

# CHAPTER-1

## INTRODUCTION

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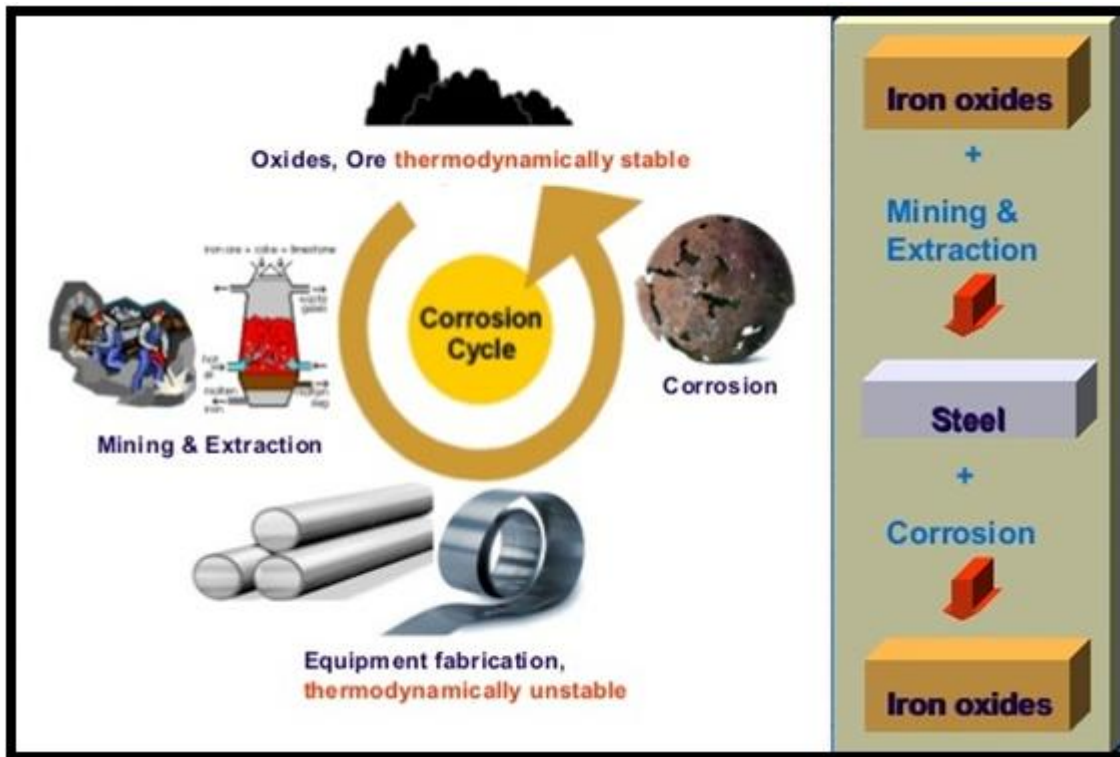
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Corrosion is a natural process which destroys the useful properties of the metals and shortens their life time. The degradation of materials and its properties due to their reactions with the environment is known as corrosion. The degradation of materials increases the complexity and diversity of materials system, which includes not only the metallic material but also ceramic, polymers, and composites. But from the practical point of view, the word materials refers to those substances, which have been used in the construction of machines, process equipments, and other manufactured products.

The fundamental reason for corrosion is the lowering of system's Gibbs free energy [Trethewey and Chamberlain (1995)]. Figure 1.1, illustrates that in the production of almost all metals involves addition of energy to the system. In terms of thermodynamic viewpoint, the metal has a strong driving force to return to its native i.e. low energy oxide state. Metals are found in nature as oxides or sulphides ores and in that state they are in higher oxidation state than the free metal. For stabilization, metal will try to lose the excess energy to become oxidized again. This return to the metal in their native oxide state called "corrosion". Due to this process the corrosion has been described as metallurgy in reverse [Fontana (1986)].

The corrosion affects the economy of the nation. A number of updated reports about enormous economic losses due to corrosion have been appeared timely in India and other countries of the world. A recent study entitled "NACE International's IMPACT Breaks New Ground in the Study of Corrosion Management" which reports the global cost of corrosion about US\$ 2.5 trillion. This is equivalent to approximately 3.4 % of global GDP [Jacobson *et al.* (2016)].

In India the cost of corrosion alone is estimated as Rs. 2 lakh crore (\$ 45 billion) every year [1<sup>st</sup> Global Corrosion Summit (2011)].



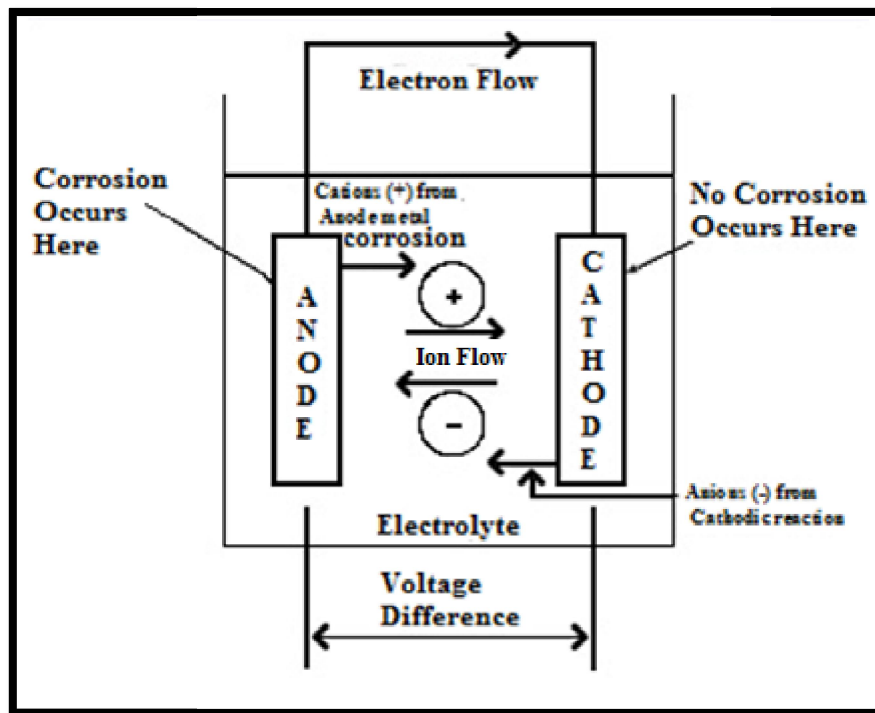
**Figure 1.1** Pictorial representation of corrosion cycle.

### 1.1 Basic concept of Corrosion

Corrosion is the destruction of a metal by a chemical or electrochemical reaction. In aqueous medium, the metal atom gets oxidized, by losing one or more electrons and leaves the bulk metal. The lost electrons are conducted through the metal to another site where they reduce the non-metallic element, which is in the contact with the metal and also the charge balance achieved by ionic current path in the opposite direction.



where  $M_m$  shows metal in metallic bonding state. In aqueous medium,  $M_m$  converts to  $M_{aq}^{2+}$  hydrated metal ion,  $e_m^-$  is electron release from the metal,  $Ox_{aq}$  is the oxidant present and Red ( $e_{aq}^-$ ) stands for reductant. So on combining both the reactions the final reaction is then written as follows:



**Figure 1.2** Schematic representation of electrochemical corrosion cell where potential difference between the two sites drives the corrosion current.

Both the sides are connected electronically by the metal and ionically by the electrolyte. This system is referred as “corrosion cell” shown schematically in Figure 1.2. From the side where metal atom losses electrons is called anode and the side where the electrons are transferred to the reducing species is called cathode. The potential difference between the two sides drives the corrosion current and the rate at which a metal corrodes depends on the magnitude of corrosion current [NACE International Basic Corrosion Course].

## 1.2 Theories of corrosion

The corrosion process is classified into two types [Fontana (1986)],

Chemical or Dry corrosion

Electrochemical or Wet corrosion

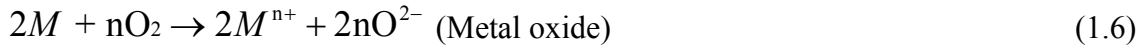
### 1.2.1 Chemical or Dry corrosion

This type of corrosion occurs due to direct chemical attack of atmospheric gasses like O<sub>2</sub>, halogens, H<sub>2</sub>S, etc in a dry environment on the metal surface. This creates a solid film of corrosion products on metal surface which protects the metal from further corrosion. But if a soluble or volatile corrosion product is formed, then the metal surface is exposed for further corrosion. The dry or chemical corrosion is divided into three types:

**(a) Oxidation corrosion:** This type of corrosion takes place by the direct action of oxygen at low or high temperatures on metals in the absence of moisture. The alkali and alkaline earth metals are readily oxidized at low temperatures and at high temperature almost all metal oxidise except Ag, Au and Pt. The oxidized alkali and alkaline earth metals deposit small volume of oxide products that create a porous layer through which oxygen can diffuse to bring out further attack of the metal. While the other metals like aluminium, tungsten and molybdenum form a greater volume of oxide layers than the metal by which they were produced. These non-porous, continuous oxide layers avoid the diffusion of oxygen, resulting in a decreases rate of further attack.



on combining both equations,

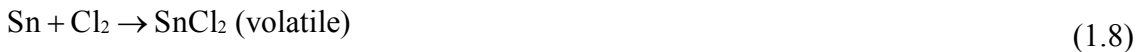


**(b) Corrosion because of other gases:** In dry atmosphere, gasses like SO<sub>2</sub>, CO<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub>, F<sub>2</sub> etc. react with metal and form corrosion products that can result in formation of protective or non-protective film on metal surface.

