

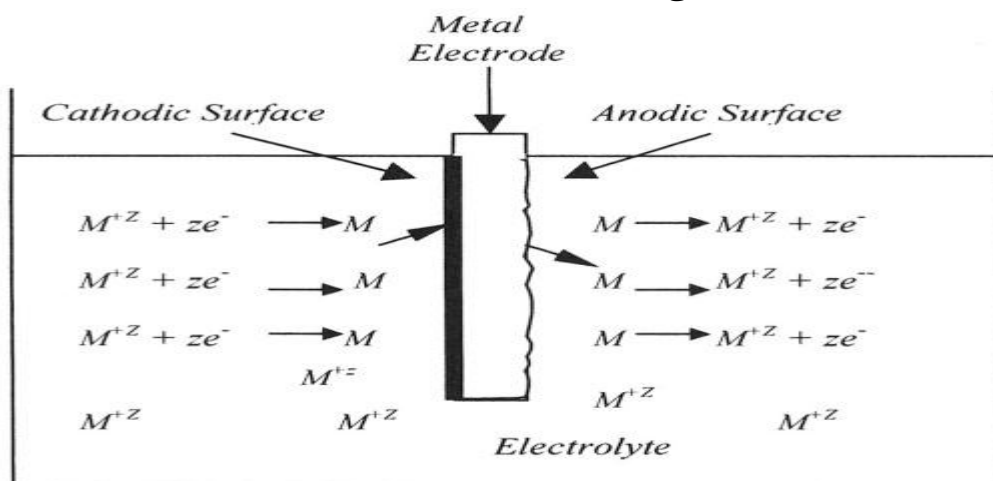
# CHAPTER (1)

# INTRODUCTION

# Introduction

## 1.1- Definition of Corrosion

Corrosion can be defined as the deterioration of a material's properties due to its interaction with its environment. Deterioration by physical causes is not called corrosion, but is described as erosion, galling, or wear. Corrosion is a chemical or electrochemical oxidation process in which the metal transfers electrons to the environment and undergoes a valence change from zero to a positive value. The environment may be a liquid, gas or hybrid soil-liquid. These environments are called electrolytes since they have their own conductivity for electron transfer. An electrolyte is analogous to a conductive solution, which contains positively and negatively charged ions called cations and anions, respectively. An ion is an atom that has lost or gained one or more outer electron (s) and carries an electrical charge. Thus, the corrosion process which can be chemical in nature or electrochemical due to a current flow requires at least two reactions that must occur in a particular corrosive environment. These reactions are classified as anodic and cathodic reactions and are defined below for a metal (M) immersed in corrosive solution as an example. Hence, metal oxidation occurs through an anodic reaction and reduction is through a cathodic reaction.



## **1.2- Cost of Corrosion**

Corrosion is not only dangerous, but also costly, with annual damages in the billions of dollars! If this is difficult to believe, consider some of the direct and indirect effects of corrosion which contribute to these costs:

- 1- Replacement of corroded equipment.
- 2- Unscheduled plant shutdowns for replacement.
- 3- Process upsets resulting from corrosion.
- 4- Product contamination.
- 5- Product loss from a vessel that has corroded.
- 6- Otherwise unnecessary preventive maintenance.
- 7- Over design to allow for corrosion.
- 8- Inability to use otherwise desirable materials.

While the economic costs are frightening, we must consider them to be of secondary importance to the potential loss of life and damage to the environment problems, which can have widespread effects upon modern industrial business. It is essential, therefore, for operators of industrial process plants to have a program for controlling corrosion.

## **1.3- Basic Causes of Corrosion**

### **1.3.1- Conditions necessary for corrosion**

For the purpose of this manual, electrochemical corrosion is the most important classification of corrosion. Four conditions must exist before electrochemical corrosion can proceed:

- 1- There must be something that corrodes (the metal anode).
- 2- There must be a cathode.
- 3- There must be continuous conductive liquid path (electrolyte, usually condensate and salt or other contaminations).
- 4- There must be a conductor to carry the flow of electrons from the anode to the cathode. This conductor is usually in the form of metal-to-metal contact such as in bolted or riveted joints.

The elimination of any one of the four conditions will stop corrosion.

### **1.3.2- Effect of material selection**

One of the fundamental factors in corrosion is the nature of the material.

Materials are usually selected primarily for structural efficiency, and corrosion resistance is often a secondary consideration in design.

### **1.3.3- Water intrusion**

Water intrusion is the principal cause of corrosion problems encountered in the field use of equipment. Water can enter an enclosure by free entry, capillary action, or condensation. With these three modes of water entry acting and with the subsequent confinement of water, it is almost certain that any enclosure will be susceptible to water intrusion.

### **1.3.4- Environmental factors**

At normal atmospheric temperatures the moisture in the air is enough to start corrosive action. Oxygen is essential for corrosion to occur in water at ambient temperatures. Other factors that affect the tendency of a metal to corrode are:

- 1- Acidity or alkalinity of the conductive medium (pH factor).
- 2- Stability of the corrosion products.
- 3- Biological organisms (particularly an aerobic bacteria).
- 4- Variation in composition of the corrosive medium.
- 5- Temperature.

The corrosion problem at KSCN is complex. The presence of salts and acids on metal surfaces greatly increases the electrical conductivity of any moisture present and accelerates corrosion. Moisture tends to collect on dirt particles.

### **1.4.1- Electrochemical theory of corrosion.**

Electrochemistry is a branch of chemistry dealing with relationships between electricity and chemical reactions. It involves oxidation and reduction (redox) reactions. Corrosion is an example of a type of electrochemical reaction, since a substance (oxidizing agent) oxidizes a metal in its environment. In the natural environment, oxygen gas is a good oxidizing agent.

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## *Introduction*

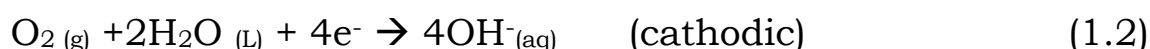
Most metals have lower reduction potentials than  $O_2$ ; therefore they are easily oxidized in the presence of oxygen. Metals such as gold, silver and platinum are not so easily oxidized and are sometimes referred to as noble metals. The reasons for the lack of oxidation in these noble metals are varied and sometimes complex.

One of the most familiar corrosion processes is the oxidation of iron (rusting). Iron metal is spontaneously oxidized in the presence of  $O_2$  and an aqueous electrolyte solution. Physical strains (scratches, dents, bends, etc...) present on the iron are more easily oxidized than other areas. This directly relates to physics, i.e., the way electric fields are generated at the surface of the metal. Stronger fields are generated at the physically strained parts of the metal. The result is that these regions are anodic (oxidation occurs) and simultaneously different areas are cathodic regions at which a reduction reaction (usually of  $O_2$ ) occurs.

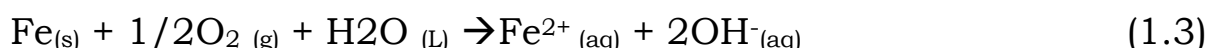
The iron atom gives up two electrons to form the  $Fe^{2+}$  ion:



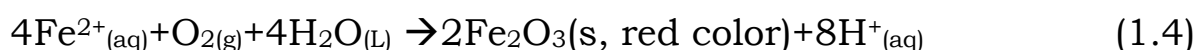
The electrons that are released flow through the iron metal to the cathodic region where they react with oxygen:



These two half reactions together give the overall reaction:



Common experience with this process (e.g., car fenders) tends to show that  $Fe^{2+}$  is eventually oxidized further to  $Fe^{3+}$ , in the compound iron (III) oxide (rust):

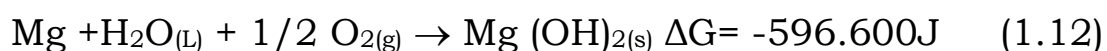


In the experimental setup, this last reaction does not occur. The  $Fe^{2+}_{(aq)}$  reacts with  $[Fe(CN)_6]^{3-}$  in the gel, forming  $Fe[Fe(CN)_6]^-$ ,

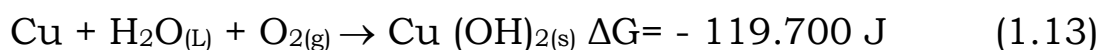
which is a vivid blue colour. The gel you use contains phenolphthalein, an indicator that is pink in basic solutions. Since the reduction of  $O_2$  results in a basic solution, one will observe a pink colour at the cathodic region. Thus, phenolphthalein and  $[Fe(CN)_6]^{3-}$  are used to show where the cathodic and anodic regions are. Further complications arise if we have a system where two different metals are in contact with each other, both in the electrolyte solution. Consider iron metal in contact with another metal. When this situation is encountered, electric fields are set up due to the difference in the reduction potential of the two metals. These fields are stronger than any effect caused by physical strains. Thus, one metal will act entirely as the anode, while the other becomes the cathode. One can use standard reduction potentials to determine which metal will act as the anode/cathode. When considering a bimetallic system, the metal with the more positive reduction potential will be reduced (cathode) and the metal with the more negative reduction potential will be oxidized (anode). For example, if copper and zinc were connected electrically and immersed in an electrolyte solution, we might expect that the copper would be the cathode and the zinc the anode, based on their relative reduction potentials.

### **1.5- Change of Gibbs Free Energy and Corrosion Tendency.**

The tendency for any chemical reaction to go, including the reaction of a metal with its environment, is measured by the Gibbs free-energy change,  $\Delta G$ . The more negative the value of  $\Delta G$ , the greater the tendency for the reaction to go. For example, consider the following reaction at  $25^\circ C$ :



The large negative value of  $\Delta G^\circ$  (reactants and products in standard states) indicates a pronounced tendency for magnesium to react with water and oxygen. On the other hand, we have



The reaction tendency is less or we can say that the corrosion tendency of copper in aerated water is not as pronounced as that of magnesium. Finally, we have the free energy is positive, indicating that the reaction has no tendency to go at all. Gold, correspondingly, does not corrode in aqueous media to form  $\text{Au(OH)}_3$ .



It should be emphasized that the tendency to corrode is not a measure of reaction rate. A large negative  $\Delta G$  may or may not be accompanied by a high corrosion rate, but, when  $\Delta G$  is positive, it can be stated with certainty that the reaction will not go at all under the particular conditions described. If  $\Delta G$  is negative, the reaction rate may be rapid or slow, depending on various factors.

## **1.6- Corrosion Inhibitors.**

### **1.6.1- Corrosion inhibition in acid solutions**

Acid solutions are widely used in industry, where the most important fields of application are acid pickling, industrial acid cleaning and oil well acidizing. Because of general aggressiveness of acid solutions, the practice of inhibition is commonly used to reduce the corrosive attack on metallic materials.

The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, temperature and velocity of flow, the presence of dissolved organic and/or inorganic substances, and on the type of metallic material exposed to the action of acidic solution.

Most of well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen <sup>(1-8)</sup>.

### **1.6.2- Factors affecting inhibitors action in aggressive acid media**

#### **1.6.2.1- Interaction of the inhibitor with a metal surface.**

Physical (or electrostatic) adsorption and chemisorptions are the principle types of interaction between an organic inhibitor and a metal surface.

