CHAPTER 1

INTRODUCTION

CHAPTER-1

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Corrosion is the term usually applied to the "deterioration or destruction of metallic materials by its surrounding" [Speller (1935)]. It is generally accepted that corrosion is a reversion or a partial reversion from the metastable condition of the metal to its stable condition accompanied by a decrease in the free energy of the system. Corrosion is actually the most common electrochemical phenomenon experienced in daily life. In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive overdesign [Landolt (2007)]. The whole process of corrosion is shown below (Figure 1.1):

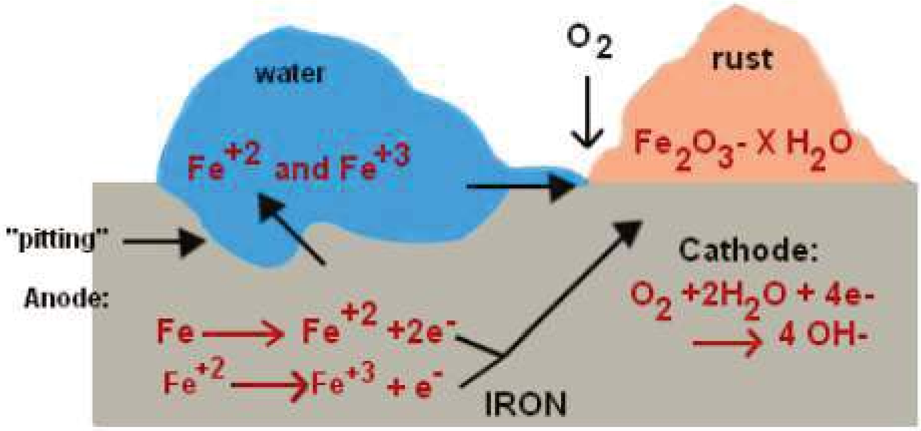
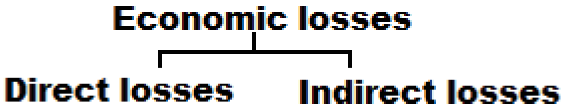


Figure 1.1 Pictorial representation of corrosion cycle.

Metals or alloys are usually attacked by water (and moisture in the air), acids, bases, salts, oil, and other solid and liquid chemicals. Metals are also susceptible to corrosion when exposed to corrosive gaseous materials like free acid vapors, formaldehyde, ammonia and sulphur in vapor state. Most metals are thermodynamically unstable under atmospheric conditions and hence have a tendency to revert back to their oxidized state as it is being favored by thermodynamics. This tendency is the characteristic of metals. The work described in this thesis aimed to develop N and O containing organic compounds to prevent dissolution of metal in acid medium. Investigation of the mode of action of the corrosion inhibition and the developments of new organic compounds and their mode of action are considered in remaining chapters.

1.1. Economic losses

Corrosion is a global phenomena, damaging the economic growth of both advanced as well as developing countries. Economic losses can be divided into direct and indirect losses. The loss to the world economy due to corrosion is in the billions of dollar per year. It is estimated that 25% of the total product of the metal and alloys go waste due to corrosion. In a widely-cited study (NACE Corrosion Costs Study) by the National Association of Corrosion Engineers, NACE, the total direct cost of corrosion in the U.S. was estimated to equal $276 Billion in 1998, approximately 3.1 % of GDP [NACE (2002)]. According to the study by CC Technologies for the Federal Highway Administration (FHWA) (2001) supported by NACE international the annual losses due to corrosion in USA were estimated to be more than $ 276 billion [Koch *et al*. (2001)]. The cost of corrosion in India is estimated approximately Rs 2 lakh crore ($ 45 billion) every year [1st Global Corrosion Summit (2011)].



Direct losses:

- Over-design to allow for corrosion.

- Inability to use desirable materials.
- Cost of anti-corrosive painting or other protection methods**.**
- The cost of repair or replacement of the corroded component.

Indirect losses:

- Product contamination.
- Loss of product.
- Damage of equipment adjacent to that in which corrosion failure occurs.
- Loss of valuable product from a container that is corroded.
- Safety, e.g., sudden failure of equipment may cause fire, explosion or release of toxic products.

1.2. General aspects of Corrosion

Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminology, corrosion processes involve reaction of metals with environmental species. or as the tendency of a metallic material to return to its original state, as it is found in nature [Fontana (1986)]; as a consequence, it is also known as metallurgy in reverse.