**(i)** The attack of Cl<sub>2</sub> on Ag results the formation of AgCl film that protects the metal from further attack.



**(ii)** The Cl<sub>2</sub> attack on Tin (Sn) forms SnCl<sub>2</sub>, which is volatile and does not protect metal from further attack.



**(c) Liquid metal corrosion:** This type of corrosion occurs at high temperature due to chemical action of molten metal through metallic pipelines. These corrosion reactions involve either dissolution of metal or cause internal penetration.

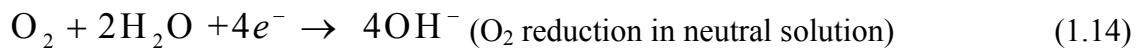
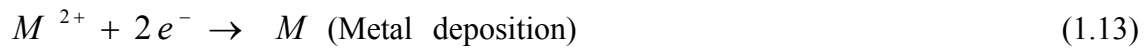
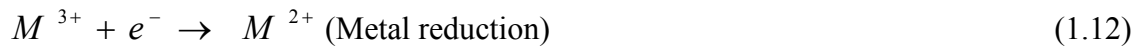
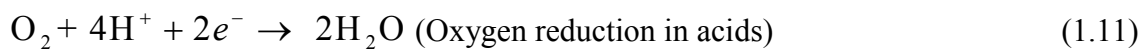
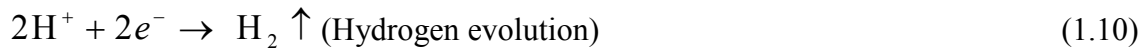
### 1.2.2 Electrochemical or Wet corrosion

The corrosion of metal in aqueous solution is an electrochemical process involving two steps: one is the oxidation of metal and the other one is the reduction. When two dissimilar metals are in contact with different electrode potential a galvanic cell is formed in a conducting solution. The EMF developed in the galvanic cell arises due to a difference in electrode potential of the metals. When these two dissimilar metals (electrodes) are joined by a wire, flow of electrons takes place from anode to

cathode i.e. at anode the metal atom get oxidized to lose electrons in the environment and itself retained as positive ions in the solution and at cathode the reduction occurs.



the cathodic reactions are more difficult to predict but can be categorized by different forms of reduction reactions:



### 1.3 Types of corrosion

The corrosion is of following types [Revie (2008)].

**(i) Uniform corrosion:** It is generally very common form of corrosion. The chemical or electrochemical reactions that occur uniformly on the entire metal surface cause uniform corrosion. In this corrosion the thickness of the metal decreases and eventually failure occurs.

**(ii) Galvanic corrosion:** This type of corrosion occurs by the contact of two dissimilar metals in a conducting medium. In the electrochemical series the metals having low reduction potential undergoes corrosion and the other one is protected i.e. called galvanic corrosion.

**(iii) Crevice corrosion:** This type of corrosion refers to localised attack on metal surface due to crevices, joints, bolts or other shielded areas on metal surface exposed to

corrosive environment. The deposition of salts, acids, and moisture results in the formation of an occluded corrosion. Anode is created in the crevice and the remaining body behave as cathode. So corrosion at the crevice is highly accelerated as well as concentrated.

**(iv) Pitting corrosion:** The cracks, holes or cavities on the developed protective film on metal surface causes pitting corrosion by formation of small anodic areas in less oxygenated part and cathodic area in oxygenated part. The flow of electrons from anode to cathode occurs via atmospheric moisture medium.

**(v) Intergranular corrosion:** This type of corrosion occurs at the grain boundaries of the metal. In that case localised corrosion attack takes place at grain boundaries while the rest part is unaffected. This can be due to the presence of impurities in the boundaries, or to local enrichment or reduction of one or more alloying elements.

**(vi) Selective leaching:** The removal of one element from an alloy due to corrosion is called selective leaching. In this process the less metal is removed from the alloy by the galvanic corrosion mechanism. The leaching is based on the position of metals in galvanic series.

**(vii) Erosion corrosion:** It is the acceleration of corrosion due to the relative movement with the corrosive fluid and the metal surface. This is promoted by high velocity fluids, turbulent flow and the impingement of the high velocity fluids on metal surfaces.

**(viii) Stress corrosion cracking:** The combined action of both applied static tensile stress and corrosive environment which forms cracks on the metals surface. In stress corrosion cracking the metal is almost un-attacked over most of the part, while fine cracks progress through it.

## 1.4 Factors influencing corrosion

The factor that affects the rate of corrosion depends on the nature of the metal and the nature of environment.

### 1.4.1 Nature of the metal

**(a) Metal position in galvanic series:** The corrosion depends upon the place of metal in galvanic series. The metal having greater oxidation potential corrodes faster. When two metals are connected in conducting solution, the metal situated higher in the galvanic series behaves as anode and suffers from corrosion. The difference between the two metals is also an important factor, if the difference is more in the series the faster is corrosion of the anodic metal.

**(b) Area of cathode and anode:** The corrosion is faster if the cathodic area is large due to a higher demand for electrons. This will increase the rate of corrosion by dissolution of metal at anodic region.

**(c) Purity of metal:** The impurity present in the metal causes the formation of a galvanic cell having cathodic and anodic area in the metal that accelerates the corrosion.

**(d) Physical state of metal:** The metal under un-uniformly distributed stress corrodes easily. In the metal the area which is more stressed tends to become anode and corrodes.

**(e) Nature of the oxide film:** If the oxide film on metal surface is porous in nature then through it the diffusion of oxygen brings further corrosion.

**(f) Solubility of the product of corrosion:** Solubility of gathered corrosion product on metal surface is also important factor. If the corrosion product is soluble in contact with any corrosive medium this will enhance corrosion otherwise, if insoluble corrosion produced can act as film to prevent corrosion.



### 1.4.2 Nature of environment

- (a) **Temperature:** The corrosion reaction is faster with temperature due increase in the rate of chemical reaction and diffusion of ions. In fact the increase in temperature can convert a passive metal condition in active state i.e. starts corrosion.
- (b) **Humidity:** The presence of moisture in the environment causes corrosion of metals due to formation of a corrosion cell in which moisture act as conducting medium.
- (c) **Nature of the electrolyte:** The nature of electrolyte plays an important role. If the electrolyte is in nature to dissolve the protective film then it will enhance corrosion. The good conductance of electrolyte causes easy flow of corrosion current; hence the rate of corrosion is increased.
- (d) **Effect of pH:** The rate of corrosion increases at maximum when the corrosive environment is acidic i.e. pH is less than 7.
- (e) **Availability of oxygen:** The rate of corrosion increases in presence of oxygen. The area where oxygen is in low proportion act as anode and another part at higher oxygenated area acts as cathode. Thus a difference in aeration causes corrosion.

### 1.5 Thermodynamic aspects

A very few of metals exist in nature in their native form, mostly are found either in the form of oxides, sulphates, carbonates or other complex form, which alludes to the fact that in their elemental state metals are inherently reactive. This tendency for the formation of natural metallic compounds is governed by the law of thermodynamics, which predicts possibility of a particular reaction. The possibility of a reaction to occur is determined by the free energy change. Corrosion of metals is an electrochemical reaction containing two half cell reactions, which occur at the anodic and cathodic sites.

The electrode potential of the half cell reactions provides a more direct approach to assessing the tendency of a reaction.



The total cell potential of the coupled two half cells can be shown as,

$$E_{\text{cell}} = E_c - E_a \quad (1.17)$$

For a reaction to take place  $E_{\text{cell}}$  must be positive, i.e.  $E_{\text{cell}} = E_c - E_a > 0$  or  $E_c > E_a$ .

The electrical potential is related to the free energy change of a corrosion process by the following equation [Fontana and Greene (1984)], [Uhlig (1971)],

$$\Delta G = -nF \Delta E \quad (1.18)$$

Where,  $n$  stands for number of electron transferred,  $F$  stands for Faraday constant and  $\Delta E$  represents the potential difference.

So, the thermodynamic condition for a corrosion process becomes:

$$\Delta G < 0 \text{ and } \Delta E > 0$$

The negative value for free energy change attributed to the spontaneous reaction, whereas a positive value suggests that the reaction has no tendency to proceed. The  $\Delta G$  can be calculated by cell potential of the electrochemical reaction, that redox potential predicts whether a metal will corrode in a given environment or not.