### **1.6.2.2-Physical adsorption**

Physical adsorption is the result of electrostatic attractive forces between inhibiting ions or dipoles and the electrically charged surface of the metal. The surface charge of the metal is due to the electric field at the outer Helmholtz plane of the electrical double layer existing at the metal/solution interface. The surface charge can be defined by the potential of the metal  $E_{\text{corr}}$  vs. its zero charge potential (ZPC) ( $E_q=0$ ) <sup>(9)</sup> when the difference  $E_{\text{corr}} - E_q = \phi$  is negative charge, cation adsorption is favored. Adsorption of anions is favored when  $\phi$  become positive. This behaviour is related not only to positively or negatively charged compounds, but also to dipoles whose orientation is determined by the value of the  $\phi$  potential.

According to Antropov <sup>(9)</sup>, at equal value of  $\phi$  for different metals, similar behavior of gives inhibiting species should be expected in the same environment.

In study the adsorption of ions at the metal/solution interface, it was first assumed that ions maintained their total charge during the adsorption. Giving rise in this way to a pure electrostatic bond. Lorenz <sup>(10-12)</sup> suggested that partial charge is present in the adsorption of ions; in this case a certain amount of covalent bond in the adsorption process must be considered. The partial charge concept studied by Shultz and Kappitz <sup>(13)</sup> and others <sup>(14-16)</sup>, they defined electrosorption valency as the coefficient for the potential dependence and charge flow of electrosorption process. The term electrosorption valency was chosen because of its analogy with the electrode reaction valency, which enters into Faraday's law as well as the Nernst equation.

### **1.6.2.3-Chemisorption**

Another type of metal/inhibitor interaction is chemisorption. This process involves charge sharing or charge transfer from the inhibitor molecule to the metal surface in order to form a coordinate type of bond.

The chemisorption process takes place more slowly than electrostatic adsorption and with higher activation energy. It depends on the higher temperature; higher degree of inhibition



should be expected at higher temperature.

Chemisorption is specific for certain metals and is not completely reversible <sup>(15)</sup>. The bonding occurring with electron transfer clearly depends on the nature of the metal and the nature of organic inhibitor. In fact, electron transfer is typical for transition metals having vacant, low-energy electron orbitals.

The structure characteristics of the rest of the molecule influence the electron density on the heteroatom and as a consequence, the strength of the chemisorption bond. Regular and systematic changes in the molecular structure, such as the introduction of substituents in various positions on the aromatic and heterocyclic compounds, may influence the electron density and the ability of compounds to inhibit corrosion.

Relationship between electronic structure and efficiency of various classes of inhibitors has been deduced from quantum mechanical calculations <sup>(17-20)</sup>. In this way, the electron density, the order of the bond along the bond line, the index of free valence and the charge of atoms in the free and adsorbed states have been calculated. Other structure parameters influencing the inhibiting efficiency may be mentioned. Thus, the projected molecular area <sup>(21)</sup>, molecular weight <sup>(22)</sup> of various series of organic compounds has been correlated with variation in inhibiting efficiencies.

#### **1.6.2.4-Interaction between adsorbed inhibitors**

When the coverage of the metal surface by adsorbed inhibitor species, lateral interaction between inhibitor molecules may arise, influencing the inhibition efficiency. Attractive lateral interactions usually give rise to stronger adsorption and higher inhibition efficiency. This effect has been shown in the case of compounds containing long hydrocarbon chains due to attractive Vander Waals forces <sup>(23,24)</sup>. In the presence of ions or molecules containing dipoles, repulsive interaction may occur, weakening the adsorption and diminishing the inhibition efficiency.

#### **1.6.2.5-Interaction of the inhibitor with water molecules**

Due to adsorption process of an inhibitor, water molecules are being removed from the metal surface. During the adsorption process of a molecule the interaction energy between molecule

and water changes as it passes from the dissolved to adsorbed state. This change forms an important part of the free energy of adsorption, i.e., the higher the solvation energy of the adsorbing species, the higher the free energy of adsorption. Increasing the size of the hydrocarbon portion of an organic molecule will increase the solvation energy of an inhibitor leading to decrease the solubility and increasing absorbability <sup>(25)</sup>.

#### **1.6.2.6-Relationship between inhibitor reactivity and efficiency**

The nature of the inhibitor initially present in acid solutions may change with the time and/or the electrode potential as a consequence of reduction reactions, polymerization reactions, or formation of surface products. The inhibition due to the reaction products is usually called secondary inhibition, whereas primary inhibition may be higher or lower than secondary inhibition, depending on the effectiveness of the reaction product <sup>(26)</sup>.

### **1.7- Adsorption Isotherms**

The adsorption isotherms describe the relationship between the coverage ( $\theta$ ) of an interface with adsorbed species and concentration of the species in solution. Various adsorption isotherms have been listed as follow <sup>(27,28)</sup>.

**1.7.1-The Henry isotherm:** It has the following form:

$$\theta = KC \quad (1.15)$$

Where:

K is the adsorption equilibrium constant.

C is the concentration of the adsorbate in the bulk phase in moles / liter.

$\theta$  is the degree of surface coverage.

**1.7.2- The Freundlich isotherm:** It has the following form:

$$\theta = KC^n \quad (1.16)$$

Where:

K and C are defined as in Henry isotherm.

N is a constant where,  $0 < n < 1$ .

**1.7.3-The Langmuir isotherm:** It has the following form:

$$\theta / 1 - \theta = K C \text{ or } C / \theta = 1/K + C \quad (1.17)$$

**1.7.4-The Volmer isotherm:** It has the following form:

$$K C = \theta / 1 - \theta \exp (\theta / 1 - \theta) \quad (1.18)$$

**1.7.5-The Amagat isotherm:** It has the following form:

$$K C^n = \theta / (1 - \theta) \exp (\theta / 1 - \theta) \quad (1.19)$$

which has the same form as the Volmer isotherm but the concentration is raised to the power n where,  $0 < n < 1$ .

**1.7.6-The Frumkin isotherm:** It has the following form:

$$K C = \theta / (1 - \theta) \exp (-2a\theta) \quad (1.20)$$

where:

a is a parameter characterizing the interaction between the adsorbed particles.

$a > 0$ , Attraction while  $a < 0$ , Repulsion.

**1.7.7-The Parsons isotherm:** It has the following form:

$$K C = \theta / (1 - \theta) \exp ((2 - \theta) / (1 - \theta)^2 - 2a\theta) \quad (1.21)$$

**1.7.8-The Temkin isotherm:** It has the following form:

$$\ln K C = a\theta \quad (1.22)$$

where all terms are defined as described above and  $\theta$  varies between  $0.1 < \theta < 0.9$ .

Interpretation of adsorption and performance of organic inhibitors can be evidenced by fitting the data to one of the adsorption isotherms.

## **1.8- Techniques Used for Studying Corrosion**

### **1.8.1- Non-electrochemical methods**

#### **1.8.1.1- Coupon method (weight loss)**

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 <sup>(29)</sup>.

### **1.8.2- Electrochemical methods**

#### **1.8.2.1- Tafel extrapolation method**

This method <sup>(30)</sup> is also described as Tafel plot method or Evans 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 i gives a figure known as polarization diagram. The intercept of anodic and cathodic Tafel lines provides the corrosion current and Tafel slopes (  $\beta_a$  and  $\beta_c$  ). In actual practice, polarization curves are obtained from galvanostatic/potentiostatic or potentiodynamic methods.

#### **1.8.2.2-Polarization resistance method**

Stern and Geary <sup>(31)</sup> have shown that there is a linear relationship between current and potential when  $\eta < 20$  mV and on measuring  $(d\eta / di)_{\eta \rightarrow 0}$  the corrosion current can be obtained from,

$$i_{\text{corr}} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \times \left( \frac{di}{d\eta} \right) \quad (1.23)$$

The above relationship is valid only for activation controlled reactions. Rajagopalan and Rangarajan <sup>(32)</sup> 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<sup>(33)</sup>, Reeve and Bech-Nielsen<sup>(34)</sup>, Oldham and Mansfeld<sup>(35)</sup>, and Periasamy and Krishnaswamy<sup>(36)</sup> have made some improvements in this method. Mansfeld<sup>(37,38)</sup> has developed a computer programme (CORFIT) for the quantitative determination of  $i_{\text{corr}}$  which requires simultaneous determination of both  $R_p$  and  $\beta$ . Various applications and the developments of this technique have been reviewed by Lorenz and Mansfeld<sup>(39)</sup>

### **1.8.2.3- Impedance measurements**

Electrochemical methods based on alternating currents can be used to obtain insights into corrosion mechanisms and to establish the effectiveness of corrosion control methods, such as inhibition and coatings. In an alternating - current circuit, impedance determines the amplitude of current for a given voltage. Impedance is the proportionality factor between voltage and current. In electrochemical impedance spectroscopy (EIS), the response of an electrode to alternating potential signals of varying frequency is interpreted on the basis of circuit models of the electrode/electrolyte interface. Figure.(1.1) shows circuit model that can be used for analyzing EIS spectra. The simplest model for characterizing the metal – solution interface, includes the three essential parameters,  $R_s$  (the solution resistance),  $C_{dl}$  (the capacitance of the double layer), and  $R_p$  (the polarization resistance). When direct - current measurements are carried out (i.e., frequency is zero), the impedance of the capacitor approaches infinity. In parallel electrical circuits, the circuit with the smallest impedance dominates, with the result that, under these conditions, the sum of  $R_s$  and  $R_p$  is measured. If  $R_s$  is significant, the corrosion rate is underestimated. When diffusion control is important, another element,  $Z_D$ , sometimes called the Warburg impedance, is added in series with  $R_p$ . In electrochemical impedance spectroscopy, the impedance of the corroding metal is analyzed as a function of frequency. A sinusoidal potential change is applied to the corroding electrode at a number of frequencies,

$\omega$ . At each frequency, the resulting sinusoidal current waveform is out of phase with the applied potential signal by an amount, the phase angle,  $\theta$ , that depends on the circuit parameters. The current amplitude is inversely proportional to the impedance of the interface. The electrochemical impedance,  $Z(\omega)$ , is the frequency – dependent proportionality factor in the relationship between the voltage signal and the current response,

$$Z(\omega) = \frac{E(\omega)}{I(\omega)}$$

where  $E$  is the voltage signal,  $E = E^0 \sin(\omega t)$ ;  $i$  is the current density,  $i = i^0 \sin(\omega t + \theta)$ ;  $Z$  is the impedance (ohm - cm<sup>2</sup>); and  $t$  is the time (seconds). Impedance is a complex number that is described by the frequency - dependent modulus,  $|Z|$ , and the phase angle,  $\theta$ , or, alternatively, by the real component,  $Z'$ , and the imaginary component,  $Z''$ . The mathematical convention for separating the real and imaginary components is to multiply the magnitude of the imaginary component by  $j$  [ $=\sqrt{-1}$ ] and report the real and imaginary values as a complex number. The equations for electrochemical impedance are

$$\begin{aligned} E &= E_{\text{real}} + E_{\text{imaginary}} = E' + jE'' \\ I &= I_{\text{real}} + I_{\text{imaginary}} = I' + jI'' \\ Z &= Z' + jZ'' = \frac{E' + jE''}{I' + jI''} \end{aligned}$$

$$\tan \theta = \frac{Z''}{Z'}$$

In electrochemical impedance analysis, three different types of plots are commonly used: Nyquist plots (complex plane, showing  $-Z''$  versus  $Z'$ ) and two different types of Bode plots, showing the impedance magnitude versus log frequency and showing phase angle versus log frequency.