$M \rightarrow M^{n+} + ne^-$ (Anodic = Oxidation) (1.1)

$nH^+ + nSO_4^{2-} + ne^- \rightarrow n/2\ H_2SO_4$ (Cathodic = Reduction) (1.2)

$M + nH^+ + nSO_4^{2-} \rightarrow M^{n+} + n/2\ H_2SO_4$ (Overall = Redox) (1.3)

where, M= Metal , H^+= Hydrogen cation , n= Valence or Oxidation state, M^{n+} = Metal cation, SO_4^{2-}= Sulfate anion

The above equations contain an anodic reaction, which is known as oxidation, where the metal losses electrons and a cathodic reaction, which is equivalent to reduction, where acceptation or gain of electrons occurs. The combination of anodic and cathodic reactions is known as redox reaction, which is also termed as overall reaction.

1.3. Corrosion problems in oil/petroleum industry

In oil/petroleum industry, corrosion of steel and other metals is a common problem such as in gas and oil well equipment, refining operations, pipeline and storage equipment [C.J. Houghton *et al.* (1984), J.R. Stanford *et al.* (1976), S.P. Sharp *et al.* (1982)]. Corrosion damage in petroleum industry occurs mainly due to several chemical factors; like high contents of corrosive gases (CO_2, H_2S, etc.), high mineralization of water, and the presence of atmospheric oxygen in pipelines, some physical factors are also involved; such as temperature, hydrodynamics flow, pressure and metallurgical factors; such as the characteristics of the metal [S. S. Prabha *et al.* (2014)]. In sweet oil wells, pipelines are mostly corroded due to H_2CO_3, which is formed by the reaction between H_2O and CO_2. Sour wells represent a more corrosive environment due to high sulfur content and severely corrode the casing in the upper part of the well. In refineries corrosion of metal occurs due to the presence of carbon dioxide, saltwater, hydrogen sulphide, nitrogen, oxygen, sulphuric acid, ammonia, hydrochloric acid, caustic soda, mercaptan, and naphthenic acid.

1.4. Acidizing treatment in oil wells

Acidization of oil well through N80 steel tubes is a frequently used stimulation technique for increasing crude oil productivity by enlarging the microscopic flow channels. Acid treatments are commonly designed to include a range of acid types or blends, such as acetic acid, formic acid, hydrochloric acid, hydrofluoric acid and fluroboric acid [M. Finšgar *et al.* (2014)]. Hydrochloric acid is commonly used to remove plugging in the bore well and stimulates production because it is cheap and the ferrous chloride formed on the surface is soluble in water [Jayaperumal *et al.* (2000)]. The acid mixture is helpful in dissolving certain components of the drilling mud which blocks the inflow of oil in the producing zone. The treatment fluid typically comprises hydrochloric acid and acidic additives depending upon the underground nature of the oil wells. Applications for the various acid types or blends are based on reaction characteristics of the prepared treatment fluid.

Generally in the petroleum industry 15% hydrochloric acid is used for the acidizing treatment because it leaves no insoluble reaction products, commercially available and cost effective [P. Rajeev *et al.* (2012)]. In some cases, hydrofluoric acid mixed with other acids is used to dissolve clays and other silicate materials. The acid is pumped inside the well through steel tubing, which enters into the drainage channels tributary and dissolves the exposed limestone surfaces of the rocks. The acid reaction may be represented by the following equations.

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2 \qquad (1.4)$$

$$CaMg(CO_3)_2 + 4HCl \rightarrow CaCl_2 + MgCl_2 + 2H_2O + 2CO_2 \qquad (1.5)$$

1.5. Classification of corrosion

1.5.1. Dry corrosion or chemical corrosion

Dry corrosion occurs in the absence of liquid phase, which involve direct chemical reaction with non-electrolytic gas or liquid such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid with metal surface in immediate proximity and involves no transport of electric charge and the metal remains film free.

The fundamental steps involves in dry corrosion are:

$$2M \rightarrow 2M^{n+} + 2ne^{-} \qquad \text{(Loss of electrons)} \qquad (1.6)$$

$nO_2 + 2ne^- \rightarrow 2nO^{2-}$ (Gain of electrons) (1.7)

Oxide film formation on aluminium surface exemplifies the dry corrosion.

