arsenic, leads to deleterious effect. Addition of 1% of antimony, phosphorous also reduces dezincification in brasses. Addition of 0.75-1.0% of tin is effective in reducing the dezincification rate of admiralty and naval brass. Addition of a few percent of aluminium to copper and zinc markedly by increases the resistance to impingement attack in turbulent high velocity saline water.

1.10.2- Coating on copper alloys

Electroplating of copper alloys with nickel, tin, chromium etc. is found to improve their life by controlling the dezincification process. Lacquering of the archaeological objects prevent the dezincification of these objects. Paints are highly complex substances capable of producing a high resistance path to ions formed on the metal surface and thus minimize the corrosion rate.

1.10.3- Applications of inhibitors

The addition of inhibitors to minimize the corrosion rate is the other mainly used method, where the protection of the metal is achieved either by changing the characteristics of the electrolyte or by forming a protective passive film on the electrode surface. This can be done by adding certain anions like chromate, nitrate and phosphate to form a protective oxide film and by retarding the cathodic current density or by increasing the flade potential to more negative values and subsequently promoting the anodic process.

Some organic compounds like azoles, amines, thiourea etc. are adsorbed or chemisorbed on the surface of the metal and form a protective layer.

1.10.4- Mechanism of inhibition

The following mechanisms are suggested to explain the phenomenon of corrosion inhibition.

1.10.4.1- Formation of a physical barrier and reduction in metal reactivity

The inhibitive action observed on the addition of organic compounds is due to the surface coverage (θ) by the compound owing to the adsorption or chemisorption. The inhibitor may be selectively adsorbed onto the cathodic or anodic sites on the surface of the metal. This results in the decrease of cathodic or anodic reaction rate and thus corrosion is retarded. The adsorption on cathodic sites increases cathodic polarization and on anodic sites increases anodic polarization.

1.10.4.2- Change in the electrical double layer structure

According to the mechanism adsorbed organic molecules physically block the sites on the metal surface resulting in the change of double layer structure at the metal/solution interface.

Though the action of inhibitors has been explained on the basis of various considerations, it is now generally accepted that organic compounds inhibit corrosion by adsorbing at the metal solution interface.

1.11- CLASSIFICATIONS OF INHIBITORS

Inhibitors are classified as acid, neutral, alkaline and vapour phase inhibitors depending upon the environment. Depending on the mechanism of inhibition, they are classified as cathodic, anodic and mixed type of inhibitors. Acid inhibitors can be further classified as inorganic and organic inhibitors. Inorganic inhibitors are not of much importance for copper and its alloys.

Usually corrosion of metals and alloys in acidic, neutral and alkaline solutions can be inhibited by a large number of organic substances. In general, nitrogen, oxygen and sulphur containing compounds with a hydrocarbon part attached to the polar group are used as inhibitors. Triple bonded hydrocarbons, acetylenic alcohols, thioureas, sulfoxides, sulphides and mercaptans, aliphatic, aromatic or heterocyclic compounds and condensation products formed by the reaction between two different species such as aldehydes, amines and schiff bases are mostly used. Schmitt [7] has reviewed the application of inhibitors for acid media. The performance of inhibitors depends on various factors like size, solubility, chemical structure, substituent effect, steric effect, carbon chain length, Hammett constant, molecular weight, basicity (pk), dipole moment, magnetic susceptibility, NMR shift, temperature, acid concentration, velocity of liquid flow, nature of metal and pH of the solution. In the case of mixture of inhibitors synergistic [8], behaviours were reported. The study of various organic compounds in relation to their different aspects of inhibition in different environments has been reviewed by Sanyal [9].

1.12- LATEST APPROACH ON THE STUDY OF INHIBITORS

The latest approach [10] which is based on the mechanism of inhibition has, however enabled the classification of the corrosion inhibitors into four major categories.

(i) Barrier layer formers.

(ii) Neutralizers.

(iii) Scavengers.

(iv) Miscellaneous.

1.12.1- Barrier layer formers

These substances form barrier layers on the corroding metal surface and reduce the corrosion rate. This type forms the largest category of corrosion inhibitors. Barrier layer formers have been further classified into oxidizers, adsorbed layer formers and conversion layer formers. In general these inhibitors are effective in reducing both the cathodic and anodic reaction rates except for the oxidizing inhibitors which shift the corrosion potential of the metal to more positive values at which a stable oxide or hydroxide is formed and protects the metal surface.

1.12.2- Neutralizers

These inhibitors remove the hydrogen ions from the corrosive environment thereby reducing the corrosivity of the environment and hence the concentration of the cathodic reactant. These inhibitors are used in the treatment of boiler waters, oil field applications and also in ethylene glycol cooling systems.

1.12.3- Scavengers

These are similar to neutralizers but used to remove corrosive species other than hydrogen ions. Typical example is hydrazine in boiler systems which removes traces of oxygen which is a cathodic reactant.

1.12.4- Miscellaneous

These inhibitors include materials such as scale forming inhibitors and biological growth inhibitors which reduce corrosion by interfering with other processes.

1.13- THEORIES OF CORROSION INHIBITION

1.13.1- Adsorption theory

Organic inhibitors which presumably are not capable of oxidizing or precipitating the metal ion, must have the ability to adsorb and impede either cathodic or anodic or both the reactions. Organic inhibitors inhibit corrosion by adsorption at metal/solution interface. Most of the heterocyclic compounds containing nitrogen were believed to be cathodic inhibitors. But it has been shown by Hoar [11] that in some cases anodic inhibition is observed.

The mode of adsorption depends on:

1) The nature of the metal surface.

2) The chemical structure of the molecule.

3) The electrochemical potential at the metal/solution interface.

The following are the different types of adsorption associated with organic inhibitors.

1) Electrostatic adsorption or electrosorption.

2) Chemisorption and π-orbital adsorption.

3) Physical or Van der Waals type of adsorption.

1.13.2- Electrosorption

In electrosorption the coulombic electrical forces which stretch out from the metal are much longer in range than the chemical forces which affect the molecules in chemisorption.

1.13.3- π-Orbital adsorption

In this type, the adsorption may result from π-orbital interaction with the metal. Organic compounds with double and triple bonds, and these containing aromatic nucleus interact with metal by their π-bond orbitals.

1.13.4- Van der Waals adsorption

The adsorbed molecules are held by weak Van der Waals forces and physically adsorbed molecules on solids forming multilayers, as the forces operating are weak Van der Waals type, the adsorbed molecules may easily be removed or desorbed from the surface by lowering the bulk concentration of the adsorbate.