Introducing the potential leads to the well known Nernst's equation [Uhlig (1971)],

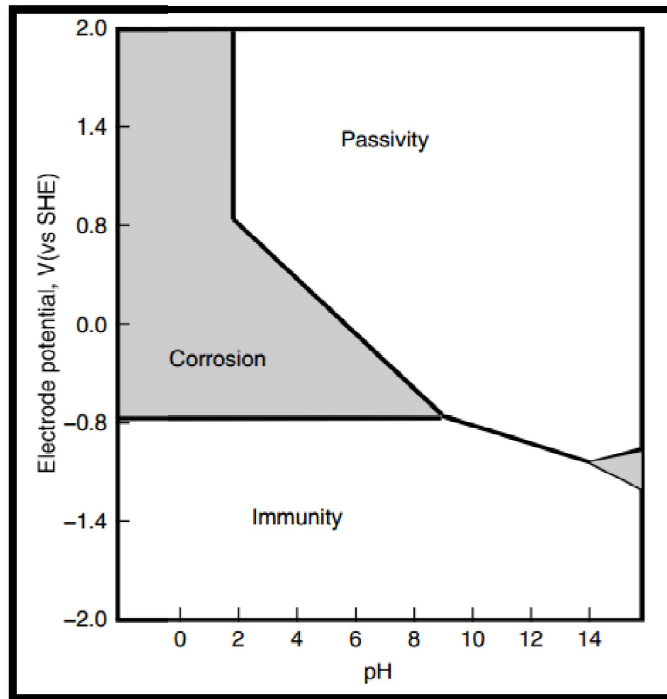
$$\Delta E = \Delta E^{\circ} - \frac{RT}{nF} \ln \frac{[Oxi]}{[Red]} \quad (1.19)$$

where,  $E^\circ$  represents Standard electrode potential,  $R$  for Gas constant ( $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ),  $F$  for Faraday constant (96,500 coulombs),  $T$  for Absolute temperature (Kelvin, K),  $n$  for Number of electrons transferred during the reaction,  $[oxi]$  for Concentration of oxidized species ( $\text{mol dm}^{-3}$ ),  $[red]$  for Concentration of reduced species ( $\text{mol dm}^{-3}$ ). The application of Nernst's equation for corrosion studies was embedded in the Pourbaix diagram.

## 1.6 Pourbaix Diagram

Marcel Pourbaix has introduced a summary of thermodynamic data in the form of potential-pH diagram. This is helpful to study the equilibrium potential variation with the pH effect, for the metal in contact with the electrolyte [Pourbaix (1974)]. Pourbaix diagram shows a glance of specific conditions of potential and pH for a metal at which, either it does not react or can react to form oxides and complex ions. Pourbaix diagram specifies the potential-pH domain by showing regimes of corrosion, immunity and passivity for metal in contact with the electrolyte.

Figure 1.3, shows potential-pH diagram for the iron/water system. Three regions are shown in the diagram. The first area in the diagram represents the active corrosion region, where the concentration of the metal ions in solution is  $\geq 10^{-6} \text{ M}$ . The second area presents immunity region where the iron concentration is less than  $10^{-6} \text{ M}$  i.e. non corroding region. The third part represents the passivity region, in such condition the metal surface is covered by the formation of oxides layer, which protects the metal from corrosion [Akid (2004)].



**Figure 1.3** Pourbaix diagram for the iron/water system.

### 1.7 Kinetic aspects

The thermodynamics of corrosion provides information about the feasibility of a particular reaction, whether it takes place or not. However, fails to give any information about the rate at which a reaction may take place. So, it is therefore very necessary to consider the kinetics of corrosion. For a reaction to proceed, the transformation rate depends upon the magnitude of the energy barriers. The maximum energy or intermediate transition states at which the entity starts transforming is the activation energy,  $\Delta G^*$  [Talbot and Talbot (2007)]. The statistical distribution of energy amongst the particles makes certain that each of the particles contains adequate energy to surmount the peaks. So, with a very short period of time the fraction of particle transforming, the reaction rate,  $r$  depends upon the activation energy. The co-relation expression between the reaction rate and activation energy is shown by Arrhenius equation,

$$r = A \exp \frac{-\Delta G^*}{RT} \quad (1.20)$$

To co-relate the equation with the electrode process, it should be restated in the electrical conditions. The ions move across through the electrode holds electrical charge. For this reason, the electric current,  $i$  can be put in place of reaction rate,  $r$ . The energy for the following process is the resultant of the charge and the potential drop,  $E$  by which it is carried.

The thermodynamic units are expressed as per mole of the substance and according to the charge on a mole of single charged ions are Faraday, thus the free energy change,  $\Delta G$  for a electrode can be expressed as,

$$\Delta G = -zF \Delta E \quad (1.21)$$

So, replacing  $r$  in the Arrhenius equation by  $i$  and putting  $\Delta G$  the equation can be represented as,

$$i = k \exp \frac{-\Delta G^*}{RT} = k \exp \frac{-zF \Delta E^*}{RT} \quad (1.22)$$

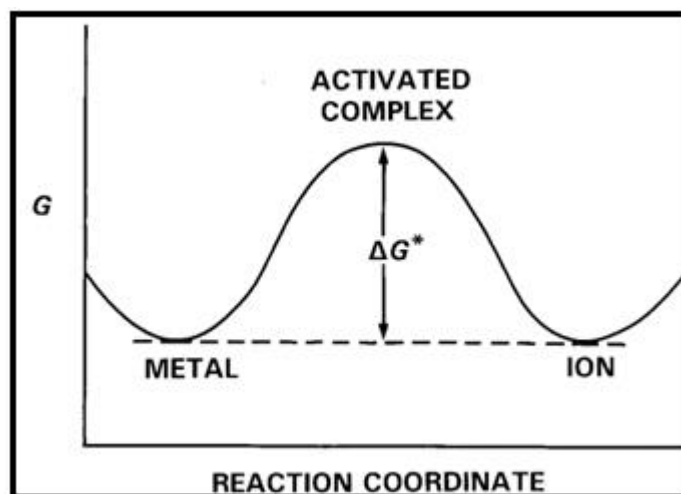
### 1.7.1 Kinetic approach for equilibrium at an electrode

When the metal electrode is at equilibrium state, it implies that both the processes i.e., the dissolution of metal as ions and the deposition of ions back to metal surface occur at equal rate. So, at equilibrium there is no net change in Gibbs free energy,  $\Delta G$  for both forward and backward processes. The chemical free energy change because of the two processes (dissolution or deposition) at metal surface is balanced by the same amount of electrical work done by the ions in crossing the electric field imposed by the equilibrium electrode potential. So, the flow of ions make up two equal

and opposite electric currents. The symbol  $\vec{i}$  and  $\overleftarrow{i}$  represents the leaving and entering current to the metal and called as partial currents and at equilibrium their magnitude is called as exchange current density,  $i_0$  [Talbot and Talbot (2007)],

$$i_0 = \vec{i} = \overleftarrow{i} \quad (1.23)$$

The excess energy needed for transformation of metal atoms from metal surface to solvated metal ions is activation energy. The completely solvated ions cannot come closer to the metal surface than outer Helmholtz plane, for the reason that they are obstructed by their own solvated metal ions sheet and the monolayer of adsorb water molecule on the surface of metal. So, the metal atoms solvated partially during the transformation, thus remain in transient higher energy state.



**Figure 1.4** Schematic energy profiles for equilibrium at an electrode.  $\Delta G^*$  is the Gibb's free energy of activation.

The pictorial representation of free energy is shown in Figure 1.4. Putting the value from the equation 1.22, we find the exchange current density as a function of activation energy,

$$i_0 = \overset{\rightarrow}{i} = \overset{\leftarrow}{i} = k \exp \frac{-\Delta G^*}{RT} \quad (1.24)$$

where  $\Delta G^*$  is activation energy,  $T$  is temperature,  $R$  is gas constant,  $k$  is a constant which depends upon the process and on the ion.

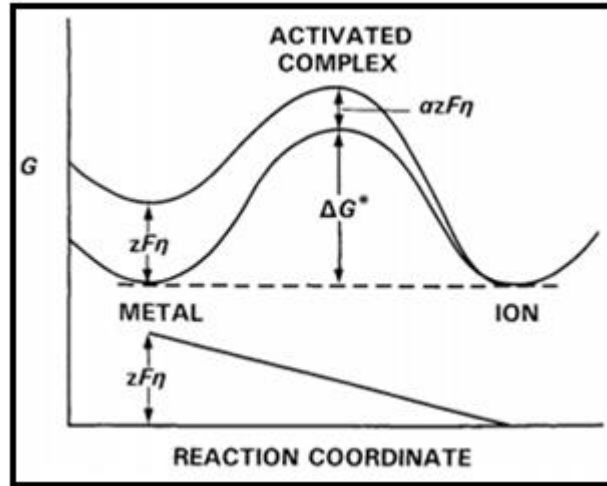
### 1.7.2 Electrochemical polarization

When the equilibrium condition at an electrode is perturbed, the net current flows through the electrode surface shifting the potential towards the direction and magnitude of current flow. That potential shift is called as polarization and its value,  $\eta$  is the over potential. There are three different type of polarization: activation, concentration polarization and Ohmic Resistance.

#### 1.7.2.1 Activation polarization

The relative changes observed in activation energy from the dissolution and deposition process at electrode surface on disturbing the equilibrium are called activation polarization. Depending on the net current flow the polarization can be defined as positive (anodic) or negative (cathodic). The pictorial representation of free energy of an electrode focused on activation polarization is shown in Figure 1.5.

If the system is polarized anodically with overpotential,  $\eta$  then due to polarization the free energy of the system  $\Delta G = -zF\Delta E$  is raised for the metal by  $zF\eta$  and for activated complex by  $\alpha zF$ , compared to the ions. Here  $\alpha$  is defined as symmetry factor. Before polarization the activation energy was equal to  $\Delta G^*$  but after polarization the activation energy for dissolution process decreased by  $[\Delta G^* - (1-\alpha)zF\eta]$  and activation energy for deposition increased by  $[\Delta G^* + \alpha zF\eta]$ .



**Figure 1.5** Schematic energy profile for activation polarization at an electrode:  $\Delta G^*$  = Gibb's free energy of activation;  $\eta/V$  anodic overpotential.