$$Z = R_s + R_p$$

At very high frequencies,

$$Z = R_s$$

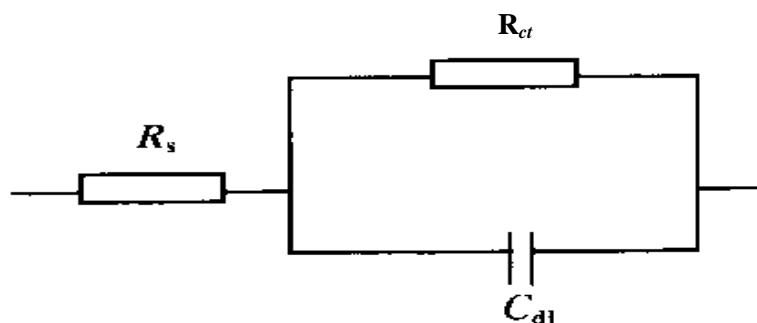


Figure (1.1); Electrical equivalent circuit model used to represent an electrochemical interface undergoing corrosion in the absence of diffusion control.  $R_p$  is the polarization resistance,  $C_{dl}$  is the double layer capacitance,  $R_p$  is the polarization resistance, and  $R_s$  is the solution resistance.

Electrochemical impedance measurements is an appropriate method for corrosion studies, particularly for corrosion rate determinations<sup>(40-59)</sup>. Mechanistic studies<sup>(60-62)</sup> passivation and passivity process<sup>(63-66)</sup> and for investigation in inhibited systems<sup>(67-73)</sup> the theoretical analysis of a.c. impedance measurements has been analyzed by Warburg<sup>(72)</sup>, to explain the frequency dispersion of the electrode-electrolyte interface and impedance in terms of mass transport (diffusion controlled) process. Haruyama and Tsuru<sup>(55)</sup> and Mansfeld et al.<sup>(62-64)</sup> have reviewed impedance methods. A review of the application of these techniques in corrosion studies has been published by MacDonald et al.<sup>(56-61)</sup>. The use of a.c. impedance technique in various cases has been reviewed by Gabrielli<sup>(73)</sup>. The schematic representation of the interface impedance are shown in Fig. 1.1. 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.

$$i_{corr} = \frac{\beta_a \cdot \beta_c}{2.3(\beta_a + \beta_c)} \cdot \frac{1}{R_t} \quad (1.24)$$

### **1.9- Pitting Corrosion**

Pitting corrosion is a complex but important problem that is at the root of many corrosion failures. It has been studied in detail for many years, yet crucial phenomena remain unclear. In pitting corrosion the surface of the metal is attacked in small-localized areas. Organisms in water or breaks in a passive film can initiate corrosion. In pitting corrosion very little metal is removed from the surface but the effect is marked.

In passivity metals or alloys that are exposed to solutions containing aggressive anions, primarily chloride, pitting corrosion results in local dissolution leading to the formation of cavities or (holes). The shape of the pits or cavities can vary from shallow to cylindrical holes and the cavity is approximately hemispherical<sup>(74)</sup>. The pit morphology depends on the metallurgy of the alloy and chemistry of the environment as well as the leading conditions. As observed first by McAdam in 1928, these pits may cause local increase in stress concentration and cracks may nucleate from them.

Pitting corrosion occurs mostly in solutions containing halide or oxyhalides. Chlorides, bromides and hypochlorites are the most aggressive anions<sup>(75)</sup>. Fluoride, iodide and iodine containing anions were thought to be without pitting tendency. However, iodide ions were found to cause pitting corrosion in many cases<sup>(76)</sup>. Solutions of certain oxidizing cations produce the worst pitting attack. Ferric, cupric and mercuric halides are the most aggressive of all pitting reagents. The non-oxidizing metal halides such as Al, Ca and Na cause pitting to a lesser degree.

Electrochemical studies of pitting corrosion have found that there exist characteristic potentials. Stable pits form at potentials noble to the pitting potential, EP, and will grow at potentials noble to the repassivation potential, ER, which is lower than EP.



During upward scanning in a cyclic polarization experiment, a stable pit starts growing at  $E_P$  where the current increases sharply from the passive current level and, upon reversal of the scan direction, repassivates at  $E_R$  where the current drops back. It is generally considered that materials exhibiting higher values of  $E_P$  and  $E_R$  are more resistant to pitting corrosion, and cyclic polarization experiments are commonly used for this purpose.

Pitting is considered to be autocatalytic in nature; once a pit starts to grow, the conditions developed are such that further pit growth is promoted. The anodic and cathodic electrochemical reactions that comprise corrosion separate spatially during pitting. The local pit environment becomes depleted in cathodic reactant (e.g. oxygen), which shifts most of the cathodic reaction to the boldly exposed surface where this reactant is more plentiful. The pit environment becomes enriched in metal cations and an anionic species such as chloride, which electro migrates into the pit to maintain charge neutrality by balancing the charge associated with the cation concentration. The pH in the pit is lower owing to cation hydrolysis and the absence of a local cathodic reaction. The acidic chloride environment thus generated in pits is aggressive to most metals and tends to propagate the pit growth.

### **1.10- Literature Survey on Corrosion of Carbon Steel.**

In the following a concise literature survey on corrosion inhibition of Carbon steel by some related organic compounds in acidic medium.

A new corrosion inhibitor, 3,5-bis(2-thieryl)-4-amino-1,2,4-trizoles (2-TAT) has been synthesized and its inhibiting action on the corrosion of mild steel in acid baths 1M HCl and 0.5M  $H_2SO_4$  has been investigated by various corrosion monitoring techniques<sup>(77)</sup> such as corrosion weight loss tests and electrochemical impedance spectroscopy. The electrochemical study reveals that this compound is an anodic inhibitor changes the impedance parameters  $R_t$  and  $C_{dl}$  are indicative of the

adsorption of (2-TAT) on the metal surface- leading to the formation of a protective film which grows with increasing exposure time (2-TAT) is able to reduce the steel corrosion more effectively in 1M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub>. The adsorption of this inhibitor is also found to obey the Langmuir adsorption isotherm in both acids [(2-TAT) is considered as a non-cytotoxic substance.

The inhibition effect of 3, 6-bis (2-methoxyphenyl)-1, 2-dihydro-1, 2, 4, 5-tetrazine (2- MDHT)<sup>(78)</sup> on the corrosion of mild steel in acidic media has been investigated by weight loss and various electrochemical techniques. Results obtained reveal that this organic compound is a very good inhibitor. 2-MDHT is able to reduce the corrosion of steel more effectively in 1M HCl than in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Potentiodynamic Polarization studies showed that 2-MDHT is a mixed-type inhibitor in 1M HCl and cathodic-type in 0.5M H<sub>2</sub>SO<sub>4</sub>. 2-MDHT acts on the cathodic reaction without changing the mechanism of the hydrogen evolution reaction. Surface analyses were also carried out to establish the mechanism of corrosion inhibition of mild steel in acidic media. The adsorption of this inhibitor on the mild steel surface in both acids obeys the Langmuir adsorption isotherm. The effect of temperature on the corrosion behaviour of mild steel in 1M HCl with addition of 100 mg/L of 2-MDHT was studied in the temperature range 25 - 60°C. The associated activation corrosion and free adsorption energies have been determined.

The influence of thiosemicarbazide<sup>(79)</sup>, phenylthiosemicarbazide Girad's-T and phenylthiosemicarbazide Girard's-P on the corrosion rate of steel in 2M HCl has been studied. The protection efficiency obtained by weight-loss and potentiostatic polarization techniques was found to be in good agreement with adsorption measurements at Pt electrode. The behaviour was correlated to the proposed skeletal representation of the adsorption mode of the inhibitors on the metal surface. Electrochemical results indicated that all the compounds investigated acted as cathodic-type inhibitors. The data obtained

provide a good fit to both the Temkin adsorption isotherm and the kinetic–thermodynamic model recently proposed.

The influence of some organic acid hydrazides, namely salicylic acid hydrazide (SAH), anthranilic acid hydrazide (AAH)<sup>(80)</sup>, benzoic acid hydrazide (BAH) and cinnamic acid hydrazide (CAH) on the corrosion inhibition of mild steel in the presence of 1N HCl was studied. The adsorptions of all the hydrazides on mild steel surface in the acid solution were found to obey Temkin's adsorption isotherm. The values of activation energy and free energy of adsorption of all the hydrazides were also calculated. The potentiodynamic polarization studies indicated that all the hydrazides except SAH are mixed inhibitors.

The influence of cetyl trimethyl ammonium bromide (CTAB) on the corrosion of carbon steel in HCl and H<sub>2</sub>SO<sub>4</sub> solutions has been studied using several techniques such as weight loss<sup>(81)</sup>, Tafel polarization, linear polarization and open circuit potential. Inhibition efficiencies have been obtaining from weight loss measurement; the effect of temperature on corrosion inhibition and the effectiveness of the inhibitor at higher acid strength have been examined. Polarization studies reveal that the inhibitor behaves as an effective inhibitor in H<sub>2</sub>SO<sub>4</sub> as well as in HCl solutions. Measurements of values of polarization resistance ( $R_p$ ) have also been carried out. The open circuit potential curve was shifted to less negative potential contrary to the blank.

The effect of a new class of corrosion inhibitors<sup>(82)</sup>, namely, Arylazobenzoyl acetonitrile derivatives, on the corrosion of carbon steel in 2M HCl and 1M H<sub>2</sub>SO<sub>4</sub> solutions has been studied by electrochemical polarization methods (potentiodynamic, Tafel extrapolation and the determination of polarization resistance). Generally, inhibition efficiency of the investigated compounds was found to increases with increasing concentration. Results obtained from both potentiodynamic and polarization resistance techniques reveal that these compounds are good inhibitors and behave better in 2M HCl than 1M H<sub>2</sub>SO<sub>4</sub>.

The adsorption of the compounds on the carbon steel in both acidic media follows a Langmuir adsorption isotherm.

The influence of some substituted dianils on corrosion of mild steel in 1N hydrochloric acid and 1N sulphuric acid has been studied using weight loss and electrochemical techniques. Among the five compounds studied, 1,4-dicinnamylidene aminophenylene (DCAP) showed the best performance. All of the compounds showed good inhibition efficiency in both the acids<sup>(83)</sup>. Inhibition efficiency of these compounds has been found to vary with nature and concentration of these compounds, solution temperature, immersion time and nature of acid solutions. The adsorption of these compounds on the steel surface from both the acids has been found to obey Temkin's adsorption isotherm. The values of activation energy and free energy of adsorption of all the dianils were calculated to investigate the mechanism of corrosion inhibition. The potentiodynamic polarization studies were carried out at room temperature, according to which all the compounds were found to be mixed type inhibitors and inhibited the corrosion of mild steel by blocking the active sites of the metal.