1.13.5- Film theory

In order to explain the inhibitive action of inhibitors in neutral and alkaline media, Evans [12] attributed the inhibition to the formation of an insoluble film. In acid solutions according to Hausler [13] and Putilova et al. [14], appreciably effective protection of metals by inhibitors is due to the formation of a layer of insoluble or slightly soluble corrosion products on the metal surface. The formation of insoluble or slightly soluble complex compounds or metal sulphide with compounds like thio-ethers, thio-alcohols and the formation of a protective film on the metal surface have been quoted as examples in support of the film theory.

1.14- ADSORPTION ISOTHERMS

An adsorption isotherm is the mathematical expression which relates the bulk concentration of an adsorbing species to its surface concentration at constant temperature. An adsorption isotherm gives the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in solution. Various adsorption isotherms have been formulated. A list of various isotherms and the corresponding equations are given in the Table 1.2 [15]. A common procedure is to convert isotherm to a linear form and plot the experimental data accordingly. The data can be fitted to any one of the adsorption isotherms from the suitable plot and the free energy of adsorption of the organic inhibitors can be obtained.

Most of the organic inhibitors obey Langmuir's or Temkin's adsorption isotherms.

an inhibitor is found to obey Langmuir's isotherm if a plot of log $\theta/1-\theta$ vs log C is linear. Similarly for Temkin's plot of θ vs log C, for Bockris Devanathan and Muller (BDM) a plot of (log C – log $\theta/1-\theta$) vs $\theta^{3/2}$ and for the Frumkin's a plot of log $\theta/(1-\theta)C$ Vs θ will be linear.

Table (1.2).

No	Isotherm	Equations
1	Langmuir	$\beta C = \frac{\theta}{(1-\theta)}$
2	Freundlisch	$\beta C = \theta(\theta < n < 1)$
3	Frumkin	$\beta C = \frac{\theta}{(1-\theta)} \exp(-2a\theta)$
4	Temkin	$\beta C = \frac{\exp(a\theta) - 1}{1 - \exp[-a(1-\theta)]}$
5	Parsons	$\beta C = \frac{\theta}{(1-\theta)} \exp \frac{2-\theta}{(1-\theta)^2} \exp[-2a\theta]$
6	Bockris, Devanathan and Muller (BDM)	$\log C \pm \log \frac{\theta}{(1-\theta)} = C + \beta\theta^{3/2}$

Note: $\beta = e^{-\Delta G_{ads/RT}}$
a = interaction Parameter
a > o = attraction
a < o = repulsion

1.15- TECHNIQUES FOR STUDYING CORROSION

1.15.1- Non-electrochemical methods

1.15.1.1- Coupon method

The corrosion rate is evaluated by measuring the change in the weight of coupon after exposing the metal specimen of known area to the particular environment for a specific period. This method yields the average rate and is inherently inaccurate for measuring very low corrosion rates. Methods of surface preparation and cleaning of corroded specimens are described by Champion [16].

1.15.1.2- Solution analysis

In this method [17] chemical or physical techniques are used to identify and estimate the concentration of ions of the metal or metals under examination dissolving in the test environment.

1.15.1.3- Gas-volumetric method

In this method [18] a definite correlation between the cathodic reaction rate and the anodic dissolution rate can be established.

1.15.2- ELECTROCHEMICAL METHODS

1.15.2.1- Electrical resistance method

An increase in the electrical resistance is a measure of corrosion [19]. A decrease in the cross section due to corrosion, increases the electrical resistance. The resistance of the exposed element is measured by Kelvin's bridge along with another element which is protected against corrosion. Instruments have been developed to measure these resistance ratios which are calibrated in mpy. The major advantage of this method is its ability to measure corrosion rates in the liquid and vapour phases and in aqueous and non-aqueous media. This method is used for continuous monitoring in chemical process industries.

1.15.2.2- Tafel extrapolation method

This method [20] is also described as Tafel plot method or Evan's diagram method or logarithmic polarization method. Actually the measurement of corrosion rate of the system involves the measurement of potential of the electrode for various applied current densities. A plot of E vs log 1 gives a figure known as polarization diagram Fig. (1.2). The intercept of anodic and cathodic Tafel lines provides the corrosion current and Tafel slopes give β_a, and β_c. In actual practice, polarization curves are obtained from galvanostatic/potentiostatic or potentiodynamic methods.

1.15.2.3- Polarization resistance method

Stern and Geary [21] have shown that there is a linear relationship between current and potential when $\eta < 20$ mV and on measuring $[d\eta/di]$ $\eta \rightarrow o$ the corrosion current can be obtained from,

$$i_{corr} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} x \left(\frac{di}{d\eta}\right) \qquad (1.12)$$

the above relationship is valid only for activation controlled reactions. Rajagopalan and Rangarajan [22] have derived the relationship with metals undergoing corrosion. The simultaneous determination of Tafel slopes and corrosion current at the corrosion potential have been suggested by many authors. Barnartt [23], Reeve and Bech- Nielsen [24], Oldham and Mansfeld [25], Periasamy and Krishnaswamy [26] have made some improvements in this method. Mansfeld [27,28] has developed a computer programme (CORFIT) for the quantitative determination of i_{corr} which requires simultaneous determination of both R_p and β. Various applications and the developments of this technique have been reviewed by Lorenz and Mansfeld [29].

1.15.2.4- Coulostatic method

This method [30,31] is suited especially for the measurement of corrosion rates of metals in high resistant media. The polarization resistance (R_p) is measured from the η-t transient of the electrode on discharging a charged capacitor (C) through the cell. The electrode potential decay is

$$\eta_t = \eta_o \exp(-t/C_{dl} R_P) \qquad (1.13)$$

η_t = overpotential at any time "t",

η_o= overpotential immediately after charging the double layer of the electrode

C_{dl} = differential capacity of the double layer.

The plot of log η_t vs t is a straight line and the slope gives $1/2.3\ C_{dl}/R_p$ and the intercept is η_o.