So, the two partial currents are not equal. Now the dissolution current  $\vec{i}$  is,

$$\vec{i} = k \exp \frac{-\{\Delta G^* - (1-\alpha)zF\eta\}}{RT} \quad (1.25)$$

$$\vec{i} = k \exp \frac{-\Delta G^*}{RT} \cdot \exp \frac{(1-\alpha)zF\eta}{RT} \quad (1.26)$$

$$\vec{i} = i_0 \exp \frac{(1-\alpha)zF\eta}{RT} \quad (1.27)$$

the deposition current  $\overleftarrow{i}$  is,

$$\overleftarrow{i} = i_0 \exp \frac{-\alpha zF\eta}{RT} \quad (1.28)$$

So, calculating the net current which is the difference of these two partial currents,

$$i_{\text{net}} = \vec{i} - \overleftarrow{i} = i_0 \left[ \exp \frac{(1-\alpha)zF\eta}{RT} - \exp \frac{-\alpha zF\eta}{RT} \right] \quad (1.29)$$

This is known as Butler-Volmer equation. If the value of anodic polarization is higher from the reversible potential i.e.  $\eta > 0.1$  V then Butler-Volmer equation simplifies to,



$$i_{\text{net}} \approx \vec{i} = i_0 \left[ \exp \frac{(1-\alpha)zF\eta}{RT} \right] \quad (1.30)$$

rearranging the equation, here  $\alpha$  and  $z$  are constant for the electrode at constant temperature,

$$\eta_{\text{anodic}} = b \log i_0 + b \log i_{\text{anodic}} \quad (1.31)$$

In the same way, the value of cathodic polarization with potential i.e.  $\eta_a > -0.1V$ , then

$i_{\text{net}} \approx \overleftarrow{i}$  and the equation is,

$$\eta_{\text{cathodic}} = b \log i_0 + b \log i_{\text{cathodic}} \quad (1.32)$$

The combination expression of both is:

$$\eta = b \log i_0 \pm b \log i \quad (1.33)$$

This is known as Tafel equation, where  $b$  is tafel slope,

$$b = \frac{2.303RT}{(1-\alpha)zF} \quad (1.34)$$

### 1.7.2.2 Concentration polarization

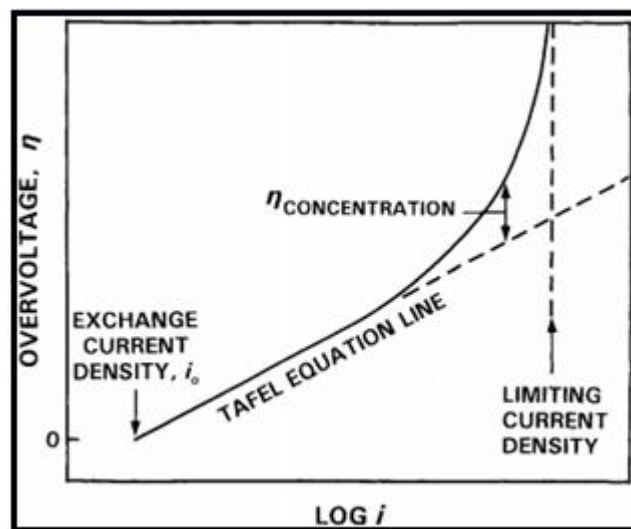
As if any electrode potential is perturbed from its equilibrium potential, in that case the net current flows either in anodic  $i_a$ , or cathodic  $i_c$ , increases at first. After that the current cannot increase indefinitely due to the limits to the rate at which the ions may carry charges via the solution towards the electrode and from the electrode. That causes excess potential above that predicted by Tafel equation. The condition is shown in Figure 1.6. This happened because the ions are produced or consumed at the

electrode surface very rapidly than by their diffusion to or from the bulk of solution. The ions concentration increases in anodic reaction, which is close to the electrode above from the bulk solution while in cathodic reaction, the local concentration is low. Result is an increase in polarization than that predicted by the Tafel equation. This excess potential is known as concentration polarization,  $\eta_c$ . Apply the Nernst equation to examine the magnitude of the effect with the assumption that it is suitable for the existing dynamic state.

In dissolution process:



Assuming that  $[^a M^{z+}]$  stands for ion activity in the bulk of solution and  $[^a M^{z+}]_p$  is the enhanced activity at the polarized electrode surface. At equilibrium potential condition for the non-polarized electrode, the potential is  $E'$ , for the reaction  $M^{z+} + ze^{-} = M$ ,



**Figure 1.6** Plot between logarithmic current density  $i$ , with overvoltage  $\eta$  (after polarization). In the plot the deviation from Tafel line and limiting current density is shown because of concentration polarization. The  $\eta$  is negative for cathodic current and positive for anodic current.

$$E' = E^{\circ} + \frac{0.0591}{z} \log [a_{M^{z+}}] \quad (1.36)$$

For polarized electrode, the potential remains not in nominal equilibrium. The potential in polarized condition is higher,  $E'_p$  as compared to equilibrium due to enhance ion activity at the polarized surface of the electrode. The equation can represent as,

$$E'_p = E^{\circ} + \frac{0.0591}{z} \log [a_{M^{z+}}]_p \quad (1.37)$$

By the difference of these two equations, we get concentration polarization  $\eta_c$  for any given current.

$$\eta_c = E'_p - E' = \frac{0.0591}{z} \log \frac{[a_{M^{z+}}]_p}{[a_{M^{z+}}]} \quad (1.38)$$

The  $[a_{M^{z+}}]_p$  and  $\eta_c$  rises with increasing current. But sooner the ion activity on the surface of electrode attains saturation with a limiting current density.

In deposition process:



The solution at the surface of electrode is depleted of  $M^{z+}$  ions. So the,  $\eta_c$  is in the opposite sense,

$$\eta_c = E' - E'_p = \frac{0.0591}{z} \log \frac{[a_{M^{z+}}]}{[a_{M^{z+}}]_p} \quad (1.40)$$

Such process have the same condition of limiting current density, because with increase in current  $[a_{M^{z+}}]_p \rightarrow 0$  and therefore  $\eta_c \rightarrow \infty$ .

### 1.7.2.3 Ohmic Resistance

In some reactions at the electrode surface the effect of resistance or ohmic polarization is very considerable. This is notable when a film is formed on electrode surface by a reaction itself or by a complementary reaction. In that condition of resistance the whole potential drop is known as resistance or ohmic polarization,  $\eta_R$ . Hence, the overall polarization at an electrode is the summation of the entire three activation, concentration and resistance polarization,

$$\eta_{\text{TOTAL}} = \eta_A + \eta_C + \eta_R \quad (1.41)$$

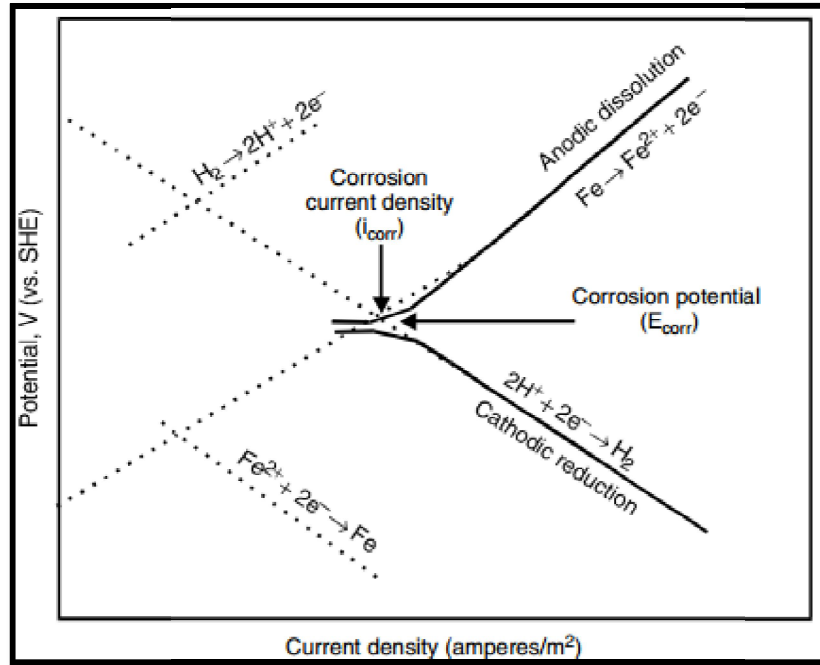
## 1.8 Mixed Potential theory and Evans Diagram

The mixed potential theory was introduced to understand about the various electrochemical reactions occurring simultaneously at the metal/solution interface. The corrosion potential developed during the electrochemical reactions (anodic and cathodic) at electrode surface is a mixed potential that lies in between the equilibrium potential of these two involved reactions.

Evans has proposed a diagram to study the kinetics of corrosion, which represents the relation between the electrode potential and current density [Akid (2004)]. Evans diagram for iron immersed in acidic solution is shown in Figure 1.7.

Theoretically four reactions can take place in such systems. These are (i) the iron dissolution to form ferrous ions ( $\text{Fe}^{2+}$ ) (ii) ferrous ions getting electrons to form Fe (iii) hydrogen gas formation from hydrogen ion in the solution and (iv) is the reverse of this process to form hydrogen ions. Therefore, four E vs.  $i$  lines are shown in the Evans diagram. Among these four reactions, the two thermodynamically feasible reactions are

represented by solid lines. The extrapolation of these solid lines gives an intersection at the corrosion potential,  $E_{\text{corr}}$  and corrosion current density,  $i_{\text{corr}}$ .