The effect of N-propyl amino lauryl amide (I) and three of its ethoxylated derivatives (II, III and IV) as corrosion inhibitors of carbon steel in 1M hydrochloric acid solution has been studied by weight loss and galvanostatic polarization techniques. A significant decrease in the corrosion rate of carbon steel was observed in the presence of the investigated inhibitors. The study revealed that, the inhibition efficiency (IE%) increases with increasing the inhibitors concentration<sup>(84)</sup>. All the tackled inhibitors seem to have obeyed the Langmuir adsorption isotherm. The galvanostatic polarization data indicated that, the inhibitors were of mixed type, but the cathodic effect is more pronounced. The slopes of the cathodic and anodic Tafel lines are approximately constant and independent on the inhibitor concentration. The relation between the surface tension of the inhibitor ( $\gamma$ ) and the logarithm of their concentrations ( $\log C$ ) was investigated to obtain the adsorption ability of the inhibitors on

the carbon steel surface. Scanning electron microscopy was used to examine the surface morphology of the carbon steel specimens after immersion in 1M HCl for 6 days in absence and presence of 500ppm of the inhibitor IV. The mechanism of inhibition was discussed in the light of the chemical structure of the undertaken inhibitors.

Potentiodynamic polarization and ac impedance studies were carried out on the inhibition of carbon steel in 0.1 M hydrochloric acid solution by various Schiff bases containing heteroaromatic substituents. The examined Schiff bases were 2-((1E)-aza2-pyrimidine-2-ylvinyl)thiophene, 2-((1Z)-1-aza-2-(2-pyridyl)vinyl)pyrimidine, 2-((1E)-2-aza-2-(1,3-thiazol-2-yl)vinyl)thiophene, 2-((1Z)-1-aza-2-(2-thienyl)vinyl) benzothiazole. Polarization curves indicates that studied Schiff bases act essentially as anodic inhibitor<sup>(85)</sup>. The variation in inhibitive efficiency mainly depends on the type and nature of the substituent's present in the inhibitor molecule. Potentiodynamic polarization and ac impedance measurements carried out at different concentration of studied Schiff bases reveal that these compounds are adsorbed on steel surface and the adsorption obeys Temkin's adsorption isotherm. From the adsorption isotherms values of equilibrium constant,  $K_{ads}$ , values of free energies of adsorption,  $\Delta G^{\circ}_{ads}$ , were calculated. Activation parameters of the corrosion process such as activation energies,  $E_a$ , activation enthalpies,  $H^*$ , and activation entropies,  $S^*$ , were calculated from the obtained corrosion rates at different temperatures.

2,5-Bis(4-dimethylaminophenyl)-1,3,4-oxadiazole (DAPO) and 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole (DAPT) have been synthesized and their inhibiting action on the corrosion of mild steel in 1M HCl and 0.5M  $H_2SO_4$  at 30°C has been investigated by various corrosion monitoring techniques. At constant acid concentration, the inhibitor efficiency of both the compounds is found to increase with inhibitor concentration <sup>(86)</sup>. DAPT is slightly more efficient in 0.5M  $H_2SO_4$  than in 1M HCl

whereas DAPO is more efficient in 1M HCl. Of the two, DAPT appears to be a better inhibitor. Potentiostatic polarization studies show that both are mixed-type inhibitors in 1M HCl but cathodic-type in 0.5M H<sub>2</sub>SO<sub>4</sub>. The inhibitors function through adsorption following Langmuir isotherm in both the acids. The electronic properties of DAPO and DAPT, obtained using the AM1 semi-empirical quantum chemical approach, have been correlated with their experimental inhibition efficiencies using the linear resistance model (LR). These inhibitors are considered as non-cytotoxic substances.

The effect of isomers of 3-pyridyl-substituted 1,2,4- and 1,3,4-thiadiazoles (3-PTHD and 3-PTH) on the corrosion of mild steel in acidic media (1M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub>) has been investigated using weight loss measurements and electrochemical techniques (impedance spectroscopy and polarization curves)<sup>(87)</sup>. A comparison of the results showed that 3-PTHD was the best inhibitor in both media. It is found to behave better in 1 M HCl than in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Polarisation curves indicate that 3-PTH and 3-PTHD are mixed type inhibitors in 1 M HCl, but in 0.5 M H<sub>2</sub>SO<sub>4</sub>, the inhibition mode of these inhibitors depends on the electrode potential and they act essentially as cathodic inhibitors. Adsorption of 3-PTH and 3-PTHD on the mild steel surface in 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> follows the Langmuir isotherm model. Molecular modeling has been conducted to correlate the corrosion inhibition properties with the calculated quantum chemical parameters.

The electrochemical behavior of 1-(2-ethylamino)-2-methylimidazoline (imidazoline), its precursor N-[3-(2-aminoethylamino-ethyl)]-acetamide (amide) and its derivative 1-(2-ethylamino)-2-methylimidazolidine (imidazolidine), is evaluated by using potentiodynamic polarization curves and electrochemical impedance spectroscopy techniques in deaerated acid media to compare their corrosion inhibition efficiency. The experimental results suggest that imidazoline is a good corrosion inhibitor at different concentrations whereas amide shows low efficiency

values; however, the properties of a corrosion inhibitor were not found in imidazolidine. The reactivity of these compounds was analyzed through theoretical calculations based on density functional theory (DFT)<sup>(88)</sup> to explain the different efficiencies of these compounds as corrosion inhibitors both in the neutral and protonated form. The theoretical results indicate that imidazoline is the more efficient corrosion inhibitor because of its two very active sites (two nitrogen atoms) and the plane geometry of the heterocyclic ring, thus promoting coordination with the metal surface.

The inhibition of the corrosion of mild steel in hydrochloric acid solutions by extract of the leaves of *Nypa fruticans* Wurmb<sup>(89)</sup> has been studied using weight loss and hydrogen gas evolution techniques. Inhibition was found to increase with increasing concentration of the leaves extract. A first-order type of mechanism has been deduced from the kinetic treatment of the results and the process of inhibition attributed to physisorption. The inhibition action of *N. fruticans* was compared with that of 1, 5-diphenylcarbazon. The highest inhibition efficiency of 75.11% was observed with *N. fruticans* and 70.18% for DPC at 30°C. The results obtained show that the solution extract of the leaves of *N. fruticans* could serve as an effective inhibitor of the corrosion of mild steel in hydrochloric acid media.

Several new isoxazolidines having varying degree of steric environment and hydrophobic chain length, prepared efficiently using single-step nitron cycloaddition reactions, are tested for corrosion inhibition of mild steel in 1M and 5M HCl at 50–70 °C range by gravimetric and electrochemical methods<sup>(90)</sup>. All compounds have shown very good corrosion inhibition efficiency (IE%) in acidic solution. Steric crowding around the nitrogen centres and hydrophobic chain lengths as well as increase in temperature (in the presence of the inhibitor in the higher concentration range (100–400 ppm) are found to increase the inhibition efficiency of the isoxazolidines. Thermodynamic parameters ( $\Delta G^{\circ}_{\text{ads}}$ ,  $\Delta H_{\text{ads}}$ ,  $\Delta S_{\text{ads}}$ ) for the adsorption process and

kinetic parameters for the metal dissolution (or hydrogen evolution) reaction in the presence of one of the isoxazolidines were determined. Experimental results agree with the Temkin adsorption isotherm. The inhibition of corrosion in 1M HCl, influenced by both physi- and chemisorption, was found to be under mixed control, but predominantly under cathodic control.

A new corrosion inhibitor, namely 2,2-bis(benzimidazole) has been synthesized and its inhibiting action on the corrosion of mild steel in acidic bath (1M HCl) has been investigated by various corrosion monitoring techniques, such as corrosion weight loss test and potentiodynamic polarization<sup>(91)</sup>. The results of the investigation show that these compounds have fairly good inhibiting properties for steel corrosion in hydrochloric acid, and are a mixed inhibitor in (1M HCl). The adsorption of this inhibitor is also found to obey the Langmuir adsorption isotherm.

The inhibition effect of some polyethylene glycols (PEGs) on carbon steel corrosion at 25°C in 0.5N hydrochloric acid as corroding solution was evaluated by weight loss method and polarization and electrochemical impedance spectroscopy techniques. In order to study the effect of polyethylene glycols' structure on the inhibition efficiency, different molecular weights (400, 1000, 4000, and 10,000 g mol<sup>-1</sup>)<sup>(92)</sup> were selected. This work has demonstrated that polyethylene glycols have inhibition effect on corrosion process and their inhibition efficiencies are between 50 and 90%. The inhibition efficiencies are increased by increasing the concentrations of inhibitors and molecular weight.

Corrosion inhibition of steel in hydrochloric acid by decylamides of  $\alpha$ -amino acids derivatives were studied using gravimetric and electrochemical techniques. Protection efficiencies of 90% were obtained with 100 ppm of tyrosine and glycine derivatives, while alanine and valine derivatives reached only 80%. The order of increasing inhibition efficiency was correlated with the modification of the molecular structure of inhibitors<sup>(93)</sup>. Potentiodynamic polarization curves indicated that



both the decylamide of tyrosine and glycine acted primarily as anodic type inhibitors, whereas the decylamide of alanine and valine were of the cathodic type. Thermodynamic parameters and Flory–Huggins adsorption isotherms described the experimental findings. The number of active sites, equilibrium constant, enthalpy and change of free energy were computed for all inhibitors studied. This information suggested that organic molecules were adsorbed and displaced water molecules from the steel surface. X-ray photoelectron spectroscopy confirmed that species of N, C and O interacted with steel to form a continuous protective film.

Some new triazole bolaamphiphiles in the series of 1,n-bis(1,2,4-triazolyl)<sup>(94)</sup> alkane where n=10,12 have been synthesized. The inhibiting action of these compounds towards the corrosion of carbon steel in 1M HCl solution was investigated using gravimetric, potentiodynamic and electrochemical impedance spectroscopy measurements. Polarization data indicate that these compounds act as very good cathodic inhibitors for carbon steel in 1M HCl. The values of the transfer resistance, obtained from impedance plots of carbon steel, increase by increasing product concentration. From all measurements carried out, the variation of the inhibition efficiency versus concentration shows the same trend. The electrochemical study shows that DTC12 is the best inhibitor and its efficiency increases with concentration and the highest value obtained is around 94%.

The inhibition effect of three amino acids against steel corrosion in HCl solutions has been investigated by potentiodynamic polarization method. Corrosion data such as corrosion rate, corrosion potential ( $E_{\text{corr}}$ ) and corrosion resistance ( $R_p$ )<sup>(95)</sup> were determined by extrapolation of the cathodic and anodic Tafel region. Adsorption isotherm was investigated by weight-loss measurement. The used amino acids were alanine, glycine and leucine. The effect of inhibitor concentration and acid concentration against inhibitor action was investigated. The

inhibition efficiency (IE%) depended on the type of amino acid and its concentration. The inhibition effect ranged from 28 to 91%. The amino acids act as a corrosion inhibitor in HCl solution through adsorption on the steel surface and adsorption follows Langmuir isotherm.