1.15.2.5- A.C. Impedance measurements

Electrochemical impedance measurements is an appropriate method for corrosion studies, particularly for corrosion rate determinations (32-51], mechanistic studies [52-54], passivation and passivity process [55-57] and for investigation in inhibited systems

[36,58-63]. The theoretical analysis of a.c. impedance measurements has been analyzed by Warburg [64], to explain the frequency dispersion of the electrode-electrolyte interface and impedance in terms of mass transport (diffusion controlled) process. Haruyama and Tsuru [47] and Mansfeld et al. [40-41] have reviewed impedance methods. A review of the application of these techniques in corrosion studies has been published by MacDonald et al. [48-49]. The use of a.c. impedance technique in various cases has been reviewed by Gabrielli [65]. The schematic representation of the interface impedance are shown in Fig. 1.3. Solution resistance is represented by R_S, charge transfer resistance is given by R_{Ct} or R_t and the double layer capacitance is represented by C_{dl}., Using Stern-Geary equation, i_{corr} is obtained from R_t since.

$$i_{corr} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \cdot \frac{1}{R_t} \qquad (1.14)$$

Thus, the cell impedance Z consists of real (Z`) and imaginary (-Z") parts. A plot of Z' vs – Z" for various frequencies is a semicircle. At high frequency, Z corresponds to R_s and at low frequency Z corresponds to $(R_s + R_t)$ and the difference between the two values gives R_t. The double layer capacitance (C_{dl}) can be calculated from the frequency ω at the top of the semicircle (Z" maximum).

$$f(Z''_{max}) = \frac{1}{2\pi C_{dl} R_t} \qquad (1.15)$$

The main disadvantage of this method is that only R_t can be determined directly while the Tafel parameters have to be obtained by other methods.

1.15.2.6- Faradaic rectification method

In a corrosion process, the anodic and cathodic reactions are unsymmetric (i.e., $\beta_a \neq \beta_c$) [66-68]. When a sinusoidal voltage is applied, a flow of direct component of current results. On measuring the rectified current and voltage, $I_{corr.}$ is obtained from the relationship:

$$I_{corr} = \frac{0.754\, i_{dc}\,(E_2 - E_{corr.})}{E_p^2(\beta_a^{-2} - \beta_c^{-2})(E_2 - E_1)} \qquad (1.16)$$

where i_{dc} = rectified current,

E_1 = mean potential of working electrode corresponding to the rectified current ratio.

E_2 = mean potential of the working electrode when $i_{dc} = o$.

E_p = peak value of a.c. component of potential

This method has been tested for corrosion reactions in which the corrosion potential is near to the equilibrium potential of metal/metal ion reaction.

1.15.2.7- Faradaic distortion method [69]

On superimposing a sinusoidal alternating voltage, i.e. $E_m \sin \omega t$ to the electrode at the corrosion potential, harmonic current components are produced due to the non-linear relationship between the current and the potential. Measurements of fundamental (i_1), second harmonic (i_2) and third harmonic (i_3) current components are made for getting $i_{corr.}$ from the following relationships.

$$I_{corr} = \frac{i_1^2}{\sqrt{48}, \sqrt{2i_1 i_3 - i_2^2}} \qquad (1.17)$$

$$\frac{1}{b_a} = \frac{1}{4.6\,E_m}\left[\frac{i_1}{i_{corr}} + \frac{4i_2}{i_1}\right] \tag{1.18}$$

$$\frac{1}{b_c} = \frac{1}{4.6\,E_m}\left[\frac{i_1}{i_{corr}} + \frac{4i_2}{i_1}\right] \tag{1.19}$$

The advantage of this method is that the measurement of corrosion current is possible at the corrosion potential without the use of anodic and cathodic Tafel slopes.

1.16-CORROSION PREVENTION OF COPPER AND ITS ALLOYS USING ORGANIC COMPOUDNS AS INHIBITORS

Benzotriazole has been used extensively as a corrosion inhibitor for copper and copper alloys for over twenty five years and it is used as an effective inhibitor for copper in an aggressive media [70-75]. Benzotriazole has also been used as a pretreatment to reduce corrosion and atmospheric oxidation of copper [76]. Walker has reviewed the utility of triazole, benzotriazole and naphthatriazole as inhibitors of corrosion in acid, neutral and alkaline media [77]. Prajapati et al. [78] have studied the utility of 2-mercapto benzimidazole, benzotriazole, benzimidazole, 2-methylbenzothiazole and indole as inhibitors for the corrosion of copper in nitric acids. It is found that the inhibition efficiency depends on the structure of the organic compounds and the reactivity of the functional groups present in them.

Fox et al. [79] have carried out measurements on the adsorption of benzotriazole on copper and found that inhibitor molecule is weakly held on the oxide covered surface until a critical solution concentration in BTA is reached above which a good corrosion inhibition results. Notoya and Poling have studied the effective action on copper in aqueous solutions by [80] benzotrizole at different temperatures ranging from 25 to 100°C by different techniques such as polarization studies, SEM study etc. All the techniques reveal the fact that the protective action given by benzotriazole increases with temperature upto 100°C. Lewis [81] studied the inhibition of copper corrosion in NaCl by benzimidazole. The chemical nature of the complex formed between copper and benzimidazole in solution has been determined with the aid of Auger Electron Spectroscopy. Some correlation is found to exist between the corrosion inhibition tendency of benzimidazole for copper and the composition of surface film formed. Fox and Bradley [82] have made use of 1:2:4 triazole as an inhibitor for the corrosion of copper in ammonium chloride. They have also made the comparison of triazole and benzotriazole as inhibitors for corrosion for copper in aqueous solutions. Soni and Bhatt [83] have studied the effectiveness of a few azoles for the corrosion of copper and brass in sodium sulphate solutions and solutions of a few organic acids.

Kuron et al. [84] have made use of surface and microanalysis methods like ESCA, AES, SIMS, ISS and LAMMA to determine the composition and thickness of protective layers formed by the adsorption of benzotriazole, tolytriazole, mercaptobenzothiazole and 2-(5-aminopentyl)-benzimidazole on copper in drinking water and artificial sea water. It is found that all the inhibitors form effective protective layers on copper after very short immersion time. Allah and Mostafa have made quantum mechanical calculations of amino pyrazole derivatives as inhibitors for the corrosion of α-brass and copper in acid chloride solutions [85]. Devi et al. [86] have studied the corrosion of copper and brass in crude oil sea water mixture. They found that copper and brass showed higher rates of corrosion in natural and artificial sea water, but lower corrosion rates in sea water containing crude oil.

Falewicz and Kuczkowska [87] have studied the utility of nitrilo-trimethylene phosphoric acid as inhibitors for the protection of copper and brass in neutral aqueous media. They found that this compound in combination with phthalic acid anhydride and zinc ions can serve as a very good inhibitor for the corrosion protection of industrial cooling and heating water installations. Zucchi et al. [88] have investigated the usefulness of pyrimidine and thiadiazole derivatives as inhibitors for the corrosion of copper in NaCl solutions.