**Figure 1.7** Evans diagram for iron in acid solution.

By the corrosion current versus potential graph the four important values, corrosion current density ( $i_{\text{corr}}$ ), corrosion potential ( $E_{\text{corr}}$ ), anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ ) tafel constants can be obtained. If the potential is moving away from  $E_{\text{corr}}$ , by  $+\Delta E$  ( $= E - E_{\text{corr}}$ ) then a straight line is observed,

$$\eta_a = \beta_a \log \frac{(i_{\text{app}})}{(i_{\text{corr}})} \tag{1.42}$$

where  $\eta_a = E - E_{\text{corr}}$  and  $\eta$  represent the overpotential.

In the same way if the potential is moving by  $-\Delta E$ , then the following equation is observed,

$$\eta_c = \beta_c \log \frac{(i_{app})}{(i_{corr})} \quad (1.43)$$

### 1.9 Tafel extrapolation method

The Tafel extrapolation technique is used to find out the corrosion rate of the metal, when the dissolution of metal is under activation control [McCafferty (2010)]. The metal immersed in de-aerated acid solution is the most common application and for that the anodic and cathodic reaction is given as,

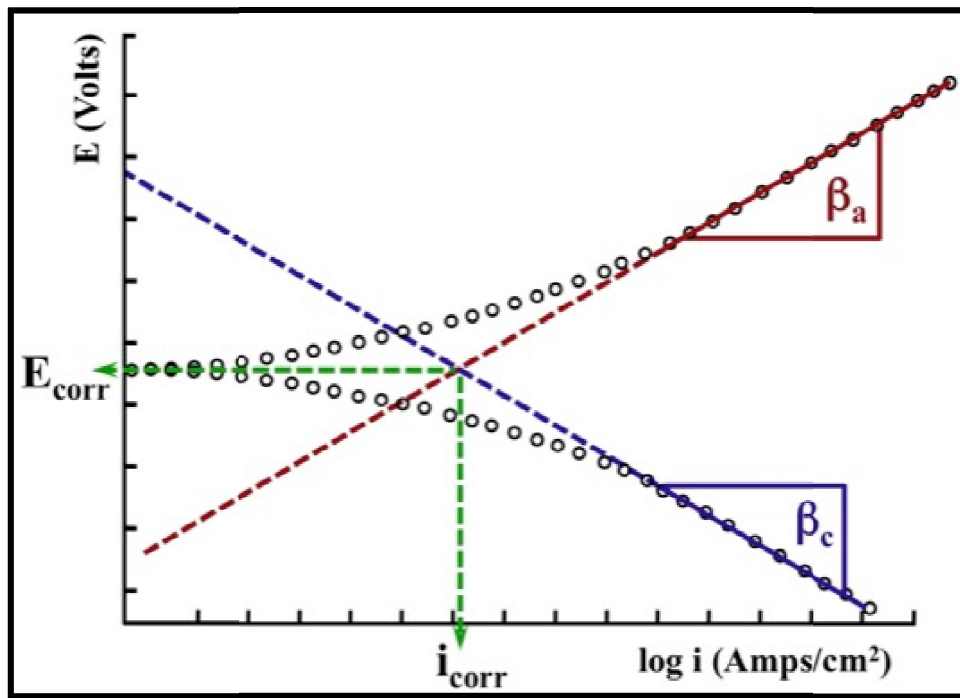


In the de-aerated condition the hydrogen evolution alone occurs as cathodic reaction rather than the cathodic reduction of oxygen. In acid solution, the oxide layer primarily present on metal surface dissolves due to contact with acid solution, which is in the route to achieve the steady state open circuit potential. Therefore, the anodic reaction solely represents the dissolution of bare metal surface. Stern and Geary [Stern (1958), and Stern and Geary (1957)] have introduced this for the measurement of corrosion kinetic parameters, by the extrapolation of the anodic and cathodic tafel branches gives the corrosion potential,  $E_{corr}$  and corrosion current density,  $i_{corr}$  as shown in the Figure 1.8.

The Tafel extrapolation technique has some limitations like,

- (i) Both the anodic and cathodic branches for the polarization curves are activation controlled.
- (ii) A clearly defined anodic and cathodic tafel region should be present (on at least one decade of current).

(iii) For the determination of polarization curve, the anodic and cathodic reaction that occurs at corrosion potential is the only reaction that can occur. It means that the changes occurring in electrode potential should not promote other electrochemical reactions in either anodic or cathodic directions.



**Figure 1.8** Extrapolated Tafel curve.

By the sole extrapolation of either cathodic or anodic region in the Tafel polarization curve, the corrosion rate can be observed. If only one polarization curve is considered, then usually the cathodic one produces the better and well defined tafel region. The anodic polarization curve may sometime fabricate concentration effect depending upon the surface conditions like rough surface which causes deviations from tafel behaviour. Therefore, the extrapolation of the cathodic tafel region back to zero overvoltage provides the corrosion rate of the cathodic reaction at the corrosion potential but it is also the net corrosion rate for the anodic reaction at corrosion potential. The use of both the tafel regions is favoured of course over just one of them.

## 1.10 Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) measures the electrode response to the sinusoidal potential modulation at different frequencies. The mathematical approach of the EIS study is based on Ohm's law about the linear correlation between the perturbed potential and the current response. Generally, the potential current responses for the electrochemical system are not linear but on considering a very small fraction of the outputs like (5-10 mV), the responses seems as linear. Accordingly, the impedance study was performed under the sinusoidal potential modulation with a small amplitude 5-10 mV. The perturbed sinusoidal potential  $E(t)$  produces a sinusoidal current  $I(t)$  of the same frequency ( $\omega$ ). This is superimposed on the steady state current with phase shift ( $\phi$ ) as regarding the potential [Cesiulis *et al.* (2016)]. The same as for the physical electric circuit, the electrochemical impedance of the electrode reaction ( $Z$ ) is studied similarly by Ohm's law as,

$$Z(\omega) = \frac{E(t)}{I(t)} = \frac{|E_0| \sin(\omega t)}{|I_0| \sin(\omega t - \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t - \phi)} \quad (1.46)$$

where  $E_0$  and  $I_0$  is the amplitude of the potential and current,  $\omega$  is the radial frequency ( $\omega=2\pi f$ ),  $f$  is frequency in Hz.

In the polar co-ordinate such functions are illustrated by the vectors of length  $|E_0|$  and  $|I_0|$  rotating counter clockwise at the radial frequency  $\omega$ . These functions can be elucidated with the help of complex numbers [Cesiulis *et al.* (2016)]. By the mathematical equation,

$$\exp(jx) = \cos x + j \sin x \quad (1.47)$$

it is obtained,



$$E(t) = |E_0| \exp(j\omega t) \quad (1.48)$$

$$I(t) = |I_0| \exp(j\omega t - \phi) \quad (1.49)$$

$j$  represents a complex unit  $j = \sqrt{-1}$ .

Therefore the earlier equation can be rewritten to describe the electrochemical impedance, the sum of the real ( $Z_{Re}$ ) and the imaginary part ( $Z_{Im}$ ) at a certain  $\omega$ ,

$$Z(\omega) = |Z_0| \exp(j\phi) = |Z_0|(\cos\phi + j\sin\phi) = |Z_0|\cos\phi + j|Z_0|\sin\phi = Z_{Re} + jZ_{Im} \quad (1.50)$$

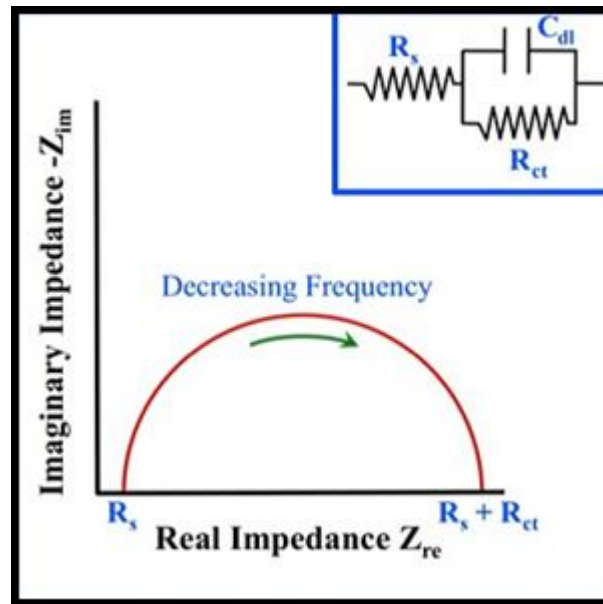
According to the theory of complex function the modulus of impedance,  $\tan\phi$  and  $\phi$  are shown by the following equation,

$$|Z(\omega)| = \sqrt{Z_{Re}^2 + Z_{Im}^2} \quad (1.51)$$

$$\tan\phi = \frac{Z_{Im}}{Z_{Re}} \quad (1.52)$$

$$\phi = \arctan \frac{Z_{Im}}{Z_{Re}} \quad (1.53)$$

The evaluation of the electrochemical impedance data depends upon the plot between the imaginary impedance components ( $Z_{Im}$ ) against the real impedance ( $Z_{Re}$ ) at the every excitation frequency of the Nyquist plot. That type of plot is known as Cole - Cole or the complex impedance plane plot. The other systems for the evaluation of electrochemical impedance are known as Bode plots, which are between  $|Z(\omega)|$  and  $\phi$  versus  $\log \omega$ . The advantage of Bode plot is that the frequency appeared in on one of the axes in that plot; by this the dependency of impedance on frequency, can be easily understood. But bode plot also has some disadvantages such as the shape of the curve can change if there is a change in circuit value.