1.5.2. Wet corrosion or electrochemical corrosion

Corrosion takes place due to electrochemical attack in presence of moisture or a conducting medium with electric charge transfer. The reactions at electrodes are:

(b) Anodic processes:

$\mathrm{M} \rightarrow \mathrm{M}^{n+} + ne^-$ (1.8)

$\mathrm{M} + n\mathrm{H_2O} \rightarrow \mathrm{M(OH)}_n + n\mathrm{H}^+ + ne^-$ (1.9)

$\mathrm{M} + n\mathrm{H_2O} \rightarrow \mathrm{M(OH)}_n + n\mathrm{H}^+ + ne^-$ (1.10)

(c) Cathodic processes:

Hydrogen evolution reaction

$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H_2}$ (1.11)

Oxygen reduction in neutral or basic environment

$\mathrm{O_2} + 2\mathrm{H_2O} + 4e^- \rightarrow 4\mathrm{OH}^-$ (1.12)

Oxygen reduction in acid environment

$\mathrm{O_2} + 4\mathrm{H}^+ + 4e^- \rightarrow 2\mathrm{H_2O}$ (1.13)

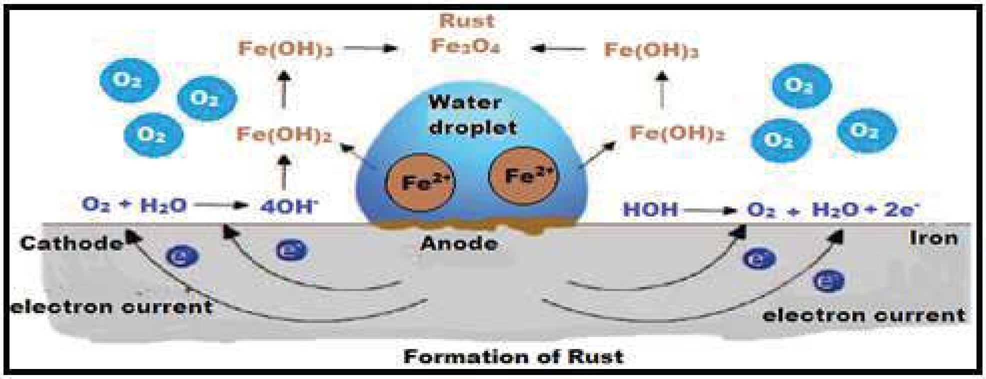


Figure: 1.2: Formation of rust

1.6. Common forms of corrosion

1.6.1. Uniform corrosion:

- Uniform corrosion, also known as general corrosion, is the uniform loss of metal over an entire surface.
- Examples: Rusting of iron, tarnishing of silver and fogging of nickel.
- Prevention: Use of metallic coatings such plating or anodizing, use of paints, use of corrosion inhibitors, cathodic or anodic protection.

1.6.2. Galvanic corrosion:

- Galvanic corrosion (also called bimetallic corrosion) is an electrochemical process in which one metal corrodes preferentially when it is in electrical contact with another, in the presence of an electrolyte. Generally, water, and especially salt water, serves as the conductive path between two metals so it is important to keep dissimilar metals separated in wet conditions.
- Examples: Corrosion at the junction of Steel-Al, Steel-Cu and Ti-Zn combinations.
- Prevention: Detail design, protective treatment, special assembly technique (sealing, electrical insulation of metals).

1.6.3. Crevice corrosion

- Crevice corrosion is a localized form of corrosion usually associated with a stagnant solution on the micro-environmental level.
- Examples: Coupling using flanges and spot welding types
- Prevention: Avoiding sharp corners, designing out stagnant areas and selection of resistant materials.

1.6.4. Pitting corrosion

- Pitting corrosion is a form of localized corrosion, which produces attacks in the form of spots or pits. Pitting corrosion may occur in stainless steels in neutral or acid solutions containing halides*, primarily chlorides (Cl^-), such as seawater.
- Prevention: Use higher alloys for increased resistance to pitting corrosion.
- Control pH chloride concentration and temperature.

1.6.5. Intergranular Corrosion

- **Intergranular corrosion occurs when the grain boundaries in a metal form an anode and the interior (the impurities) of the grain acts as a cathode. In serious cases this can lead to the grains falling apart.**
- Selection of stabilized materials and control of heat treatments
- Processing to avoid susceptible temperature range.

1.6.6. Stress Corrosion

- Stress corrosion cracking (SCC) is a process that requires the simultaneous action of corrodent and sustained tensile stress.

- SCC, involving the initiation of cracks and their propagation, possibly up to complete failure of a component, due to the combined action of tensile mechanical loading and a corrosive medium.
- Prevention: control the hardness and stress level. Avoid the chemical sepsis that involves the SCC.

1.6.7. Fretting corrosion

- Fretting corrosion refers to the deterioration at the interface between contacting surface as the result of corrosion and slight oscillatory slip between two metals surface.
- Prevention: lubricate the surface
- Regularly inspect and maintain the lubrication.