Gonzalez et al. [89] have investigated whether chemicals like benzotriazole, thiourea and potassium ethyl xanthate can inhibit the corrosion of copper either alone or in synergistic combination. The combination of potassium ethyl xanthate and benzotriazole exhibits synergistic inhibition in NaCl solutions. They attribute synergistic effect to in the compactness of the polymer like passivating layer of potassium ethyl xanthate and copper which form in the presence of benzotriazole and chloride ions. Zhou et al. [90] have studied the inhibition of corrosion of copper in low conductivity solutions by 2-mercapto benzothiazole. Schultze and Wipperman [91] have found that 3-amino-5-heptyl-1,2,4 triazole (AHT) is a very effective inhibitor for the corrosion of copper in neutral and acidic solutions. Beier and Schultze [92] have also studied the formation of inhibitive layer on copper by AHT in H_2SO_4 using potentiostatic pulse measurements Bastidas and Otero [93] have made a comparative study of the performance of benzotriazole (BT) and 2-amino-5-mercapto-1,3,4 thiadiazole (AMT) as inhibitors for the corrosion of copper in acidic solutions using different techniques such as weight loss, polarization curves, polarization resistance and electrochemical impedance spectroscopy. AMT showed more inhibition than BT in acidic solution. Notoya et al. [94] have studied the poalrization and corrosion behaviour of copper in domestic water in the presence of calcium, magnesium and sodium salts of phytic acid. Sodium salt of phytic acid is found to perform well as an inhibitor for the corrosion of copper in potable water. Itsh et al. [95] have studied the chemical modification of alkane thiol self-assembled monolayers with alkyl trichloro silanes for the protection of copper against corrosion. Guo et al. [96] have made use of a two component coupling agent layer for copper with epoxy resin and polyamide produced by the immersion of copper plate in polybenzimidazole solution. It showed better anticorrosive performance and higher adhesive strength.

Penninger et al. [97] have investigated the inhibitive performance of triazole derivatives, benzotriazole and other heterocyclic compounds on the corrosion of copper in NaOH to reveal the relationship between the molecular structure of the compounds and their inhibitive efficiency. Carron et al. [98] have studied the synergistic inhibition of corrosion of copper in corrosive media by tolybenzimidazole and mercaptobenzimidazole at high temperatures using cyclic voltammetry and surface enhanced Raman Scattering Spectroscopy. Rehan [99] has studied, the utility of 1-2-amino thiazole derivatives as inhibitors for the corrosion of commercial copper and brass in acidic solutions using techniques such as weight loss, polarization and capacity measurements Yi Ping Wu et al. [100] have made a comparative study of the inhibitive effect of benzotriazole and its derivatives on the corrosion of copper in NaCl and $Na_2B_4O_7$. Tromans and Silva [101] have made a comparative study of the performance of tolytriazole and benzotriazole as inhibitors for the corrosion of copper in NaCl solution using potentiodynamic studies. It is found that tolytriazole is more inhibitive than benzotriazole. Tommesani et al. [102] have recently investigated influence of a few derivatives of benzotriazole on the corrosion of copper in 3.5% NaCl and 0.1M $NaClO_4$ using polarization curves, EIS Spectra and XPS analysis.

Brass is one of the important non-ferrous alloys used in industries due to its comparative cheapness, long life and remarkable physical and mechanical properties. Copper based alloys are resistant to alkaline solutions over a wide range of conditions but may be appreciably attacked by strong solutions [103-105]. Patel et al. [106] have studied the influence of benzimidazoles on the corrosion of 63/37 brass in NaOH solution. Vakil and Oza [107] have studied the influence of halides on the corrosion behaviour of 70/30 brass in 3.5% NaCl solution. It is found that iodide is least effective as an inhibitor whereas fluoride and bromide can influence the corrosion reactions. Notoya and Poling [80] have made use of four different types of zinc complexing agents with benzotriazole for 70/30, and 60/40 brass in aerated 3.5% NaCl solutions. It is found that the combination of benzotriazole and dimercapto thiadiazole is more effective for both types of brasses, except for 70/30 brass in acidic NaCl solution [108]. A derivative of thioglycolic acid in combination with benzotriazole is found to be more effective as a corrosion inhibitor for brasses [109-110]. Effect of chloro, dichloro, trichloro, bromo and iodo acetic acid on the corrosion of brass in dilute nitric acid has been studied by Dinnappa and Mayanna [111] using weight loss and polarization technique. It is found that haloacetic acids are effective corrosion inhibitors in acidic medium. Gadiyar et al. [112] have studied the inhibitive performance of 3-methyl-4-amino-5-mercapto-1,2,4 triazole for copper and α-brass in marine environments. Pushpa Gupta et al. [113] have studied the influence of mixed inhibitors such as malachite green, congo red, crystal violet, alizarin and methyl orange along with benzotriazole on the inhibition of corrosion of 63/37 brass in sulphuric acid by weight loss and polarization studies. It is found that with the combination of benzotriazole with other organic compounds provide better protection for the corrosion and dezincification of 63/37 brass in H_2SO_4 solution. Aymen Hussain and Gurmeet Singh [114] have studied the inhibitive action of dimethyl acrylamide on the corrosion of α-brass in acetic acid solutions by galvnostatic polarization and XPS measurements in the temperature range of 15 to 50°C. The compound is found to be a very good inhibitor. The effect of addition of aluminium on brass on the corrosion behaviour of α-brasses has been studied by Beccaria et al. [115,116] by weight loss measurements, atomic absorption spectrometry and X-ray diffractometry. the retarding effect of some benzaldehyde derivatives on the dissolution of brass alloy in nitric acid

Abduelwafa [117] by thermometric method. It has been found that all the compounds act as inhibitors and o-OH and o-CH_3 derivatives have the highest inhibiting effect. The inhibition of corrosion of α-brass (67/33) in acid chloride solutions by 3-amino 5-heptyl-1-2-4 triazole (AHT) was evaluated by weight loss, polarization and capacitance measurements [118]. Alsuhybani et al. [119] have studied the corrosion behaviour of brass in nitric acid solutions in presence of different inorganic anions. It is found that nitrate ion accelerates the corrosion at low acid concentrations and Inhibits corrosion at high acid concentrations. Oza et al. [120] have evaluated the efficiency of urea and its derivatives as inhibitors for the corrosion of brass in binary acid mixture of nitric and hydrofluoric acids by thermometric technique and conventional weight loss method. It is found that urea and its derivatives are considerably very effective inhibitors. Dacosta et al. [121] have investigated the electrodissolution of brass in 1M HCl using rotating ring disc electrode. They have also studied the effect of benzotriazole on the electrodissolution. Shih and Tzou [122] have studied the effect of benzotriazole on stress corrosion cracking and electrochemical polarization of 70/30 brass in fluoride solutions. Torchio [123] has studied the effect of citrate ions on the corrosion inhibition and stress corrosion cracking of aluminium brass in acetic sulphate solutions. Citrate is found to be inhibitive at high concentrations. Beg et al. [124] have studied the inhibitive action of benzimidazole and its derivatives on the corrosion and dezincification of 70/30 brass in ammonia by weight loss method, galvanostatic poalrization technique and solution analysis.