**Figure 1.9** Nyquist plot along with constant phase element (CPE).

So, preferentially EIS method analysed both the Nyquist and Bode plots. For the analysis of EIS results an equivalent circuit model is used for data fitting that consists  $R_s$  (solution resistance), CPE (constant-phase element) parallel to the  $R_{ct}$  (charge-transfer resistance) as shown in the Figure 1.9 [Cesiulis *et al.* (2016)].

### 1.11 Corrosion control methods

There are various methods for corrosion control:

- (i) Proper selection of the material
- (ii) Modification of the materials
- (iii) Modification of the design
- (iv) Use of the inhibitors
- (v) Modification in the corrosive environment
- (vi) Modification of the surface

From the available various corrosion control methods the use of corrosion inhibitors is the most efficient and cost effective method.

## **1.12 Corrosion inhibitors**

Corrosion inhibitors are the chemical substance, which effectively prevent corrosion by the addition in a very low concentration without any significant change to the environment. The proposed definition about corrosion inhibitors is given as:

Corrosion inhibitors are the substances, which when added in small quantity to corrosive environment lower the corrosion rate. They reduce corrosion by either acting as a barrier by forming an adsorbed layer or retarding the cathodic and/or anodic process [Sastri (1998)].

### **1.12.1 Classification of corrosion inhibitors**

These are briefly classified [Revie and Uhlig (2011)] as listed in Table 1.1.

### **1.12.2 Environmental conditioners**

By removing the corrosive species in the medium the corrosion can be controlled. The inhibitor which reduces corrosiveness in the medium by scavenging the aggressive substances is known as environmental conditioners.

### **1.12.3 Interface inhibitor**

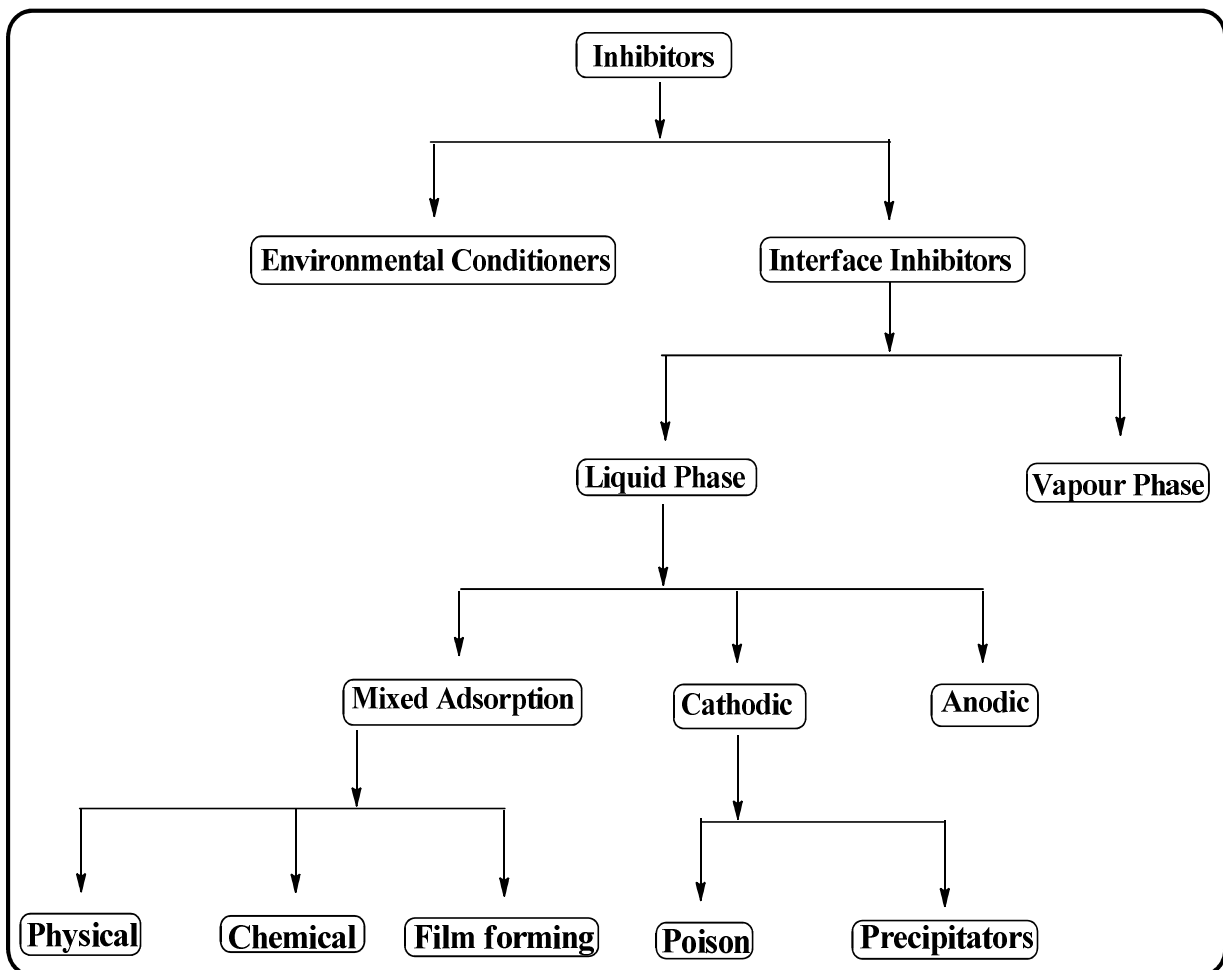
Interface inhibitors are divided into two parts: liquid phase and vapour phase inhibitors. The liquid phase inhibitors are further divide into three parts.

**1.12.3 (a) Anodic inhibitors:** The anodic types of inhibitors are used in near neutral solutions in which soluble corrosion product like oxides, hydroxides or salts are formed. Such type of corrosion product creates formation of a passive layer on metal surface that inhibits corrosion via preventing anodic dissolution. When the concentration of

anodic type inhibitor is not sufficient then the corrosion process can be accelerating instead of inhibition.

**1.12.3 (b) Cathodic inhibitors:** The cathodic type of inhibitors control corrosion by reducing the reaction rate at cathodic side in the electrochemical corrosion cell. They can perform by blocking the cathodic sites by precipitation. As, Bi, and Sn are referred as cathodic poison, which decreases the reaction rate of hydrogen reduction therefore lowers the corrosion rate. The elimination of oxygen from the corrosive environment reduces the corrosion rate.

**Table 1.1** Classification of corrosion inhibitors.



**1.12.3 (c) Mixed inhibitors:** They protect the metal from corrosion in three possible ways such as physisorption, chemisorption and film formation. The performance of mixed type of inhibitors depends on their adsorption tendency and coverage of metal surface. The planar molecular structure of the inhibitor facilitates the adsorption. The mixed type of inhibitor may retard both the electrode processes. According to the environment inhibitors are further classified as acid, base, and neutral inhibitors. They are further classified into inorganic and organic inhibitors.

**(a) Inorganic inhibitors:** The salts of metals are added in the corrosive medium in order to improve inhibition. The metal is protected due to reduction of the present electropositive ions and then the accumulation on the metal surface. This results in lowering the overvoltage of the main cathodic depolarization process [Tomashov (2012)]. The effectiveness of the inorganic anions has been studied along with the organic compound in various acid solutions for metals. In the neutral medium, the contact of inhibitor to the metal surface covered with oxide layer and prevention of oxygen reduction at cathode side takes place. These inhibitors protect the metal surface from aggressive medium. Firstly the displacement of already adsorbed water molecules from metal surface occurs by the inhibitor molecules via chemical or electrochemical reactions. Thus the inhibitors which prevent oxygen reduction at cathode at the metal surface are known as cathodic inhibitors.

**(b) Organic inhibitors:** Heterocyclic compounds containing unshared electron pairs and  $\pi$  electrons act as good corrosion inhibitors [Li *et al.* (2011) (a)]. Various organic compounds have been reported that effectively inhibit corrosion and show high inhibition performance [Cruj *et al.* (2004)], [Wahdan and Gomma (1997)], [Bentiss *et al.* (2000)], [Abdennabi *et al.* (1996)], [Granese *et al.* (1992)], [Gomma (1998)], [Qu *et al.* (2007)].

They can be of anodic, cathodic or mixed type depending upon their reaction occurring at metal surface and potential shift. The effectiveness of these compounds depends on their molecular structure, size, planarity, aromaticity, conjugation etc [Schmitt and Bedbur (1985)].

#### **1.12.4 Interface inhibitors (Vapour phase)**

The vapour phase inhibitors are used to prevent atmospheric corrosion of metals in the closed spaces. These are substances having low but significant vapour pressure. The vapours of such inhibitors come in contact with the metal surface and the adsorption of inhibitor occurs followed by the hydrolysis due to moisture and liberation of protective ions that have corrosion inhibition properties.