1.6.8. Corrosion fatigue

- Corrosion fatigue is the fatigue in the corrosive environment. The combined action of cyclic stresses and a corrosive environment reduce the life of components below that expected by the action of fatigue alone.
- Prevention: reducing the fatigue by minimising vibration and pressure fluctuation. Reducing the corrosion by coating of the material and also used high performance alloys resistance to corrosion fatigue.

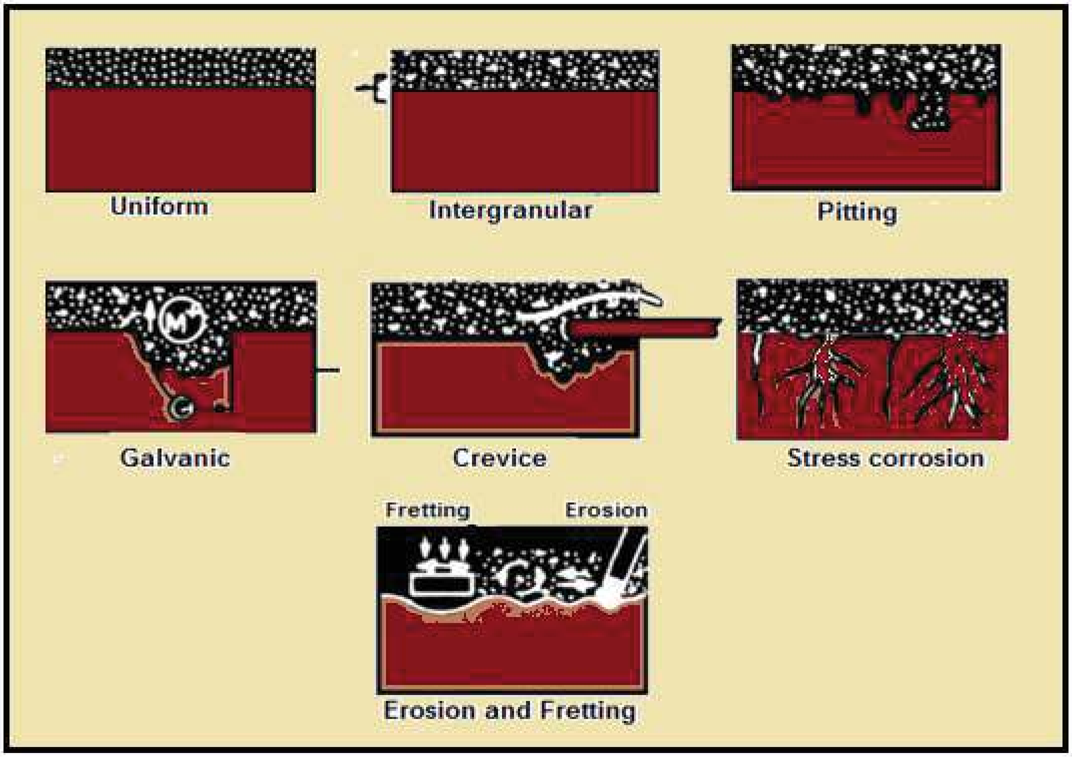


Figure 1.3: Common forms of corrosion

1.7. Factors affecting corrosion

The knowledge of the factors and the mechanism is essential with which corrosion rate is affected because the rate of corrosion is different in different atmosphere.

Two important factors are:

1.7.1. Metal behaviour

(a) Position in the galvanic series

When two metals are in electrical contact, the metal higher up in the galvanic series becomes anodic and suffers corrosion. Further, the rate and severity of corrosion depend upon the difference in their positions in the galvanic series. The greater is the difference, the faster is the corrosion of anodic metal.

(b) Relative areas of the anode and cathode

The rate of corrosion is more when the area of the cathode is larger. When the cathodic area is larger, the demand for electrons will be more and this results in increased rate of dissolution of metals at anodic regions.

(c) Physical state

The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc). The smaller the grain size of the metal or alloy, the greater will be its solubility and hence greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

(d) Solubility of the corrosion products

Solubility of the corrosion product formed is an important factor in corrosion. If the corrosion product is soluble in the corroding medium, the corrosion of the metal will proceed faster.

1.8. Theories of Corrosion

There are three theories of corrosion:

(i) Homogeneous theory

(ii) Heterogeneous theory

(iii) Mixed potential theory

(i) Homogeneous theory: According to this theory corroding metal is treated as a single electrode on which corrosion reactions occurs. Due to corrosion charge transfer reaction occurs at the metal solution interface and this makes metal to become unstable. So, it becomes essential to make the potential more negative than the equilibrium potential for cathodic reaction (electronation) or more positive than the equilibrium potential for anodic reaction (metal dissolution).