1,1,2-bis(1,2,4-triazolyl)dodecane (dTC12) is an excellent corrosion inhibitor for carbon steel in deaerated 1M HCl solution<sup>(96)</sup>. Electrochemical and analytical techniques were used to study the inhibition of corrosion on carbon steel in acidic medium. The carbon steel corrosion inhibition of dTC12 was attributed to the synergistic effect between chloride anion and quaternary ammonium ion. The protective efficiency of the film was higher than 90%, indicating that corrosion of carbon steel in 1M HCl is reduced by dTC12. The effect of dissolved oxygen on the inhibition efficiency was also investigated. The results show that the inhibition efficiency increases in early stage and decreases for a long immersion time.

The effect of some prepared compounds, namely pyridine derivatives on the corrosion of carbon steel in 2M HCl solutions has been studied by electrochemical polarization method<sup>(97)</sup> (potentiodynamic, Tafel extrapolation) as well as weight loss method. Generally, inhibition efficiency of the investigated compounds was found to depend on the concentration and the nature of the inhibitor. Results obtained from both potentiodynamic and weight loss techniques reveal that these compounds are good inhibitors. The presence of substitution in pyridine ring plays an important role in the percentage inhibition of the compounds under investigation. The adsorption of these compounds on the carbon steel follows a Langmuir adsorption isotherm.

A triazole-based cationic gemini surfactant, 3,5-bis(methylene octadecyl dimethyl ammonium chloride)-1, 2, 4-triazole (18-triazole-18) <sup>(98)</sup> has been synthesized, and its effect on corrosion inhibition of A3 steel in 1M HCl has been studied using

the weight-loss method. The result showed that 18-triazole-18 acted as an excellent inhibitor in 1M HCl. It was found that the adsorption mechanism of 18-triazole-18 on the steel surface in acid medium was quite different from that of cationic gemini surfactants containing dimethylene as a spacer, as well as that of conventional cationic single-chained surfactants, which is due to unique molecular structure of 18-triazole-18. 18-Triazole-18 may be adsorbed on the steel surface in acid medium through a maximum of four atoms or groups, i.e., the two nitrogen atoms of triazole ring and two quaternary ammonium head groups. Four regions of surfactant concentration could be divided to illustrate the adsorption of 18-triazole-18 on the steel surface, and four different adsorption mechanisms may take place in different regions of surfactant concentration.

Two new telechelic compounds have been synthesised and tested as inhibitors for the corrosion of steel in 1 M HCl solution <sup>(99)</sup>. Weight loss measurements, potentiodynamic polarisation and impedance spectroscopy (EIS) methods are used. The inhibiting action increases with the concentration of methyl 4-{2-[(2-hydroxyethyl) thio] ethyl} benzoate (T2) and 11-[(2-hydroxyethyl) thio] undecan-1-ol (T3) to attain 92% at  $10^{-3}$ M and 90% at  $10^{-4}$ M, respectively. Good agreement between gravimetric and electrochemical methods (potentiodynamic polarisation and EIS) was observed. Polarisation measurements show also that T2 and T3 act as mixed inhibitors. The cathodic curves indicate that the reduction of proton at the steel surface happens with an activating mechanism. Adsorption of T3 on the steel surface obeys to the Langmuir adsorption model. Effect of temperature studied between 308 and 353 K shows that efficiency remains almost constant.

The effect of succinic acid (SA) on the corrosion inhibition of a low carbon steel (LCS) electrode has been investigated in aerated non-stirred 1M HCl solutions in the pH range (2–8) at 25°C. Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques were

applied to study the metal corrosion behaviour in the absence and presence of different concentrations of SA under the influence of various experimental conditions. Measurements of open circuit potential (OCP) as a function of time till steady-state potentials ( $E_{st}$ ) were also established. Surface analysis using energy dispersive X-ray (EDX) <sup>(100)</sup> and scanning electron microscope (SEM) allowed us to clarify the mechanistic aspects and evaluate the relative inhibition efficiency. Results obtained showed that SA is a good “green” inhibitor for LCS in HCl solutions. The polarization curves showed that SA behaves mainly as an anodic-type inhibitor. EDX and SEM observations of the electrode surface confirmed existence of a protective adsorbed film of the inhibitor on the electrode surface. The inhibition efficiency increases with increase in SA concentration, pH of solution and time of immersion. Maximum inhibition efficiency ( $\approx 97.5\%$ ) is obtained at SA concentrations  $>0.01M$  at  $pH = 8$ . The effect of SA concentration and pH on the potential of zero charge (PZC) of the LCS electrode in 1M HCl solutions has been studied and the mechanism of adsorption is discussed. Results obtained from weight loss, polarization and impedance measurements are in good agreements.

2,3-Quinoxalinedione (QD) was tested as corrosion inhibitor for mild steel in 1M HCl solution using electrochemical (potentiodynamic polarisation) and non-electrochemical technique (weight loss and UV-vis spectrophotometric measurement). Results of weight loss and Tafel polarization measurements showed that this compound has fairly good inhibiting properties for steel corrosion in acidic bath, with efficiencies of around 88% at a concentration of  $10^{-3}M$ . The inhibition is of a mixed anodic-cathodic nature. Langmuir isotherm is found to provide an accurate description of the adsorption behaviour of the investigated compound <sup>(101)</sup>. Negative value was calculated for the energy of adsorption indicating the spontaneity of the adsorption process. The formation of complex between metal cations and 2, 3-quinoxalinedione is also proposed as additional inhibition mechanism of mild steel corrosion.

The inhibition effect of *Zenthoxylum alatum* plant extract on the corrosion of mild steel in 5% and 15% aqueous hydrochloric acid solution has been investigated by weight loss and electrochemical impedance spectroscopy (EIS)<sup>(102)</sup>. The corrosion inhibition efficiency increases on increasing plant extract concentration till 2400 ppm. The effect of temperature on the corrosion behaviour of mild steel in 5% and 15% HCl with addition of plant extract was studied in the temperature range 50–80°C. Surface analysis (SEM, XPS and FT-IR) was also carried out to establish the corrosion inhibitive property of this plant extract in HCl solution. Plant extract is able to reduce the corrosion of steel more effectively in 5% HCl than in 15% HCl. The adsorption of this plant extract on the mild steel surface obeys the Langmuir adsorption isotherm.

Inhibition efficiency of some water-soluble hydrazones for C-steel corrosion in hydrochloric acid has been tested by weight loss, polarization measurements and open circuit technique. The inhibition effect was attributed to the adsorption of the additives on the C-steel surface as supported by adsorption measurements at Pt electrode using cyclic voltammetry<sup>(103)</sup>. Electrochemical measurements indicated that all the additives behave as cathodic-type inhibitors. The data obtained fit well to both the Temkin adsorption isotherm and the kinetic-thermodynamic model. The inhibition behaviour and its order were explained with the help of the proposed skeletal representation.

The inhibitive action of the aqueous extract of olive (*Olea europaea* L.) leaves toward the corrosion of C-steel in 2M HCl solution was investigated using weight loss measurements, Tafel polarization, and cyclic voltammetry<sup>(104)</sup>. It was found that the extract acts as a good corrosion inhibitor for the tested system. The inhibition efficiency increases with increasing extract concentration. The inhibitive action of the extract is discussed with a view to adsorption of its components onto the steel surface, making a barrier to mass and charge transfer. The adsorption of

extract components onto the steel surface was found to be a spontaneous process and to follow the Langmuir adsorption isotherm. It was found also that such adsorption increases the activation energy of the corrosion process. The results of cyclic voltammetry showed that the presence of olive extract decreases the charge density in the transpassive region. The inhibition efficiency is greatly reduced as the temperature is increased.

Quinolin-5-ylmethylene-3-[[8-(trifluoromethyl) quinolin-4-yl]thio]propanohydrazide(QMQTPH) was synthesized, characterized and tested as a corrosion inhibitor for mild steel in 1M and 2M HCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Polarization resistances calculated from the EIS measurements were in good agreement with those obtained from direct current (DC) polarization measurements. The mild steel samples were also analyzed by scanning electron microscopy (SEM) <sup>(105)</sup>. The results showed that QMQTPH is an excellent inhibitor for mild steel in acid medium. The inhibition was assumed to occur via adsorption of the inhibitor molecule on the metal surface. It acts as an anodic inhibitor. In the temperature range (30 to 60°C), the QMQTPH adsorption follows Langmuir isotherm model. The protection efficiency increased with increasing inhibitor concentration in the range  $10^{-5}$  -  $10^{-3}$ M, but slightly decreased with increasing temperature.

The efficiency of three furan derivatives (2-methylfuran, furfuryl alcohol and furfurylamine)<sup>(106)</sup>, as corrosion inhibitors for carbon steel in 1M HCl, has been determined by gravimetric and electrochemical measurements. These compounds inhibit corrosion even at very low concentrations, and furfuryl alcohol is the best inhibitor. Polarization curves indicate that all compounds are mixed inhibitors, affecting both cathodic and anodic corrosion currents. Adsorption of furan derivatives on the carbon steel surface is in agreement with the Langmuir adsorption isotherm model, and the calculated Gibbs free energy values confirm the chemical nature of the adsorption. The structural and electronic

properties of these inhibitors, obtained using AM1, PM3, MNDO and MINDO/3 semi-empirical self-consistence field methods, are correlated with their experimental efficiencies.

The effect of some prepared compounds, namely thiazole derivatives on the corrosion of C-steel in 2 M HCl solutions has been studied using the weight loss and electrochemical polarization methods. The results showed that the inhibition efficiency of the investigated compounds was found to depend on the concentration and the nature of the inhibitor. The presence of the substituted donating group ( $-\text{OCH}_3$ ) <sup>(107)</sup> plays an important role in the inhibition percentage of these investigated compounds. The effect of temperature on the corrosion behavior of C-steel in 2M HCl without and with the inhibitors was studied in the temperature range from 30 to 50°C. The activation and thermodynamic parameters  $E_a^*$ ,  $\Delta H^*$  and  $\Delta S^*$  were calculated. The inhibitors were adsorbed on the C-steel surface according to Frumkin's adsorption isotherm. The synergistic effect of some cations ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ca}^{2+}$ ) on the corrosion inhibition of C-steel in 2M HCl in the presence and absence of the investigated compounds was also studied by the weight loss method.

The effect of ammonium polymolybdate (APM) on the corrosion of carbon steel in a solution of 1M HCl was studied by weight loss and Mossbauer spectrometry. Inhibition efficiencies (IE) have been obtained from weight measurement <sup>(108)</sup>. The inhibition efficiencies increased with increase APM concentration. Mossbauer spectrometry shows that a superficial compound is formed on the electrode surface as a result of corrosion.