#### **1.13 Adsorption of inhibitors**

The inhibitor molecules get adsorbed and form a layer on the metal surface. The adsorption can be as physical and chemical type. The adsorption of inhibitor molecules impedes the anodic or cathodic reaction or both the reactions at electrode surface in presence of electrolyte. The three adsorption types are as:

**1.13.1 Electrostatic adsorption:** This type of adsorption occurs due to the columbic or electrical forces which stretched out by the metal are longer in the range than the chemical forces, by which the inhibitor molecules are attracted to the metal surface

**1.13.2 Physisorption:** The physisorption occurs due to electrostatic interaction between inhibitor ions and charged metal surface. The metal surface is charged because of the electric field at the outer Helmholtz plane of the electrical double layer that exists at metal/solution interface. The surface charge of metal can be defined by the OCP (open

circuit potential) versus PZC (potential of zero charge) of that particular metal. If the difference is negative, the cation adsorption is favoured and if it is positive anion adsorption is favoured.

**1.13.3 Chemisorption:** This occurs by charge sharing from inhibitor molecules with metal which results in a coordinate type of bonding. Heterocyclic compounds containing multiple bonds are considered as good corrosion inhibitors due to easy electron transfer. The adsorption of inhibitor molecules covers the metal surface. The increase in the surface coverage leads to stronger adsorption and high corrosion inhibition efficiency.

#### **1.14 Adsorption isotherms**

The organic inhibitors inhibit corrosion by adsorption on the metal surface. When the corrosion rate is decreased by organic inhibitor due to adsorption, a state of quasi equilibrium is formed. This equilibrium adsorption state can be investigated using appropriate adsorption isotherm [Wranglén (1972)]. Different adsorption isotherms as listed in Table 1.2 were used to fit for the interpretation of the inhibition characteristics of organic molecules [Damaskin *et al.* (1971)].

**Table 1.2** Adsorption isotherms.

Serial number	Isotherms	Equations
1.	Langmuir	$\beta C_{\text{inh}} = \frac{\theta}{1 - \theta}$
2.	Freundlich	$\beta C_{\text{inh}} = \theta$
3.	Temkin	$\beta C_{\text{inh}} = \frac{\exp(a\theta) - 1}{1 - \exp[-a(1 - \theta)]}$
4.	Frumkin	$\beta C_{\text{inh}} = \frac{\theta}{1 - \theta} \exp(-2a\theta)$

Where  $\beta$  = adsorption constant  
 $\theta$  = surface coverage  
 $C_{\text{inh}}$  = Inhibitor concentration  
 $a$  = molecular interaction constant  
 $a > 0 \Rightarrow$  attraction and  $a < 0 \Rightarrow$  repulsion

### 1.15 Corrosion inhibition of mild steel in mineral acids

Mild steel is a widely used construction material due to its low cost and high mechanical properties. Some industrial processes such as acid pickling and acid descaling require the use of mineral acids, especially hydrochloric and sulphuric acids. Hydrochloric acid is the most commonly used mineral acid because it pickles faster in comparison to sulphuric acid [Subramaniam *et al.* (1990)]. These processes are important because they remove unwanted scale and salt deposits or mill scales that are formed during manufacturing [Obot and Obi-Egbedi (2010)], [Rocha *et al.* (2010)]. Unfortunately, the acids used in the course of these processes promote corrosion. The damage due to corrosion of metals engenders high cost for renovation, replacement of



various equipments and causes public and environmental risks. The use of chemical corrosion inhibitors is a good option to protect metals from such type of corrosion. The adsorption of inhibitor molecules on metal surface prevents direct contact between the metal and the acid solution. Usually, heterocyclic compounds are considered as good corrosion inhibitors because of the ease of electron donation to the metal [Ostovari *et al.* (2009)], [Schmitt (2013)], [Quraishi and Sardar (2003)]. Molecules with triple or conjugated double bonds and aromatic rings are also promising corrosion inhibitors. The adsorption of inhibitor molecules builds a protective film on corroding surface of the metal that results to lessen the corrosion rate.

### **1.16 Application of theoretical methods in corrosion inhibitor studies**

The quantum study and molecular dynamics simulations provide an approach about the reactivity, planarity, binding properties of any organic molecule along with the attached substituents [Sasikumar *et al.* (2015)]. The calculation of theoretical parameters have some advantages like the organic molecules can be easily characterised based on their molecular structure and their proposed mechanism of action in terms of chemical reactivity can be studied [Levine (1991)]. The quantum chemically calculated parameters are fundamentally different from the experimentally calculated results, though there is some natural overlap. There is no statistical error in quantum chemical calculations just like in experiment. There can be some inherent error but, as associated with the assumptions require facilitates the calculation. By the help of computational simulation software's it is easy to predict the corrosion inhibition efficiency of the investigated molecules. Density function theory (DFT) is a computational quantum parameters mechanically modelling method to calculate HOMO, LUMO, Mulliken charges, fraction of electron transfer from inhibitor to metal, chemical hardness,

softness, proton affinity, electronegativity, electrophilicity and nucleophilicity are very useful to predict chemical reactivity of organic molecules [Gece (2008)], [Mousavi and Baghcoli (2016)]. Koopman's theorem gives immense facilities in the calculation of these mentioned chemical properties [Koopmans (1934)]. According to the theory, the ionization energy and electron affinity values of any chemical species are associated to their HOMO and LUMO energy values. The hard-soft acid and base (HSAB) theory by Pearson states that "The hard acids prefer to co-ordinate with hard bases and same as soft acid with soft bases" [Chattaraj *et al.* (1991)], [Pearson (1963)], [Pearson (1968)]. The polarisable chemical compounds are based on soft concept. Thus the effectiveness of organic molecule towards metal corrosion inhibition can be estimated by using the DFT study.

The molecular dynamics simulations have been also considered a useful modern tool to study the adsorption manner of studied inhibitor molecules for the concern metal surface [Khaled (2009)]. The adsorption of studied organic inhibitor at (110) surface of Fe single crystal was also investigated using Adsorption Locator module developed in BIOVIA Materials Studio programme package. The simulations were performed to find the preferential adsorption sites and their adsorption energy modelling of the selected compounds situated at the surface of the Fe crystal [Musa *et al.* (2012)].

### **1.17 Literature survey on organic compounds as corrosion inhibitors**

The use of corrosion inhibitors is one of the finest methods to protect metal corrosion. Most of the used corrosion inhibitors in industries are the organic compounds having heteroatoms (O, N, and S) with high electron density and multiple bonds in the molecule through which they get adsorbed on the metal surface. Various researchers have made attempts to investigate the corrosion inhibition performance of organic

compounds for mild steel in acid medium. A brief review of the research work carried out by them is given below.

Inhibitors/Metal Alloy/Medium	Remark	Reference
3,5-bis (2-thienyl)-4-amino-1,2,4-triazoles (2-TAT)/Mild steel/1 M HCl, 0.5 M H <sub>2</sub> SO <sub>4</sub>	2-TAT inhibits the corrosion of mild steel in both acids but better performance is seen in the case of HCl i.e. 98.3% at 100 mg/l. 2-TAT behaves as an anodic inhibitor.	[Bentiss <i>et al.</i> (1999) (a)]
2 5- 2-pyridyl -1,2,4-triazol-3-yl phenol (PPT)/ Mild steel/1 M HCl	PPT inhibits the corrosion showing 96.3% at 80 mg/l. PPT is found to affect both the anodic and cathodic process, i.e. PPT is a mixed type inhibitor. The adsorption of PPT obeys a Langmuir adsorption isotherm.	[Bentiss <i>et al.</i> (1999) (b)]
4-amino-3-butyl-5-mercapto-1,2,4-triazole (ABMT)/ Mild steel/1 N H <sub>2</sub> SO <sub>4</sub>	ABMT shows 89% at 1000 ppm. It is a mixed type of inhibitor. It inhibits the corrosion by getting adsorbed on the metal surface follows Temkin's adsorption isotherm.	[Quraishi and Sharma (2003)]
3,5-bis(4-methoxyphenyl)-4-amino-1,2,4-triazole (4-MAT) /Mild steel/1 M HCl	4-MAT) shows excellent inhibition 98% at optimum conc. $4 \times 10^{-4}$ M. Based on the polarization results, the investigated 4-aminotriazole can be classified as mixed inhibitor. With increase in concentration, increase obtained in $R_{ct}$ values and decrease in of the capacitance, $C_{dl}$ obtained. The adsorption model obeys to the Langmuir adsorption isotherm and the negative value of the Gibbs free energy of adsorption ( $\Delta G_{ads}$ ) indicates that the adsorption of the 4-MAT molecules is a spontaneous process.	[Bentiss <i>et al.</i> (2009)]
4,4-dimethyl-3-oxo-2 (1,2,4)triazol-1-yl-pentanethioic acid phenylamide (DTP) / Mild steel/0.5M H <sub>2</sub> SO <sub>4</sub>	Polarization curves proved that the DTP was the mixed-type inhibitor. EIS plots indicated that the inhibitor increased the charge transfer resistance and it showed that the inhibitive performance depended on the adsorption of the molecule on the metal surface. The adsorption model obeyed Langmuir adsorption isotherm. The adsorption	[Tao <i>et al.</i> (2009)]