Syed et al. [125] have studied the inhibitive effects of benzotriazole on the stress corrosion cracking of α-brass in nitrate solutions.

Some triaryl and trialkyl phosphites were investigated as corrosion inhibitors for Cu in HNO_3 solutions [126]. The values of inhibitor efficiency from weight loss measurements were in agreement with those obtained from polarization studies. The potential and polarization data indicate that the action of all compounds used are a mixed type, since they hinder both anodic and cathodic reactions. The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm. The effect of temperature on the rate of corrosion with and without inhibitors was also determined. Some thermodynamic functions were also computed.

A study has been made to investigate the effect of some azoheterocyclic dyes of the type 3-arylazo 1,2,4-triazole (AT) on the corrosion of copper exposed to 0.5M nitric acid solution at different temperatures and at different AT concentrations [127]. Using Potentiodynamic polarization and Tafel electrochemical methods, it can be shown that AT compounds are good inhibitors of copper corrosion in HNO_3 solution. the kinetic and thermodynamic parameters of the inhibited system were determined. The high inhibition efficiency of these compounds may be due to the adsorption of the additive itself and/or the adsorption of the formed Cu(II)-AT complexes at the polarized electrode interface. Cathodic polarization measurements showed that AT dyes are predominantly cationic inhibitors.

In this work Fast Green, $C_{37}H_{34}N_2Na_2O_{10}S_3$, was used during the study of copper corrosion in a hydrochloric acid solution [128]. The parameters studied were aerated and de-aerated solutions with nitrogen, temperature of the electrolyte (from 298 to 328 K), and content of Fast Green inhibitor ($1x10^{-3}$ to $5x10^{-3}$M). The hydrochloric acid concentration was 0.1N. The duration of the experiments was 3 h. Two electrochemical techniques were used, electrochemical impedance spectroscopy (EIS), and polarization curves. Weight loss measurements were also recorded. Results for the inhibited solution indicated that the corrosion rate decreased as the temperature increased, this is particularly evident at the two highest temperatures tested. EIS results show two time consists in the presence of inhibitor. Weight loss results agree with the electrochemical data.

The efficiency of two newly developed organic compounds of the triazoles type namely: bis [4-amin-5-hydroxy-1,2,4-triazol-3-yll methane "compound D_1" and bis [4-amino-5-hydroxy-1,2,4-triazol-3-yll butane "compound D_2" as corrosion inhibitors for copper in 4.0M HNO_3 solutions at 25°C was investigated using both weight loss and galvanostatic polarization techniques [129]. The results showed that the predominant action of the inhibitors was cathodic. The two inhibitors proved to be effective (>99%) with long term effectiveness. Galvanostatic polarization measurements confirm weight loss measurements.

The inhibition of copper corrosion in aerated 0.5M sulfuric acid (30°C) by 1-[(1`,2`-dicarboxy)ethyl]benzotriazole (BTM) was assessed by Potentiodynamic and surface enhanced Raman scattering (SERS) techniques [130]. The inhibition efficiency increased with increasing BTM concentration to maximum (52%) at the 1 $x10^{-3}M$ level. Benzotriazole (BTAH) is -20% more efficient as an inhibitor for copper corrosion under the same conditions. BTM ($1x10^{-3}M$) showed increased inhibition with increasing pH reaching maximum value of 78.3% at pH = 8. Polarization studies showed that BTM suppressed both the cathodic and anodic corrosion reactions. The SERS studies suggest that, like BTAH, BTM inhibits copper corrosion by adsorption through the azole nitrogen. Also mixtures of BTM and potassium iodide are very efficient in protecting copper in acid solutions down to pH = 3. The synergistic effect of iodide was explained by the adsorption of iodide ions on the copper surface followed by an over layer of protonated BTM molecules to form a more compact and corrosion resisting polymeric Cu-I-BTM complex. Addition of KI caused a deterioration in the quality of the SERS spectrum and this supports the initial adsorption of iodide ions on the metal.

The effect of benzimidazole (BZ) and substituted benzimidazoles, viz., 2-amino-benzimidazole (2-ABZ) and 2-hydroxy-benzimidazole (2-HBZ) on the corrosion of composition 70/30 brass in 0.5N nitric acid has been investigated as functions of acid concentration, inhibitor concentration and temperature using weight loss and polarization techniques [131]. The additives increased both anodic and cathodic polarization and the latter process is predominant. The energy of activation (E_a) and thermodynamic parameters (ΔG, ΔH and ΔS) for adsorption revealed that the inhibition occurred by blocking the reaction

The efficiency of imidazole and its derivatives (4-methylimidazole, 4-methyl-5-hydroxyimidazole, 1-phenyl-4-methylimidazole 1-[p-tolyl]-4-methylimidazole) for corrosion inhibition of Cu in 0.5M HCl was investigated [134]. Corrosion inhibition was studied using impedance spectroscopy and potentiodynamic methods. Polarization resistances calculated from the AC impedance measurements were in good agreement with those obtained from DC polarization measurements. Copper specimens also were analyzed by SEM and X-ray microanalysis. These studies showed that 1-(p-tolyl)-4-methylimidazole had the best inhibitory efficiency.

The homologous series of aromatic secondary amines with various substituents have been investigated [135]. The results of the electrochemical and gravimetric measurements on copper in hydrochloric and sulfuric acid have shown that the nonsubstituted secondary amine (N-(2-furfuryl)-p-toluidine) has the least-effective inhibiting properties. The introduction of substituents (-Cl, -Br, $-NO_2$, $-CH_3$) in the 5-position of N-(2-furfuryl-p-toluidine) increased the degree of copper protection in acid media. The comparison of results obtained in hydrochloric acid with those related to sulfuric acid point to the activity of electrolyte anions.

The inhibitive efficiency of imidazole and its derivatives 4-methylimidazole, 4-methyl-5-hydroxymethylimidazole, 1-phenyl-4-methylimidazole, and 1-(p-tolyl)-4-methylimidazole of copper in 0.5M hydrochloric acid [136]. Corrosion inhibition was studied using Potentiodynamic methods. 1-(p-Tolyl)-4-methylimidazole has the best inhibitory efficiency. Activation energies were obtained by measuring the temperature dependence of the corrosion current. The activation energies in the presence of the various inhibitors are low (3-5 kJ/mol), with the best inhibitor showing the highest value. The adsorptive behaviour of the imidazole derivatives on the copper electrode surface follows a Freundlich-type isotherm. The studied free energies of adsorption are also low (14-16 KJ/mol), indicating that imidazole and its derivatives physical adsorbed on the copper surface. Possible mechanisms of corrosion inhibition for these molecules are discussed.