The synergism between rare earth cerium(IV) ion and vanillin on the corrosion of cold rolled steel (CRS) in 1M HCl solution was first investigated by weight loss, potentiodynamic polarization, ultraviolet and visible spectrophotometer (UV-vis), X-ray photoelectron spectroscopy (XPS)<sup>(109)</sup> and atomic force microscope (AFM). The results revealed that vanillin had a

moderate inhibitive effect, and the adsorption of vanillin obeyed the Temkin adsorption isotherm. For rare earth  $\text{Ce}^{4+}$ , it had a negligible effect. However, incorporation of  $\text{Ce}^{4+}$  with vanillin significantly improved the inhibition performance, and produced strong synergistic inhibition effect. Depending on the results, the synergism mechanism was proposed.

New compounds of alkylamides derived from  $\alpha$ -amino acids were tested as corrosion inhibitors for carbon steel in an aqueous solution of hydrochloric acid. The chemical synthesis of these amides performed by aminolysis of  $\alpha$ -amino acid methyl esters resulted in good yields. Electrochemical testing was carried out using polarization scans and weight loss measurements. Polarization scans indicated that compounds act as mixed corrosion inhibitors with an efficiency of 80–90% when dissolved in the testing solution at  $\geq 50$  ppm, whereas gravimetric results displayed a similar tendency. Microtox testing indicated a correlation with the molecular structure of inhibitors. Apparently, a long aliphatic chain ( $C > 12$ )<sup>(110)</sup> promoted not only higher corrosion efficiency, but also a higher toxicity. The higher efficiency of dodecyl amine of tyrosine was apparently derived from its longer aliphatic chain, with some contribution from its phenyl ring, which reinforces the molecular interactions of  $\pi$  type bonding to the d orbital metal favouring film formation.

Corrosion inhibition of indole-3-acetic acid on mild steel in acidic medium (0.5M HCl) containing the desired amount of inhibitor has been investigated at different temperatures by using potentiodynamic polarization<sup>(111)</sup>, electrochemical impedance spectroscopy, and polarization resistance measurements. The experimental results showed that corrosion potential shifted toward a more negative potential region in the presence of indole-3-acetic acid than that of blank solution. According to the obtained results from all measurements, inhibition efficiency was about 77% with  $1.7 \times 10^{-3}\text{M}$  inhibitor present, increasing to about 93% at the  $1 \times 10^{-2}\text{M}$  inhibitor concentration. Potentiodynamic polarization measurements showed that the current at anodic



and cathodic regions obtains a smaller value in the presence of inhibitor at almost all potentials than that of the Blank solution. The degree of the surface coverage was determined by using the calculated corrosion current, and it was found that adsorption process of the studied inhibitor on mild steel surface obeys the Langmuir adsorption isotherm. Corrosion of the mild steel increased with a rise in temperature both in the presence and absence of the inhibitor. Activation energy ( $E_a$ ), Gibbs free energy ( $\Delta G^\circ_{\text{ads}}$ ), enthalpy ( $\Delta H_{\text{ads}}$ ), and entropy ( $\Delta S_{\text{ads}}$ ) of corrosion process were calculated by using experimental measurements. Effect of immersion time to corrosion of mild steel was also tested in this study.

The corrosion inhibition effect of 3H-phenothiazin-3-one, 7-dimethylamin as a new inhibitor was studied using different electrochemical and weight loss methods. It was found that this compound acts as a strong inhibitor for mild steel in 1 M HCl even at very low concentration (1 ppm) <sup>(112)</sup>. Results showed that this compound acts as a mixed type inhibitor. As the inhibitor concentration increased, the charge transfer resistance of mild steel increased and double layer capacitance decreased. The results of EN measurements after trend removal were in good agreement with other methods results. It was found that this inhibitor acts through adsorption on the metal surface. Also, adsorption obeys the Langmuir isotherm.

The cycloaddition reactions of the cyclic nitrones 1-pyrroline 1-oxide and 3, 4, 5, 6-tetrahydropyridine 1-oxide with alkenes, 11-phenoxy- 1-undecene and 11-p-methoxyphenoxy-1-undecene, afforded cycloaddition products <sup>(113)</sup> (bicyclic isoxazolidines) in excellent yields. One of the cycloadducts on reaction with propargyl chloride and ring opening with zinc in acetic acid afforded quaternary ammonium salt and aminoalcohol, respectively. All the new inhibitor molecules in the presence of 400 ppm at 60°C achieved inhibition efficiencies, determined by gravimetric method, in the range 99–99.6% and 85–99% for mild steel in 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively.

Comparable results were obtained by the electrochemical methods using Tafel plots and electrochemical impedance spectroscopy for the synthesized compounds. The isoxazolidine derivatives were also found to be good inhibitors of mild steel corrosion in synthetic brine. Negative values of  $\Delta G^\circ_{\text{ads}}$  in the acidic media ensured the spontaneity of the adsorption process. While the corrosion inhibition by these molecules was predominantly under cathodic control in 1 M HCl, the inhibition in 0.5 M H<sub>2</sub>SO<sub>4</sub> was found to be under anodic control. The isoxazolidines and their derivatives were found to be among a rare class of molecules, which provide suitable inhibition mechanism for the corrosion inhibition in HCl as well as in H<sub>2</sub>SO<sub>4</sub> media.

The inhibitive action of leaves (LV), seeds (SD) and a combination of leaves and seeds (LVSD) extracts of *Phyllanthus amarus* on mild steel corrosion in HCl and H<sub>2</sub>SO<sub>4</sub> solutions was studied using weight loss and gasometric techniques<sup>(114)</sup>. The results indicate that the extracts functioned as a good inhibitor in both environments and inhibition efficiency increased with extracts concentration. Temperature studies revealed an increase in inhibition efficiency with rise in temperature and activation energies decreased in the presence of the extract. A mechanism of chemical adsorption of the plants components on the surface of the metal is proposed for the inhibition behaviour. The adsorption characteristics of the inhibitor were approximated by Temkin isotherm.

The efficiency of three furan derivatives (2-methylfuran, furfuryl alcohol and furfurylamine)<sup>(115)</sup>, as corrosion inhibitors for carbon steel in 1 M HCl, has been determined by gravimetric and electrochemical measurements. These compounds inhibit corrosion even at very low concentrations, and furfuryl alcohol is the best inhibitor. Polarization curves indicate that all compounds are mixed inhibitors, affecting both cathodic and anodic corrosion currents. Adsorption of furan derivatives on the carbon steel surface is in agreement with the Langmuir adsorption isotherm model, and the calculated Gibbs free energy values confirm the

chemical nature of the adsorption. The structural and electronic properties of these inhibitors, obtained using AM1, PM3, MNDO and MINDO/3 semi-empirical self-consistence field methods, are correlated with their experimental efficiencies.

Uniform polyaniline (PANI) nanofibers were synthesized by interfacial polymerization. Transmission electron microscopy (TEM) image shows that the nanofibers have average diameter of 30–60 nm and length of 200–400 nm. And the PANI nanofibers have the good dispersion stability in the ethanol <sup>(116)</sup>. The anti-corrosion performance of PANI nanofibers and aggregated PANI-coated carbon steel samples exposed to 5% NaCl aqueous solution was evaluated by electrochemical corrosion measurements. The results show that the carbon steel coated with PANI nanofibers has more excellent corrosion protection than that with aggregated PANI. Raman spectroscopy analysis indicates that the surface of carbon steel coated with PANI nanofibers formed better passive layer, which is composed of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>.

The inhibitive action of the aqueous extract of the root of shirsh el zallouh (*Ferula harmonis*) toward the corrosion of C-steel in HCl solution was investigated. The inhibition efficiency was measured using weight loss and potentiostatic polarization techniques. The electrochemical behavior of the extract was investigated using cyclic voltammetry. It was found that the addition of the extract reduces the corrosion rate of C-steel. The inhibition efficiency increases with increasing extract concentration <sup>(117)</sup>. The inhibitive effect of the tested extract was discussed in view of adsorption of its components on the steel surface. The adsorption of the extract components on the C-steel surface follows Langmuir adsorption isotherm. The inhibition efficiency decreases as the temperature is increased. The presence of extract increases the activation energy of the corrosion process of C-steel. The curves of cyclic voltammetry technique showed that the adsorbed molecules reduce the charge density on the steel surface.

Corrosion inhibition of C-steel in 2M HCl was investigated in the absence and presence of different concentrations of some thiosemicarbazide derivatives namely, 1-ethyl-4(2,4-dinitrophenyl) thiosemicarbazide(I), 1,4-diphenylthiosemicarbazide(II), 1-ethyl-4-phenylthiosemicarbazide(III). Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques were employed. Impedance measurements showed that the double layer capacitance decreased and charge transfer resistance increased with increase in the inhibitors concentration and hence increasing in inhibition efficiency<sup>(118)</sup>. Potentiodynamic polarization study showed that all the inhibitors act as mixed-type inhibitors. Results obtained reveal that the inhibition efficiency (IE%) follows the sequence: I>II>III. The adsorption of these compounds on C-steel surface obeys Temkin's adsorption isotherm and has a chemisorptions mechanism.

In this investigation, benzotriazole (BTAH), a well known corrosion inhibitor for copper, has been evaluated as a possible corrosion inhibitor of a carbon steel (CA-50) used as reinforcement in concrete. BTAH was added to a simulated pore solution of an aged concrete with addition of 3.5 wt% NaCl to imitate marine environments. The effect of BTAH in a concentration of 1.5 wt% on the corrosion resistance of CA-50 carbon steel was investigated by electrochemical impedance spectroscopy (EIS)<sup>(119)</sup> and potentiodynamic polarization tests. The improvement of the corrosion resistance due to BTAH addition was superior to that associated with nitrite in similar concentration, suggesting that BTAH is a potentially attractive alternative to nitrites for inhibiting corrosion of reinforcement steel in concrete.

Cold plasma nitriding treatment was performed to improve the corrosion resistance of C38 carbon steel. Nitriding process was conducted using a radiofrequency nitrogen plasma discharge for different times of treatment on non-heated substrates. The modification of the corrosion resistance characteristic of the C38

steel due to the treatment in acid medium (1M HCl) were investigated by gravimetric and electrochemical tests such as potentiodynamic polarisation curves and electrochemical impedance spectroscopy (EIS)<sup>(120)</sup>. It was shown that the plasma nitriding treatment improves the corrosion resistance. Indeed, in the gravimetric tests, nitrided samples showed lower weight loss and lower corrosion rate in comparison to untreated one. In the Tafel polarisation tests, the nitrided samples showed greatly reduced corrosion current densities, anodic dissolution and also retarded the hydrogen evolution reaction. Using EIS method, an adequate structural model of the interface was used and the values of the corresponding parameters were calculated and discussed. The results obtained from weight loss and electrochemical studies were in reasonable agreement. X-ray photoelectron spectroscopy (XPS) was carried out to establish the mechanism of corrosion inhibition of nitrided C38 steel in 1MHCl medium. The enhancement of the corrosion resistance is believed to be related to the iron nitride compound layer formed on the C38 steel surface during plasma nitriding, which protected the underlying metal from corrosive attack in the aggressive solutions.