	equilibrium constant ( $K_{ads}$ ) decreased with the temperature.	
2-(2-trifluoromethyl-4,5-dihydro-imidazol-1-yl)-ethylamine(1-IM), 2-(2-trichloromethyl-4,5-dihydro-imidazol-1-yl)-ethylamine(2-IM) /Mild steel /0.5 M HCl	1-IM and 2-IM act as good inhibitors. When the temperature increases, the inhibitive effect of 1-IM decreases while that of 2-IM does not significantly change. The halogen-substituted imidazoline indicates that the chloride substituted inhibitor functions more effectively than the fluoride version.	[Zhang <i>et al.</i> (2015) (a)]
2-methyl-4-phenyl-1-tosyl-4,5-dihydro-1H-imidazole (IMI)/ P 110 carbon steel/ 1 M HCl	IMI shows excellent inhibition 94% at 300 mg/l. MI inhibitor can be defined as an excellent mixed-type inhibitor. The adsorption behaviour of IMI inhibitor on metal surface obeys the Langmuir adsorption model. SEM analysis indicates that the addition of IMI into the aggressive solution can remarkably protect carbon steel material	[Zhang <i>et al.</i> (2015) (b)]
2-aminobenzimidazole (AB), 2-(2-pyridyl)benzimidazole (PB), 2-aminomethylbenzimidazole (MB), 2-hydroxybenzimidazole (HB), benzimidazole (B)/ iron/ 1 M HCl	All the benzimidazoles act as good inhibitors and show the following order of inhibition AB>PB > MB> HB>B. A good correlation between the highest occupied molecular orbital $E_{HOMO}$ and inhibition efficiencies was sought.	[Khaled <i>et al.</i> (2003)]
9H-pyrido[3,4-b]indole (norharmane), 1-methyl-9Hpyrido[3,4-b]indole (harmane)/ C38 steel/1 M HCl	Norharmane and harmane were found to inhibit corrosion for C38 steel and their inhibition efficiency increased with increasing concentration. The $i_{corr}$ values decrease considerably in the presence of harmane and norharmane with increasing inhibitor concentration. The values of $E_a$ determined in 1 M HCl containing indole derivatives are higher than that for uninhibited solution. The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage.	[Lebrini <i>et al.</i> (2013)]

4-hydroxy- <i>N'</i> -[( <i>E</i> )-(1 <i>H</i> -indole-2-ylmethylidene)] benzohydrazide(HIBH)/Mild steel/1 M HCl	HIBH showed maximum inhibition efficiency, more than 90% at its optimum concentration 0.8 mM at all the studied temperatures. HIBH acts as mixed type inhibitor. The adsorption of HIBH on the mild steel surface obeys Langmuir adsorption isotherm. The corrosion inhibition mechanism of HIBH follows mixed adsorption type with predominately chemisorption.	[Kumari <i>et al.</i> (2014)]
Pyridine-2-thiol (P2T) ,2-Pyridyl disulfide (2PD) /Mild steel/0.1 M HCl	P2T and 2PD show good inhibitive performance and increase in each of the inhibitors concentration gives a noticeable improvement on their efficiencies. Adsorption of the present compounds obeys Langmuir isotherm and they show both chemisorption and physisorption onto the mild steel surface. Optical microscopy obviously reveals the corrosion attack morphology in absence and presence of inhibitors in 0.1 M HCl solution and it depicts that the mild steel surface will severely corrode if inhibitors are not used.	[Kosari <i>et al.</i> (2014)]
2-amino-6-methoxy-4-(4-methoxyphenyl) pyridine-3,5-dicarbonitrile (PC-1), 2-amino-6-methoxy-4-(4-methylphenyl) pyridine-3,5-dicarbonitrile (PC-2),2-amino-6-methoxy-4-phenylpyridine-3,5 di carbonitrile (PC-3) /Mild steel/1 M HCl	The percentage inhibition efficiency of PCs follows the trend PC-1 > PC-2 > PC-3. The potentiodynamic polarization curves indicated that PCs are acting as mixed inhibitors predominantly cathodic. Surface morphology revealed the formation of a protective film of PCs over the mild steel. The adsorption of PCs on mild steel surface has been described by Langmuir adsorption isotherm.	[Ansari <i>et al.</i> (2015)]
8-hydroxyquinoline/ Cold rolled steel /0.5 M/ H <sub>2</sub> SO <sub>4</sub>	The adsorption of 8 hydroxyquinoline onto the steel surface can be explained by the Temkin adsorption isotherm. The apparent activation energy increases with concentration of 8 hydroxyquinoline, and the elevation of apparent activation energy inhibits the steel corrosion in sulphuric acid. Polarization study reveals that it is cathodic type	[Tang <i>et al.</i> (2006)]

	inhibitor.	
8-hydroxy quinoline (HQ), 3-formyl 8-hydroxy quinoline (FQ) /Mild steel/1 M HCl	The compound FQ (90%) showed comparatively enhanced inhibition efficiency than HQ (86%) at 1.6% of inhibitor. The increased inhibition efficiency in case of FQ is due the presence of electroactive functional group that encourages higher interaction with metal for better adsorption. Adsorption of compounds on steel surface is spontaneous and obeys Langmuir's isotherm.	[Achary <i>et al.</i> (2008)]
N-((2-chloroquinolin-3-yl)methylene)aniline (CQM), N-((2-chloroquinolin-3-yl)methylene)-5-methylthiazol-2-amine (CQMA) /Mild steel/1 M HCl	CQM and CQMA were effective corrosion inhibitors. The polarization curves inferred that both acted as mixed-type inhibitors. The reduction in $C_{dl}$ is due to decrease of local dielectric constant or increase in thickness through adsorption of inhibitor molecules at the metal-solution interface. Adsorption of CQM and CQMA found to obey the Langmuir adsorption isotherm.	[Mistry <i>et al.</i> (2013)]
5-benzoyl-4,6-diphenyl-1,2,3,4-tetrahydro-2-thiopyrimidin (DHPM-I) /Stainless steel/0.5 M/ H <sub>2</sub> SO <sub>4</sub>	The addition of DHPM I induces a decrease in both anodic and cathodic currents. The corrosion potential ( $E_{corr}$ ) of DHPM I was observed to shift towards more noble potentials with increasing additive concentration, indicating the inhibitors to be of anodic character and formation of a surface film. The negative values of $G_{ads}$ show that the adsorption of inhibitor molecules on the metal surface is spontaneous. Dubinin Radushkevich model suggests that DHPM are adsorbed on stainless steel surface by physical adsorption mechanism.	[Caliskan and Akbas (2011)]
2-amino-3,5-dicarbonitrile-4-(4-methoxyphenyl)-6-(phenylthio)pyridine (ADTP I), 2-amino-3,5-dicarbonitrile-4-phenyl-6-(phenylthio) pyridine (ADTP II), 2-amino-3,5-dicarbonitrile-4-(4-nitrophenyl)-6-(phenylthio) pyridine (ADTP III) ) /Mild	This study has revealed that ADTPs are good corrosion inhibitors for mild steel in 1 M HCl. The order of inhibition efficiency is ADTP I > ADTP II > ADTP III at optimum concentration. Polarization measurements show that they are mixed-type inhibitors. However, the cathodic inhibiting effect is more prominent. Impedance data	[Sudheer and Quraishi (2014)]

steel/1 M HCl	and SEM results specify that dissolution of mild steel was prevented by the adsorption of ADTPs on its surface. The adsorption of ADTPs on mild steel followed the Langmuir adsorption.	
2-amino-4-(4-methoxyphenyl)-1,8-naphthyridine-3-carbonitrile(ANC-1), 2-amino-4-(4methylphenyl)-1,8 naphthyridine-3-carbonitrile (ANC-2) and 2-amino-4-(3 nitrophenyl)- 1,8 naphthyridine-3-carbonitrile (ANC-3) /N80 / 15% HCl.	The synthesized ANCs are effective inhibitor for N80 steel in 15% HCl. EIS spectra showed only one capacitive loop. The addition of ANCs increases $R_{ct}$ and decreases $C_{dl}$ values. Quantum chemical calculation supports well to the experimental results. Tafel polarization measurements showed that ANCs are mixed type but predominantly cathodic inhibitors. Langmuir adsorption isotherm model is best fitted to studied inhibitors.	[Ansari and Quraishi (2015) (a)]

The literature survey reveals clearly that inhibitors investigated by other authors exhibit good inhibition efficiency above 200-1000 mg/l. Conventional routes for synthesis of inhibitors was adopted by other authors which involves large amount of energy, high reaction time with low yield. In the present investigation green route for synthesis has been adopted which involved use of ultrasound and microwave methods that consumes less energy, giving high yields at moderate conditions in one step using green principles of green chemistry.

Although there are several papers on inhibitors for mild steel in hydrochloric acid. But our present work clearly creates a difference in inhibition characteristic of steel in hydrochloric acid. The compounds synthesized in present investigation give inhibition efficiency as high as 98% at very low concentration of 25 mg/l. while the other investigators have developed inhibitors which exhibit good inhibition efficiency at concentration as high as 200-1000mg/l.

In the present work the focus is on the application of greener techniques ultrasound and microwave which consumes less time, low energy, giving very pure compounds with high yield at moderate experiment conditions while the other investigator follows the conventional route which involves multistep synthesis of compounds using high energy, more time, giving fewer yields with side products.

In earlier investigations above points were not studied systematically so these gaps prompted me to undertake synthesis of highly functionalised organic inhibitors using principles of green chemistry.

The research objectives for the present work was:

### **1.18 Research objectives**

So my research objective for the present work is:

1. To synthesize effective corrosion inhibitors for mitigating of corrosion of mild steel in acid solution.
2. To evaluate the corrosion inhibition efficiency of synthesized compounds for mild steel in hydrochloric acid solution using weight loss, electrochemical impedance spectroscopy and potentiodynamic polarization methods.
3. To study the surface morphology of the inhibited mild steel specimen by using SEM/AFM/XPS.
4. To systematically study the reactivity and adsorption behaviour of the synthesized inhibitor on the mild steel surface by DFT and Monte Carlo simulations