(ii) Heterogeneous theory: According to this theory, metal corrosion occurs when it comes in contact with moist atmosphere. In this generation of local galvanic cell arises over the corroding metal due to the structural heterogeneity. Though many theories have been put forward, the most acceptable theory is electrochemical or acid theory of corrosion [R.Walker (1907)]. The other old theories such as direct chemical attack theory [C.D. Bengoung *et al.* (1922)], Colloidal theory [J.N. Friend (1921)] and Biological theory [H.G. Reddic *et al.* (1932)] were either proved to form a part of electrochemical theory or found to be rarely applicable. The factors that are mainly responsible for corrosion are those associated with the metal, environment or both.

(iii) Mixed Potential Theory: According to this theory, electrochemical reactions are divided into two or more partial oxidation and reduction reactions [N. Perez (2010)]. During an electrochemical reaction there is no net accumulation of electrical charge, i.e. metal cannot spontaneously accumulate electrical charge when immersed in an electrolyte. For the corrosion of an electrically isolated metal sample, the total rate of oxidation must be equal to total rate of reduction [(R.H. Husler (1985)]. The polarization curves for corroding metal can be demonstrated by applying the mixed potential theory. More generally polarization of anodic and cathodic reactions occurs to same extent and thus corrosion is said to be under mixed control. The extent of polarization not only depends on the nature of metal and electrolyte, but also depends on the exposed area of the electrode [(I.N. Putilova *et al.* (1960)].

1.8.1. 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.

$$M \rightarrow M^{z+} + ze^{-} \qquad (1.14)$$

$$2\mathrm{H}^{+} + 2e^{-} \rightarrow \mathrm{H}_2 \qquad (1.15)$$

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

$$E_{\mathrm{cell}} = E_{\mathrm{c}} - E_{\mathrm{a}} \qquad (1.16)$$

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

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

$$\Delta G = -nF\Delta E \qquad (1.17)$$

Where, n stands for number of electron transferred, F stands for Faraday constant and ΔE represents the potential difference.

So, the thermodynamic condition for a corrosion process becomes:

$$\Delta G < 0 \text{ and } \Delta E > 0 \qquad (1.18)$$

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 ΔG 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)*],

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

where, E° represents Standard electrode potential, R for Gas constant (8.314 $JK^{-1}mol^{-1}$), 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 (mol dm^{-3}), [*red*] for Concentration of reduced species (mol dm^{-3}). The application of Nernst's equation for corrosion studies was embedded in the Pourbaix diagram.

1.8.2. Potential pH-diagram

To overcome some of the limitations of E.M.F. and galvanic series, a system showing the effect of both potential and pH has been evolved by Pourbaix in the form of E/pH diagrams. These diagrams often called Pourbaix diagrams or Potential-pH diagrams are plotted for various equilibria on normal Cartesian coordinates with potential on vertical axis and pH on horizontal axis or abscissa. The diagram takes account of electrochemical and chemical equilibria of metals in conjunction with water, and since there are several such equilibria for each metal, only one metal can be clearly represented on one diagram. Such diagrams are constructed using electrochemical calculations based on solubility data, equilibrium constants and the Nernst equation. The potential-pH diagram for iron exposed to water has been shown in Figure 1.4. It is necessary to consider the following equilibria before drawing the potential diagram for iron:

$$\mathrm{Fe} + \mathrm{Fe}^{2+} + 2\mathrm{e}^{-} \qquad \text{(Corrosion reaction)} \tag{1.20}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad \text{(Oxidation reaction)} \qquad (1.21)$$

$$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O \qquad \text{(Precipitation reaction)} \qquad (1.22)$$

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)^{2+} + 2H^+ \qquad \text{(Hydrolysis reaction)} \qquad (1.23)$$

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^- \qquad \text{(Corrosion reaction)} \qquad (1.24)$$

$$Fe + 3H_2O \rightarrow HFeO_2^- + 3H^+ + 2e^- \qquad \text{(Corrosion reaction)} \qquad (1.25)$$

$$HFeO_2^- + H_2O \rightarrow Fe(OH)_3 + e^- \qquad \text{(Precipitation reaction)} \qquad (1.26)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad \text{(Precipitation reaction)} \qquad (1.27)$$

Reactions (1.20), (1.21) and (1.26) are independent of pH and are represented by straight horizontal lines; while reactions (1.22), (1.24) and (1.25) are dependent upon pH and potential and are represented by the E_H/pH plots by sloping lines. Reactions (1.23) and (1.27) which only depend on pH are represented by vertical lines. Oxygen is evolved above but not below (line 'cd') in accord with the reaction:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad (1.28)$$