The high affinity of surfactant molecules to adsorb onto interfaces is responsible for their applications in several interfacial systems. For this reason, surfactants can be used as good corrosion inhibitors on metallic surfaces. The main objective of this work was to examine the anticorrosion ability of three novel surfactant molecules synthesized from ricinoleic acid, a castor oil derivative. The surfactants are: sodium 12- N,N-diethylamino-9-octadecenoate (AR1S), sodium 12-N,N-diethylamino-9,10-dihydroxy-octadecanoate (AE2S) and sodium 12-N,N-diethylamino-9-octadecanoate (AE1S)<sup>(121)</sup>. Their ability to inhibit corrosion in AISI 1010 carbon-steel has been investigated by preparing specific micellar solutions and microemulsion systems. Adsorption phenomena have been electrochemically studied with the Frumkin model, indicating that the surfactant solutions tested can inhibit corrosion with levels as high as 95%.

On the other hand, the micro emulsion systems, although featuring relatively lower performance, are advantageous in that they are able to dissolve more active matter. These results are useful as a basis to propose and study particular applications such as the transport of oil in petrochemical industries.

The dodecyl cysteine hydrochloride surfactant was synthesized. The surface properties of this surfactant were studied using surface tension technique <sup>(122)</sup>. The nanostructure of this surfactant with the prepared gold nanoparticles was investigated using TEM technique. The synthesized surfactant and its nanostructure with the prepared gold nanoparticles were examined as non-toxic corrosion inhibitors for carbon steel in 2 M HCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results show that the percentage inhibition efficiency (IE %) for each inhibitor increases with increasing concentration until critical micelle concentration (CMC) is reached. The maximum inhibition efficiency approached 76.6% in the presence of 175 ppm of dodecyl cysteine and 90.8% in the presence of the same concentration of dodecyl cysteine hydrochloride self-assembled on gold nanoparticles. Polarization data indicate that the selected additives act as mixed type inhibitors. The slopes of the cathodic and anodic Tafel lines ( $b_c$  and  $b_a$ ) are approximately constant and independent of the inhibitor concentration. Analysis of the impedance spectra indicates that the charge transfer process mainly controls the corrosion process of carbon steel in 2M HCl solution both in the absence and presence of the inhibitors. Adsorption of these inhibitors on carbon steel surface is found to obey the Langmuir adsorption isotherm. From the adsorption isotherms the values of adsorption equilibrium constants ( $K_{ads}$ ) were calculated. The relatively high value of ( $K_{ads}$ ) in case of dodecyl cysteine hydrochloride self-assembled on gold nanoparticles reveals a strong interaction between the inhibitor molecules and the metal surface.

This investigation aims to analyze the effect of  $\text{Cl}^-$  ion on the atmospheric corrosion rate of carbon steel. The metal samples were exposed to a marine atmospheric environment (95 and 375 m from the sea line) <sup>(123)</sup> as well as an industrial atmospheric environment. The effects of  $\text{Cl}^-$  ions on the protective characteristics of the rust layers were assessed by IR spectroscopy, SEM-EDAX analyses, linear polarization resistance and electrochemical impedance spectroscopy. The results show that  $\text{Cl}^-$  ion influences the corrosion rate, as well as the morphology and composition of the rust layer.

The behavior of the Schiff base N,N-bis(salicylidene)-1,2-ethylenediamine (Salen), its reduced form (N,N-bis(2-hydroxybenzyl)-1,2-ethylenediamine)<sup>(124)</sup> and a mixture of its preceding molecules, ethylenediamine and salicylaldehyde, as carbon steel corrosion inhibitors in 1 mol L<sup>-1</sup> HCl solution was studied by corrosion potential measurements, potentiodynamic polarization curves, electrochemical impedance spectroscopy and spectrophotometer measurements. The experimental results showed that the reduced Salen presented the highest efficiency among the inhibitors studied. The results obtained in the presence of Salen were similar to those obtained in the presence of the salicylaldehyde and ethylenediamine mixture, showing that in acid medium the Salen molecule undergoes hydrolysis, regenerating its precursor molecules.

We report here the use of macrocyclic polyether compounds containing 1,3,4-thiadiazole moiety (n-MCTH)<sup>(125)</sup> in the corrosion inhibition of C38 carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> acid medium. n-MCTH n = 1, 2, 3, 4, 5. The aim of this work is devoted to study the inhibition characteristics of these compounds for acid corrosion of C38 steel using electrochemical impedance spectroscopy (EIS). Data obtained from EIS show a frequency distribution and therefore a modeling element with frequency dispersion behavior, a constant phase element (CPE) has been used. The experimental results obtained revealed that these

compounds inhibited the steel corrosion in acid solution and the protection efficiency increased with increasing inhibitors concentration. The difference in their inhibitive action can be explained on the basis of the number of oxygen atoms present in the polyether ring which contribute to the chemisorptions strength through the donor acceptor bond between the non bonding electron pair and the vacant orbital of metal surface. Adsorption of n-MCTH was found to follow the Langmuir's adsorption isotherm. The thermodynamic functions of adsorption process were calculated and the interpretation of the results is given. These results are complemented with quantum chemical study in order to provide an explanation of the differences between the probed inhibitors. Correlation between the inhibition efficiency and the structure of these compounds are presented.

The inhibitive action of henna extract (*Lawsonia inermis*) and its main constituents (Lawson, Gallic acid,  $\alpha$ -D-Glucose and tannic acid) on corrosion of mild steel in 1M HCl solution was investigated through electrochemical techniques and surface analysis (SEM/EDS)<sup>(126)</sup>. Polarization measurements indicate that all the examined compounds act as a mixed inhibitor and inhibition efficiency increases with inhibitor concentration. Maximum inhibition efficiency (92.06%) is obtained at 1.2 g/l henna extract. Inhibition efficiency increases in the order: Lawson > henna extract > Gallic acid >  $\alpha$ -D-Glucose > tannic acid. Also, inhibition mechanism and thermodynamic parameters are discussed.

The inhibition effect of glycine (Gly) towards the corrosion of low alloy steel ASTM A213 grade T22 boiler steel was studied in aerated stagnant 0.50 M HCl solutions in the temperature range 20–60°C using potentiodynamic polarization (Tafel polarization and linear polarization) and impedance techniques, complemented with scanning electron microscope (SEM) and energy dispersive X-ray (EDX). Electrochemical frequency modulation (EFM)<sup>(127)</sup>, a non-destructive corrosion measurement technique that can directly give values of corrosion current



without prior knowledge of Tafel constants, is also presented here. Experimental corrosion rates determined by the Tafel extrapolation method are compared with corrosion rates obtained by electrochemical, namely EFM technique, and chemical (i.e., non-electrochemical) method for steel in HCl. The chemical method of confirmation of the corrosion rates involved determination of the dissolved cation, using ICP-AES (inductively coupled plasma atomic emission spectrometry) method of analysis. Corrosion rates (in mm y<sup>-1</sup>) obtained from the electrochemical (Tafel extrapolation and EFM) and the chemical method, ICP, are in a good agreement. Polarization studies have shown that Gly is a good “green”, mixed-type inhibitor with cathodic predominance. The inhibition process was attributed to the formation of an adsorbed film on the metal surface that protects the metal against corrosive agents. Scanning electron microscopy (SEM) and energy dispersion X-ray (EDX) examinations of the electrode surface confirmed the existence of such an adsorbed film. The inhibition efficiency increases with increase in Gly concentration, while it decreases with solution temperature. Temkin isotherm is successfully applied to describe the adsorption process. Thermodynamic functions for the adsorption process were determined.

The inhibition ability of benzimidazole and its derivatives against the corrosion of mild steel in 1M HCl solution was studied. The change of impedance parameters observed by variation of inhibitors concentration within the range of 50–250 ppm was an indication of their adsorption <sup>(128)</sup>. The thermodynamic adsorption parameters proposed that these inhibitors retard both cathodic and anodic processes through physical adsorption and blocking the active corrosion sites. The adsorption of these compounds obeyed the Langmuir’s adsorption isotherm. The inhibition efficiency was increased with inhibitor concentration in the order of 2-mercaptobenzimidazole > 2-methylbenzimidazole > benzimidazole, which is in accordance with the variation of apparent activation energy of corrosion.

The corrosion inhibition of 2-hydrazino-4,7-dimethylbenzothiazole on low carbon steel in industrial water has been investigated at different temperatures and fluid velocities at different concentrations of the inhibitor using mass loss, potentiodynamic polarization and electrochemical impedance spectroscopy measurements. The results showed that corrosion resistance increased by increasing the inhibitor concentration <sup>(129)</sup>. Optimization of the three variables has been made and correlating the results obtained using Box–Wilson statistical method. The adsorption process on low carbon steel surface obeys Flory–Huggins isotherm. The values of  $\Delta G_{\text{ads}}^{\circ}$  obtained suggest that, the adsorption process of 2-HMBT on low carbon steel is chemisorption. The activation energy increased with increasing the concentration of inhibitors leading to decrease of the pre-exponential factor, and the entropy of activation increased negatively in the presence of inhibitor. SEM was used to identify the film formed on the metal surface.

The corrosion inhibition and adsorption behaviour of 2-undecyl-1-ethylamino imidazoline (2UEI) on N80 mild steel in CO<sub>2</sub>-saturated 3% NaCl solutions was investigated using potentiodynamic polarization, electrochemical impedance spectroscopy techniques and SEM observation. Inhibitor efficiency increased with increase in 2UEI concentration. Temperature studies revealed an increase in inhibition efficiency with rise in temperature and corrosion activation energies decreased in the presence of 2UEI. A mechanism of chemical adsorption of 2UEI on the metal's surface is proposed <sup>(130)</sup>. The adsorption characteristics of the inhibitor were approximated by Temkin isotherm. The inhibition efficiency of 2UEI was enhanced in the presence of iodide ions.

The synergistic inhibition effect of rare earth cerium(IV) ion and 3,4-dihydroxybenzaldehyde (DHBA) <sup>(131)</sup> on corrosion of cold rolled steel (CRS) in H<sub>2</sub>SO<sub>4</sub> solution was first investigated by weight loss and potentiodynamic polarization methods. Effects of

inhibitor concentration, temperature, immersion time and acid concentration on synergism are discussed in detail. The results reveal that DHBA has moderate inhibitive effect and its adsorption obeys Temkin adsorption isotherm. For the cerium (IV) ion, it has negligible effect. However, incorporation of  $\text{Ce}^{4+}$  with DHBA improves the inhibition performance significantly, and produces strong synergistic inhibition effect.

Methanolic extract of *Artemisia pallens* was tested as corrosion inhibitor for mild steel in 4N HCl and conc. HCl.<sup>(132)</sup> Weight loss and polarization techniques were used for evaluating corrosion inhibition in 4N HCl, whilst weight loss, SEM and FT-IR studies were carried out in conc. HCl. The inhibition efficiency was found to increase with increase of the inhibitor concentrations due to the adsorption of the inhibitor molecules on the metal surface and the adsorption follows Langmuir's adsorption isotherm. The inhibition Efficiency was found to be 93% at  $1.5 \text{ g l}^{-1}$  in 4N HCl and 96.5% at  $40 \text{ g l}^{-1}$  in conc. HCl.