A synergistic effect exists when BTAH and iodide ions are used together to prevent the corrosion of Cu in H_2SO_4 [137]. The nature of this effect was studied systematically by using electrochemical techniques and XPS. The synergistic effect is due to the formation of a film of Cu(IBTA) complex and is probably polymeric. This new complex film greatly depresses Cu dissolution

The inhibitive action of α-brass in 1N acetic acid solution in presence of dimethyl acrylamide was studied by galvanostatic polarization and XPS measurements at 15-150°C [138]. The electrochemical results showed that the additive is cathodic predominate inhibitor and inhibition efficiencies up to 90% can be obtained at 0.1M concentration of the additives. The inhibition efficiency decreases as the temperature increases and concentration decreases. XPS measurements showed the adsorption of the additive through the lone pair of electron of the nitrogen atom. The surface morphology was studied by SEM.

Benzotriazole, thiourea, and potassium ethylxanthate behave as Cu corrosion inhibitors under certain conditions [139]. These chemicals were investigated to establish whether they provide synergistic effects. Cu corrosion inhibition was followed through changes in the electrochemical characteristics. Cu specimens were tested at 25°C in 0.1M NaCl and 1M $NaClO_4$ by using the linear potential sweep technique at 0.001 V/s and by SEM of Cu specimens subjected to potentiodynamic and potentiostatic routines. Comparative behaviour of the different substances for Cu was presented in the $6.6 \leq pH \leq 11$ range. For the ethylxanthate – benzotriazone mixtures, synergistic inhibition effects were found in 0.1M NaCl pH 7-11. The apparent synergistic inhibition was explained tentatively by an increase in the compactness of the polymer-like passivating layer, which formed in the presence of benzotriazone and Cl^- ions.

The action of BTA on the corrosion behaviour of Cu and on the formation of protective films on electrode surface in acetate buffer solution pH 5.8 were studied using cyclic voltammetry, photopolarization and impedance spectroscopy [140]. The Cu-electrode surface in the absence and presence of benzotriazole (BTA) was covered with the film of a double layer structure. An inner barrier film grown on the Cu-substrate has an outer porous film of corrosion, products. Photopolarization measurement performed in situ revealed nonstoichiometric structure of inner Cu_2O layer related to the characteristic of a thin semiconducting film of p-type. In the presence of BTA, stoichiometric structure of an inner layer corresponds to the formation of a polymeric complex of Cu(I) BTA on the metal surface. Cyclic voltammetry and impedance spectroscopy measurements confirmed these results. High values of the Gibbs adsorption energy $\Delta G_{ads.} = -36.67$ KJ mol^{-1}, calculated from anodic c.d., pointed out a strong inhibiting effect of BTA on the charge transfer kinetics.

Normally oxide layers are formed on metal surfaces which can passivate them to prevent reaction with their environment [141]. In acid solutions most of these oxide films are not stable. Thus a protection scheme must be used in order to slow or stop corrosion. Application of inhibitors is one possibility to reduce the metal surface corrosion. The aim of this work was to investigate the surface properties of copper in 0.1M sodium sulfate (at pH 2.95 and room temperature) with and without the addition of aromatic sulfoxides as corrosion inhibitors. The aromatic sulfoxides investigated were: Dibenzyl-sulfoxide (DBSO), Diphenylsulfoxide (DPSO) and Di-p-tolylsulfoxide (DPTSO). The application of the electrochemical quartz crystal microbalance technique (EQCMB) allows us to determine and monitor the corrosion rate and observe the chemical adsorption behaviour of the inhibitor on the copper surface. Differences in the inhibitor adsorption or copper dissolution velocity, copper surface potential and the film thickness were also monitored simultaneously. This method revealed that the addition of the above mentioned sulfoxides lowered the velocity at which the copper surface was dissolving into the solution. Adsorption of the inhibitor on the electrode surface modified the surface potential to more stable values. In order to get more precise information about the influence of these chemicals on copper corrosion polarization measurements were carried out. Potentiostatic polarization results concerning the effectiveness of the adsorbed inhibitor film were consistent with the results obtained from the EQCMB measurements. Deviations from Tafel behaviour were observed both in the anodic and cathodic regions.

The corrosion behaviour of brass 70 Cu/30 Zn in deaerated solutions of pure dilute HCl and acidified 4% NaCl of pH 1.8-2 was studied at different temperatures between 25 and 60°C by the weight loss method [142]. The curves representing the variation of loss in weight with time indicate that there is an induction period followed by a linear relation. Analysis of the solution by atomic absorption technique and investigation of the surface by SEM indicate that the linear relation begins at a critical value of copper-ion concentration of the corrodent due to autocatalysis. The addition of different concentrations of $CuCl_2$ eliminates the induction period and increases the corrosion rate. The effect of the addition of different concentrations of 2-methyl benzimidazole (MBIA) and Armohib 28 inhibitors on the dissolution of the alloy in both media was tested at 60°C. MBIA has no effects in the case of acidified 4% NaCl, but with pure dilute HCl the inhibition efficiency in the presence of 300 ppm MBIA amounted to 84.6%. The inhibition efficiency reached 93.4% and 94.6% in the presence of 10 ppm Armohib 28 inhibitor in pure dilute HCl and acidified 4% NaCl, respectively

A review with 53 reference of different approaches trying to explain the mechanism of action of copper corrosion inhibitors, mainly azole derivatives [143]. The copper/benzotriazole system is one for which the contribution of the surface oxide layer has been deeply examined in relation with the effect of the inhibitor. The mechanisms seem to be relatively well resolved when the inhibiting molecule reacts on a clean surface, i.e. in the case of a Cu/Cu_2O system. They are much more complicated if the molecule has to react in realistic practical conditions, i.e. for Cu/Cu_2O/corrosive layer systems.