Hydrogen is evolved below but to above (line 'ab') in accord with the reaction:

$$H^+ \rightarrow \frac{1}{2}H_2 + e^- \qquad (1.29)$$

As can be seen in Figure 1.1 the redox potential of hydrogen electrode (line 'ab') lies above immunity region along all the pH scale. This means that Fe may be dissolved with evolution of hydrogen in aqueous solutions of all pH values. In the pH interval (9.4-12.5), however, a passivating layer of $Fe(OH)_2$ is formed (reaction 1.26). At higher values of pH soluble hypo ferrite can form within a restricted active potential range. At higher redox potential in the corroding medium, the passivating layer consist of $Fe(OH)_3$ or Fe_2O_3, nH_2O or Fe_2O_3 in different situations. Soluble ferrate (FeO_4^{-2}) can form in alkaline solutions at a very noble potential, but the stable field is not well defined.

Though the potential-pH diagram is quite useful in showing at a glance specific conditions of potential and pH under which the metal will corrode, there are several limitations regarding their use in practical corrosion problems. Since the data in potential-pH diagram are thermodynamic, they convey no information about the rate of reactions.

The major uses of such diagram which can be constructed for all metals are:

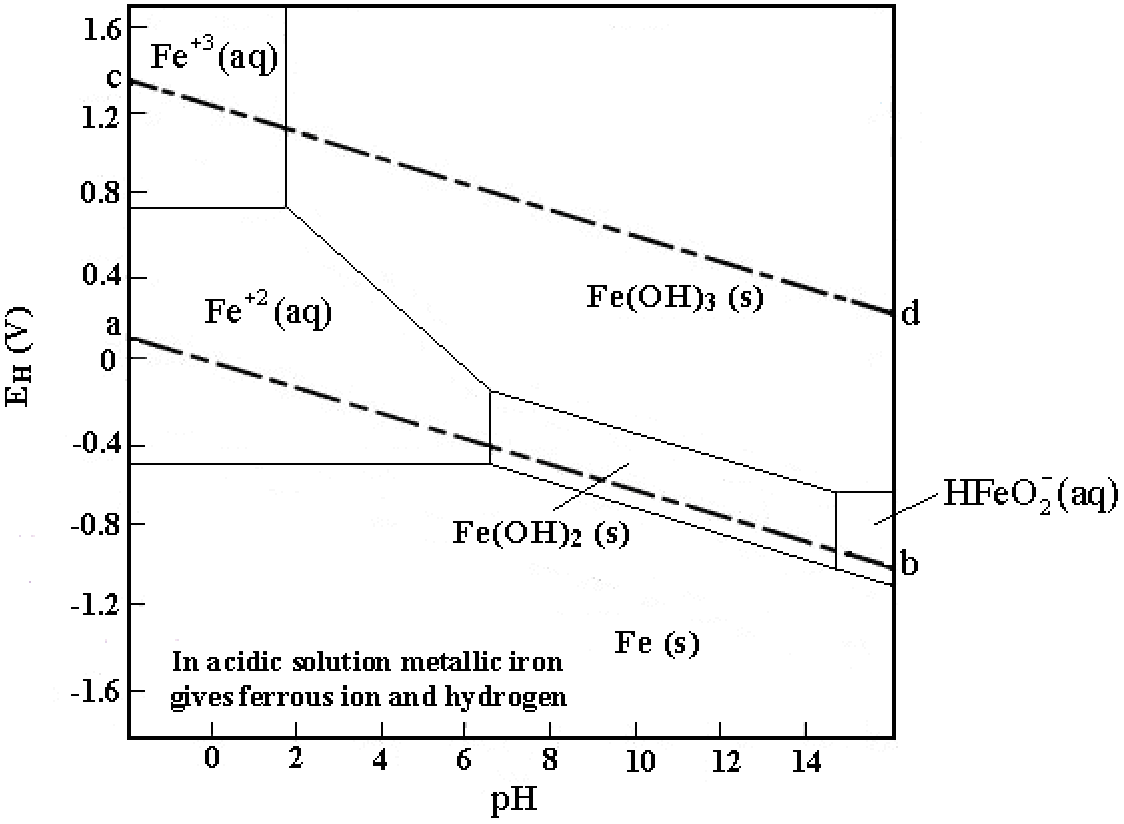


Figure 1.4: Pourbaix diagram for iron/water system at 298 K.