Tris-hydroxymethyl-(2-hydroxybenzylidenamino)-methane (THHM) was synthesized. The effect of THHM on the corrosion of cold rolled steel (CRS) in 0.1 Mhydrochloric acid was then investigated by Tafel polarization curve and electrochemical impedance spectroscopy (EIS). Polarization curve results clearly reveal the fact that THHM is a good cathodic type inhibitor. EIS results confirm its corrosion inhibition ability. The inhibition efficiency increases with increasing THHM concentration but decreases with immersion time. Atomic force microscopy (AFM)<sup>(133)</sup> reveals that a protective film forms on the surface of the inhibited sample. The adsorption of this inhibitor is found to follow the Langmuir adsorption isotherm. THHM adsorbs on the sample probably by chemisorption.

The oxo-triazole derivative (DTP) was synthesized and its inhibiting action on the corrosion of mild steel in sulphuric acid was investigated by means of weight loss, potentiodynamic polarization, EIS and SEM. The results revealed that DTP was an

excellent inhibitor and the inhibition efficiencies obtained from weight loss experiment and electrochemical experiment were in good agreement. Potentiodynamic polarization studies clearly revealed that DTP <sup>(134)</sup> acted essentially as the mixed-type inhibitor. Thermodynamic and kinetic parameters were obtained from weight loss of the different experimental temperatures, which suggested that at different temperatures (298–333 K) the adsorption of DTP on metal surface obeyed Langmuir adsorption isotherm model.

The corrosion inhibition effect of cationic surfactants, DTAB (Dodecyl Trimethyl Ammonium Bromide) and TTAB (Tetradecyl Tri methyl Ammonium Bromide), on low carbon steel was studied using weight loss, open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS)<sup>(135)</sup> measurements. The effect of chain length compatibility on corrosion inhabitancy of surfactant and co-surfactant was investigated by C<sub>7</sub>OH (1-heptanol), C<sub>12</sub>OH (1-dodecanol) and C<sub>15</sub>OH (1-pentadecanol) as nonionic co-surfactants in acidic media at different concentrations of DTAB and TTAB. Data represented that the corrosion rate decreased by increasing concentration of DTAB and TTAB, independently. The effect of chain length compatibility on surfactant behavior was discussed. Decreasing of corrosion rate for DTAB+C<sub>12</sub>OH was more pronounced than other mixtures.

In this investigation, attempts have been made to study the inhibitive effect of N,N-ortho-phenylen acetylene acetone imine (S1) and 4-[(3-[[1-(2-hydroxy phenyl)methylidene] amino} propyl] ethanemidol]- 1,3-benzenediol (S2) in the concentration range of 50–400ppm for mild steel with two different microstructures resulted from two different heat treatments (annealed (A) and quenched and tempered (Q&T)) <sup>(136)</sup> in 1M hydrochloric acid by ac impedance spectroscopy. The tests were conducted in acid solutions in the absence and presence of different concentrations of S1 and S2 Schiff bases for both microstructures. A sole time constant was observed from Bode-phase angle plots in the presence of inhibitors which reveal that the action of inhibitors is

through adsorption on the surface. The charge transfer resistance and inhibition efficiency increases with the increase in Schiff bases concentration for both microstructures. The perlite samples in the absence of inhibitors in 1M hydrochloric acid indicated slightly less corrosion than martensite ones, which was because of more protective oxide layers. Furthermore in the presence of S1 and S2, these samples showed better adsorption than martensite one. Schiff base S1 showed a better inhibition against corrosion in comparison with S2. Both S1 and S2 adsorbed on steel surface according to a Langmuir adsorption isotherm model. The associated Gibbs free energies for S1 on both microstructures are more than S2.

The corrosion inhibition characteristics of the synthesized cationic gemini surfactants, namely bis(p-(N,N,N-decyldimethylammonium bromide) benzylidene thiourea (10-S-10), bis(p-(N,N,N-dodecyldimethylammonium bromide)benzylidene thiourea (12-S-12) and bis(p-(N,N,N-tetradecyldimethyl ammonium bromide)<sup>(137)</sup>benzylidene thiourea (14-S-14) on the carbon steel corrosion in 1 M hydrochloric acid have been investigated at 25°C by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The inhibition efficiencies obtained from all methods employed are in good agreement with each other. The obtained results show that compound 14-S-14 is the best inhibitor with an efficiency of 97.75% at  $5 \times 10^{-3}$  M additive concentration. Generally, the inhibition efficiency increased with increase of the inhibitor concentration. Changes in impedance parameters (charge transfer resistance,  $R_{ct}$ , and double-layer capacitance,  $C_{dl}$ ) were indicative of adsorption of 14-S-14 on the metal surface, leading to the formation of a protective film. The potentiodynamic polarization measurements indicated that the inhibitors are of mixed type. The adsorption of the inhibitors on the carbon steel surface in the acid solution was found to obey Langmuir's adsorption isotherm. The free energy of adsorption processes were calculated and discussed. The surface parameters of each synthesized surfactant were calculated from its surface tension including the critical

micelle concentration (CMC), maximum surface excess ( $C_{\max}$ ) and the minimum surface area ( $A_{\min}$ ). The free energies of micellization ( $\Delta G^\circ \text{ mic}$ ) were calculated. The surface morphology of carbon steel sample was investigated by scanning electron microscopy (SEM).

The hydrogen evolution reaction (HER) (cathodic reaction) of low carbon steel electrode immersed in hydrochloric acid was investigated as a source for hydrogen production. Corrosion rate, hydrogen evolution rate, and current density increase with the increase of HCl concentration. Theoretically and practically, every 1 g of iron produces about 0.036 g of hydrogen. Therefore, the hydrogen production efficiency over the immersion period is about 100%. High correlation coefficient<sup>(138)</sup> (close to 1) statistically indicates that there is a strong relation between loss in weight and the amount of evolved hydrogen (as dependent variable) and both time of immersion and acid concentrations (as independent variables). Application of the hydrogen produced by low carbon steel electrode has been performed on storage material. The tested material absorbs about 6 wt. % of hydrogen under atmospheric pressure and room temperature.

The inhibition effect of novel nonionic surfactants on the corrosion of carbon steel (CS) in 1M HCl was studied at different temperatures (20–60°C) by weight loss, electrochemical impedance spectroscopy (EIS)<sup>(139)</sup> and potentiodynamic polarization methods. The CS surface morphology was investigated by SEM. The obtained results showed that the prepared nonionic surfactants are excellent inhibitor in 1M HCl, and the inhibition efficiency (g) increases with the inhibitor concentration and temperature increasing. The adsorption of inhibitors on the CS surface obeys the Langmuir adsorption isotherm equation. Thermodynamic parameters have been obtained by adsorption theory. Polarization curves show that the synthesized inhibitors are mixed-type inhibitors in hydrochloric acid.

The protection influence of glycine (Gly) and a one of its derivatives, namely 2-(bis(2-aminoethyl)amino) acetic acid, designated here as GlyD; where GlyD stands for “glycine derivative”, against cold rolled steel (CRS) corrosion was studied in aerated stagnant 1.0 M HCl solutions at 25°C. Measurements were conducted under various experimental conditions using Tafel polarization, linear polarization and impedance techniques. These studies have shown that Gly and GlyD are very good <sup>(140)</sup> “green”, mixed-type inhibitors. GlyD is more effective than Gly itself in inhibiting the acid corrosion of CRS. Electrochemical frequency modulation (EFM) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) method of analysis are also presented here for monitoring corrosion. Corrosion rates obtained from both EFM and ICP-AES methods are comparable with those recorded using Tafel extrapolation method, confirming validation of corrosion rates measured by the latter. Adsorption via H-bond is discussed here, based on the presence of oxide film on the electrode surface as well as the number of NH linkages in the inhibitor molecule. Quantum chemical method was also employed to explore the relationship between the inhibitor molecular properties and its protection efficiency. The density function theory (DFT) is used to study the structural properties of Gly and GlyD in aqueous phase in an attempt to understand their inhibition mechanism. The protection efficiencies of these compounds showed a certain relationship to highest occupied molecular orbital (HOMO) energy, Mulliken atomic charges and Fukui Indices.

The inhibition of the corrosion of mild steel in hydrochloric acid solutions by 4-amino-5-phenyl-4H-1,2,4-triazole-3-thiol (APTT)<sup>(141)</sup> inhibitor was studied using weight loss technique. Basic kinetic parameters of the corrosion inhibition process were obtained by reaction kinetic equations. Rustles show that the inhibition increases with increasing of inhibitor concentration. Kinetic calculations show that the maximum value of time for which the corrosion rate increases twice the initial one, while time for which the mass of the sample subjected to corrosion

decreases twice the initial one were at  $8 \times 10^{-4}$  M of APTT. The dynamics were described by an exponential kinetic equation of self-accelerating reactions in the absence of inhibitor and by an equation of a zero order in its presence.

The inhibitor effect of tryptamine on the corrosion of mild steel in 0.5 M hydrochloric acid at 30°C was investigated using linear polarization, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) <sup>(142)</sup> techniques. The inhibition efficiency increases with an increase in concentration of tryptamine. At 500 ppm tryptamine the inhibition efficiency calculated by these techniques is around 97%. Cathodic and anodic polarization curves of mild steel in the presence of different concentrations of tryptamine at 30°C reveal that it is a mixed type inhibitor. Tryptamine follows Langmuir adsorption with adsorption free energy of  $-35.07 \text{ kJ mol}^{-1}$ .



## AIM OF THE PRESENT WORK

Carbon steel is used as construction materials for corrosion resistant equipment in most of the major industries, particularly in the nuclear, petroleum, power, food production, medical, chemical and electrochemical industries. Corrosion studies have become important due to awareness of the world's metal resources. Though corrosion is unavoidable, through better appreciation of its basic principles, the losses can be considerably reduced. Studies of carbon steel properties in general and especially electrochemical have been received a great attention. In such aspect, the corrosion and corrosion inhibition of carbon steel in the different media become very interesting and important owing to its wide applicability in industry and domestic life. Numerous studies on iron and Carbon steel were done including the corrosion nature and its mechanism in different media.

### ***The present work was designed to:***

- 1- Investigate the inhibiting effect of some pharmaceutical compounds towards the corrosion of carbon steel C1018 in hydrochloric acid solution.
- 2- Determine the rate of corrosion of carbon steel C1018 in hydrochloric acid solution, in the absence and presence of different concentrations of these pharmaceutical compounds

by electrochemical methods (potentiodynamic polarization and impedance methods) at 30°C.

- 3- Determine the type of adsorption isotherm at 30°C.
- 4- Study the effect of temperature on the rate of corrosion carbon steel 1018 in hydrochloric acid solution by one of the two methods to:
  - (a) Calculate the thermodynamic parameters of both adsorption and activation processes.
  - (b) Determine the kind of adsorption (physical or chemical).
- 5- Determine the mechanism and percentage inhibition of these investigated pharmaceutical compounds.
- 6- Determine the effect of investigated pharmaceutical compounds on pitting of Carbon Steel C1018 in 1M NaCl solution.
- 7- Determine the corrosion rate of carbon steel in hydrochloric acid solution, in absence and presence of different concentrations of these pharmaceutical compounds by using more modern techniques likes electrochemical impedance spectroscopy (EIS).
- 8- Finally, ordered these pharmaceutical compounds according to their percentage inhibition.