Ethoxylated fatty acids from soybean oils having the general formula $R\text{-}COO(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$, where R is mainly a mixture of $C_{17}H_{29}$, $C_{17}H_3$ and $C_{17}H_{33}$ and (n) is the number of ethylene oxide per mol (n = 10, 16, and 30) have been used as corrosion inhibitors for copper in 2M HNO_3 [144]. The inhibition efficiency of these compounds as determined from weight loss and polarization measurements increases with their concentration up to a critical value. At higher additives concentrations the inhibition efficiency starts to decrease. A behaviour which could be attributed to a steric hindrance effect produced by accumulation of the inhibitor molecules on the metal surface which results in a loosely attached layer that stimulate corrosion rather than inhibition. In presence of one and the same inhibitor concentration, the surface coverage increases with increasing the number (n) of ethylene oxide. Inhibition of Cu corrosion by these compounds is assumed to take place via a blocking adsorption mechanism, i.e. they inhibit both the cathodic and anodic reactions. That this is actually the case is supported from comparison of both the protection efficiency of the corrosion reaction, $P_{i_{corr.}}$ and the protection efficiency of the cathodic reaction, $[P_{i_o} / P_{i_{corr.}} - 1]$.

The anodic polarization behaviour of copper in 1M NaI at -24° was compared with calculations. based on thermodynamic equilibrium. and is consistent with the potential –pH diagram for the $Cu\text{-}I^-\text{-}H_2O$ system [145]. An active region was predicted and observed where cuprous complexes, CuI_2- complexes are formed. The active region exhibited a Tafel slope of 60 mV, similar to that observed in 1M NaCl where $CuCl_2$- complexes are present. The active region occurred at less noble potentials in 1M NaI than in 1M NaCl and was consistent with an anodic dissolution model based on mass-transport control of the cuprous complexes. Polarization studies were conducted on copper in the presence of two related inhibitors, benzotriazole and tolytriazole. The inhibitors behaved in a similar manner to each other in 1M NaI and 1M NaCl and promoted passivation. Inhibitor-induced passivation commenced in the active region on oxide-free surfaces. The shape of the passive polarization curve in 1M NaI differed from 1M NaCl, suggesting structural differences between the inhibitor films in the two solutions. Possible differences are discussed in terms of the presence of copper oxides in the film, together with an assessment of the critical step in the initiation of passivation.

The studies the use of 5% (wt) citric acid without inhibitor, inhibited with benzotriazole (BTA) and 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) and deaerated with nitrogen in the cleaning of 18th and 18th century chalcog. plates. dc and ac electrochemical techniques have been used to characterize the effect of the inhibitors and to quantify the aggressiveness of the cleaning treatment [146]. Citric acid removes copper surface tarnish. BTA and AMT inhibitors are similarly efficient.

De-aeration reduces corrosion to levels similar to those obtained with inhibitors.

The corrosion behaviour of copper with various organic inhibitors in aerated solutions. at pH 1 to pH 2 was studied using a potentiostat [147]. The inhibitors studied included benzotriazole (BTAH), hydroxyl benzopehnoximes, 1-hydroxy-5-nonylacetophenone oxime, and sodium acetyl hydroxamate (SOH). BTAH was the most effective of the inhibitors tested. Morphol. of the copper substrate after corrosion in the presence and absence of BTAH was examined using SEM. Fourier transform IR spectroscopy (FTIR) was used to identify the spectra of the adsorbed complexes (BTA). The surface film was identified as a polymeric Cu(I)-BTA complex that totally covered the copper surface, exhibiting strong corrosion inhibition. The formation of Cu(I)-BTA was found to were accomplished after the adsorption of BTAH on the copper surface. The effect of annealing of copper plate on the rate of corrosion also was investigated, and results indicated that the annealed copper exhibited better corrosion resistance than copper plate that had not been annealed.

The corrosion behaviour of a copper electrode in a 1M HCl solution was studied potentiokinetically at different temperatures ranging from 25 to 55°C [148]. The inhibition efficiency of four amino acids was then tested for three concentrations in the range 10^{-5}-10^{-3}M. The amino acids, in the presence of HCl solution, caused a shift, mainly in the anodic direction of the corrosion potential at low current densities as well as the linear part of the cathodic Tafel line. The protection efficiency of each amino acid was calculated for different temperatures and concentrations. The amino acids act as a corrosion inhibitor in HCl solution through adsorption on the copper surface. The kinetic results, operating through a compensation effect, could well account for the variation of the inhibiting capacities of the various amino acids. The results reported in this paper elucidate the effect of temperature and the molecule structure on the inhibition efficiency. α-alanine was the most efficient of the four amino acids for inhibiting the corrosion of copper in HCl solution. Thermodynamic parameters for adsorption of the amino acids are calculated