(i) Predicting whether or not corrosion will occur,

(ii) Estimating the composition of corrosion products formed, and

(iii) Predicting environmental changes which will prevent or reduce corrosive attack

1.8.3. Kinetic aspects - Polarization diagrams

1.8.3.1. Kinetic of equilibrium

When a metal in solution is at equilibrium, it implies rates of dissolution and deposition reactions are equal. When the two above reactions (anodic and cathodic) are in equilibrium, the rates (equal and opposite) of each of the two reactions are referred to as exchange current density. Expressing reaction rates in terms of current density,

$$r_{oxid} = r_{red} = \frac{i_0}{nF} \quad \text{(Based on Faraday's law)} \qquad (1.30)$$

where, $r_{red.}$ and $r_{ox.}$ are the equilibrium reduction and oxidation rates. i_0 is exchange in the current density which is the rate of oxidation and reduction at equilibrium. There is no net current under the above conditions even through the concept is a useful method of representing rates at equilibrium.

$$i_c = i_a = i_0 \qquad (1.31)$$

$$i_{net} = i_a - i_c = 0 \qquad (1.32)$$

There is no hypothetical method for precisely deciding the exchange current for any given system. This must be determined experimentally. For the characterization of electrochemical processes, it is always preferable to normalize the value of the current by the surface area of the electrode and use the current density, often expressed as a small i, i.e., i = I/surface area.

1.8.3.2. Kinetics of polarization

A system is out of equilibrium when the potential is displaced from the equilibrium potential by the application of an external voltage or by the spontaneous production of a voltage away from equilibrium. This deviation in potential is defined as polarization (η) [Fontana (1987)]. The polarization is said to be either anodic, when the anodic processes on the electrode are accelerated by changing the sample potential in the positive (noble) direction or cathodic when the cathodic processes are accelerated by moving the potential in the negative (active) direction. There are three distinct types of polarization and these are additive, as expressed in equation:

$$\eta_{\mathrm{total}}=\eta_{\mathrm{act}}+\eta_{\mathrm{conc}}+i\mathrm{R} \tag{1.33}$$

where η_{act} is the activation over potential, a complex function describing the charge transfer kinetics of an electrochemical reaction. η_{act} is always present and mostly dominant at small polarization currents or voltages, η_{conc} is the concentration over-potential, a function describing the mass transport limitations associated with electrochemical processes. η_{conc} is predominant at larger polarization currents or voltages; i_{R} is the ohmic drop.

1.8.3.3. Activation controlled polarization

A system is referred to be as activation controlled when the rate of the electrochemical process is controlled by the charge transfer across the metal solution interface. Activation polarization is a manifestation of the relative changes in the activation energies for dissolution and deposition, when equilibrium is disturbed. It is always a component of the total polarization, whether or not there are also significant contributions from concentration and resistance effects. The polarization is positive, i.e., *anodic*, or negative, i.e., *cathodic*, according to whether the net current is a dissolution or deposition current. A general representation of the polarization of an electrode supporting one specific reaction is given in the **Butler-Volmer equation**:

$$i_{reaction}=i_0\left\{\exp\left(-\beta\frac{nF}{RT}\eta_{reaction}\right)-\exp\left((1-\beta)\frac{nF}{RT}\eta_{reaction}\right)\right\} \tag{1.34}$$

where i_{reaction} is the anodic or cathodic current, β is the charge transfer barrier (symmetry coefficient) for the anodic or cathodic reaction, usually close to 0.5, n is the number of participating electrons, R is the gas constant, whose value is 8.314 J mol^{-1} K^{-1}, T is the absolute temperature (K), F corresponds to 96,485 C/ (mole of electrons).

When η_{reaction} is cathodic, i.e. negative, the second term in the **Butler-Volmer equation** becomes negligible and the cathodic current density (i_{c}) can be expressed by a simpler equation and its logarithm:

$$i_{reaction} = i_c = i_0 \exp\left(-\beta \frac{nF}{RT} \eta_{reaction}\right) \tag{1.35}$$

$$\eta_{reaction} = \eta_c = b_c \log_{10}\left(\frac{i_c}{i_0}\right) \tag{1.36}$$

where b_{c} is the cathodic Tafel coefficient which can be obtained from the slope of a plot of η against log i, with the intercept yielding a value for i_0

$$b_c = -2.303 \frac{RT}{\beta nF} \tag{1.37}$$

Similarly, when η_{reaction} is anodic, i.e. positive, the first term in the Butler-Volmer equation becomes negligible and the anodic current density (i_{a}) can be expressed by equation and its logarithm with ba obtained by plotting η_{reaction} vs. log i:

$$i_{reaction} = i_a = -i_0 \exp\left(1-\beta \frac{nF}{RT} \eta_{reaction}\right) \tag{1.38}$$