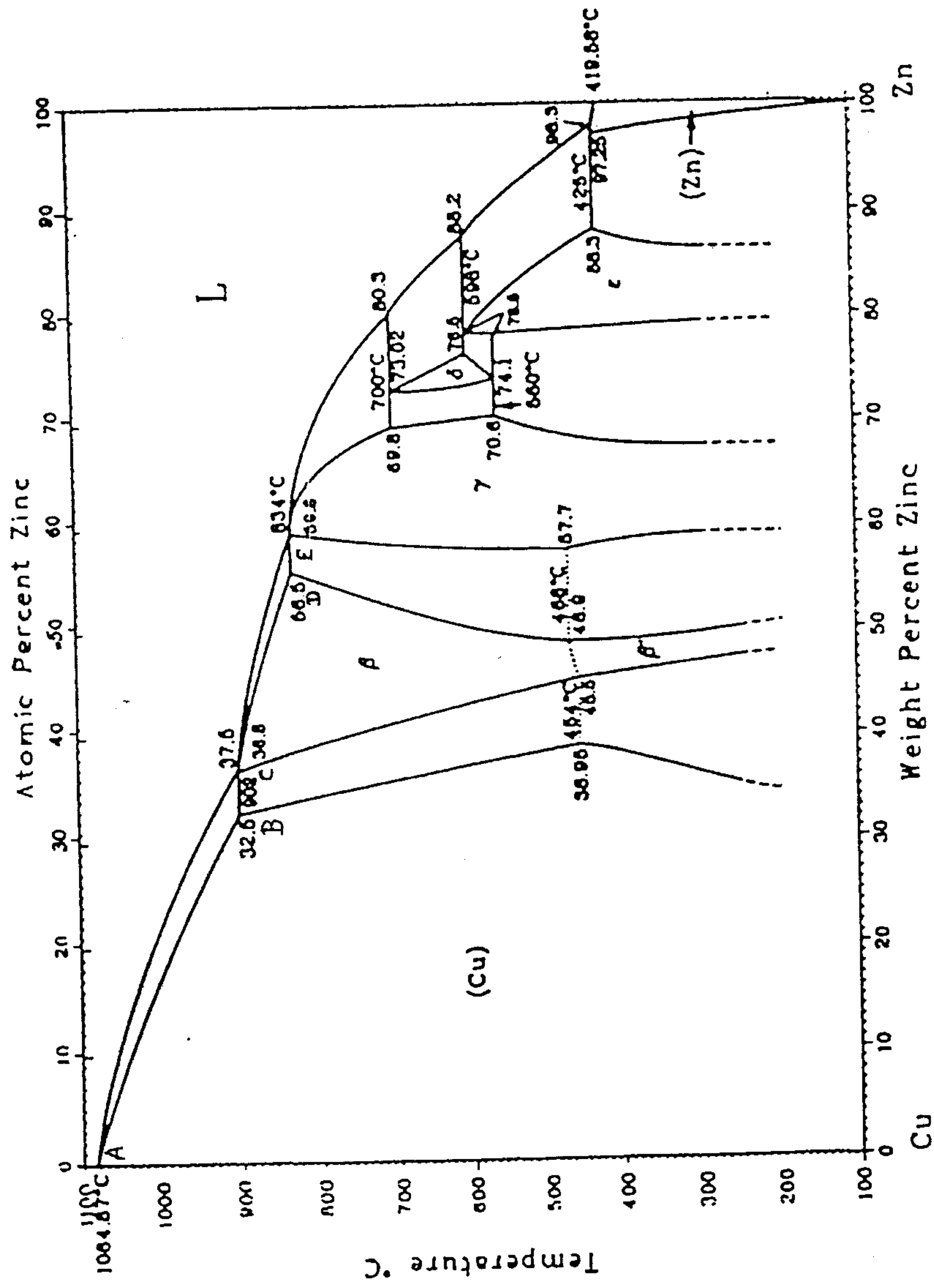


FIG.1.1.Binary Alloy Phase Diagram of Cu-Zn

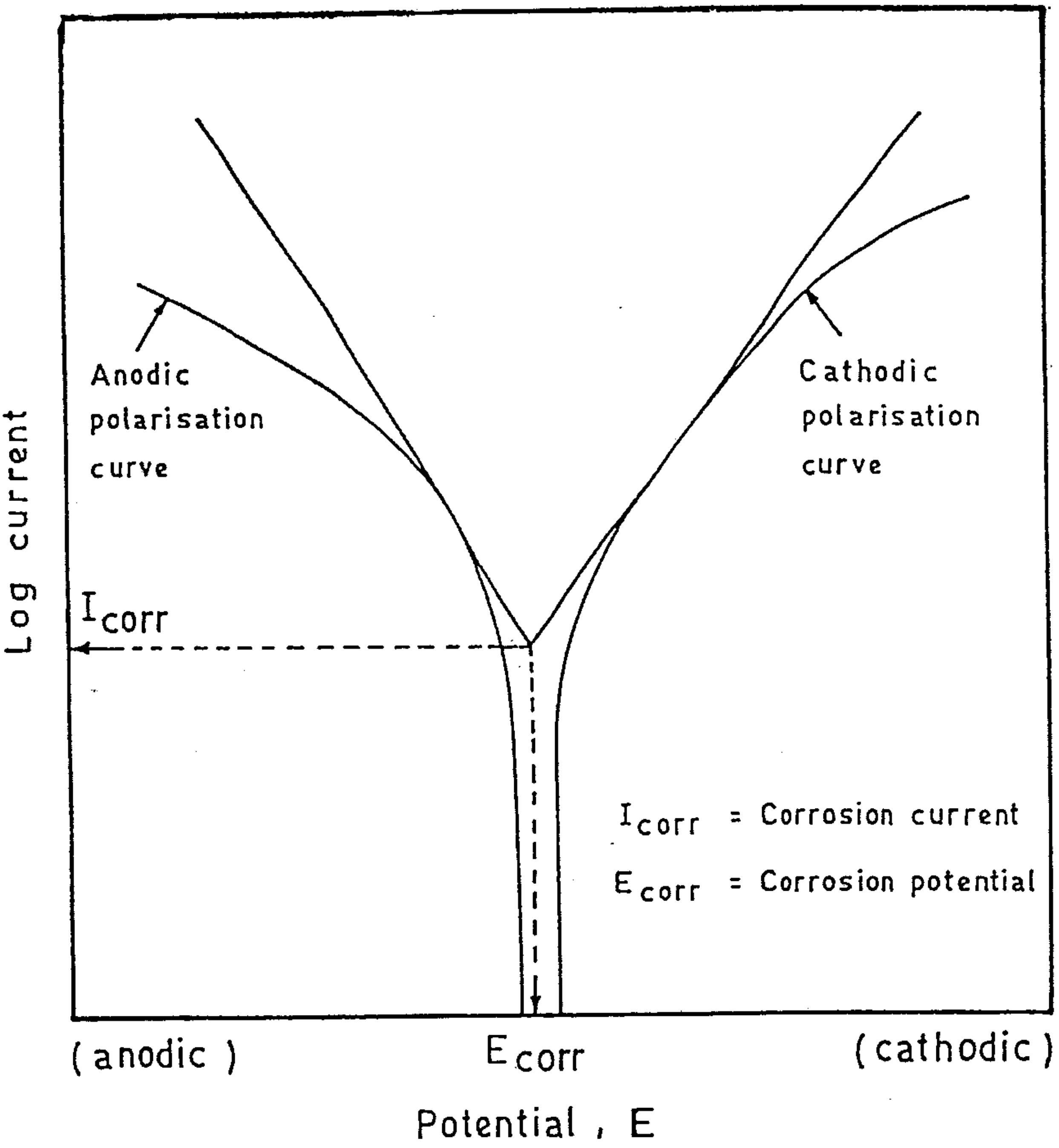
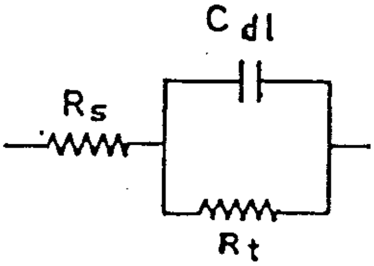


Fig. (1.2) : Polarisation diagram



R_s = Solution resistance

C_{dl} = Electrochemical double layer capacitance

R_t = Charge transfer resistance

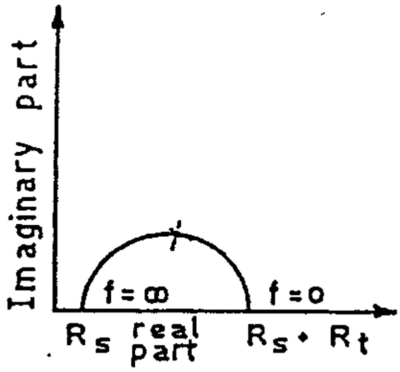


Fig.(1.3): Schematic representation of interface impedance.