$$\eta_a = b_a \log_{10}\left(\frac{i_a}{i_0}\right) \tag{1.39}$$

$$ba = 2.303 \times \frac{RT}{\beta nF} \tag{1.40}$$

1.8.3.4. Concentration polarization

When a chemical species participating in a corrosion process is in short supply, the mass transport of that species to the corroding surface can become rate controlling. The effect arises because ions are produced or consumed at the electrode surface faster than they can diffuse to or from the bulk of the solution. In an anodic reaction, the concentration of ions in the immediate vicinity of the electrode is raised above that in the bulk solution; conversely, in a cathodic reaction, the local concentration is depressed. As a consequence, the polarization for a given current is greater than that predicted by the Tafel equation. The excess potential is called the concentration polarization, η_{conc} For a chemical species which is consumed by the cathodic reaction at the corroding surface, the concentration gradient ($\delta C_0/dx$) is greatest when the concentration of that species is completely depleted at the surface, i.e. $C_0 = 0$. It follows that the cathodic current is limited in that condition, as expressed by equation:

$$i_c = i_L = -nFD_0 \frac{C_0^{\text{bulk}}}{\delta} \qquad (1.41)$$

For intermediate cases, i.e. when the cathodic current is smaller than i_L, η_{conc} can be evaluated using an expression derived from Nernst equation:

$$\eta_{conc} = \frac{2.303 \times RT}{nF} \log_{10}\left(1 - \frac{i}{i_L}\right) \qquad (1.42)$$

where 2.303 $RT/F = 0.059$ V when T = 298.16 K.

1.9. CORROSION KINETICS

1.9.1 Graphical representation of kinetic data

Electrode kinetic data are typically presented in a graphical form called Evans diagrams or mixed-potential diagrams. However, the representation of the mixed potential behavior is often associated with Professor Evans who has popularized this representation of corrosion polarization measurements.

1.9.2 Evans diagram

Evans diagram is a kinetic diagram which represents electrode potential in volts verses corrosion current in ampere per unit area. Figure 1.5 represents the Evans diagram for iron corrosion in an acid solution.

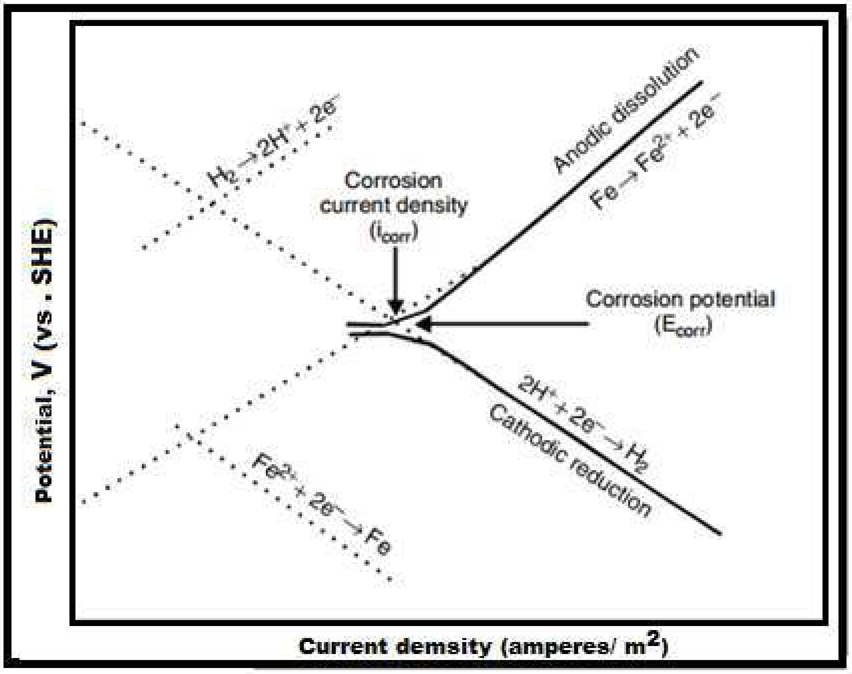


Figure 1.5: Schematic representation of Evans diagram for iron in acid solution.

For this kind of system theoretically four reactions are possible, i.e. oxidation of iron atoms to form ferrous ions (Fe^{+2}), reverse of this process i.e. ferrous ions gain electrons to form iron (Fe), hydrogen ions present in the electrolyte forming hydrogen gas and reverse of this reaction. And therefore, there are four potential (E) vs. current (i) are possible which are represented in the Evans diagram. For celerity purpose of the thermodynamically feasible reactions are shown in solid lines. The extrapolation these two solid lines give rise to an intercept at the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) for the system.

Generally, Evans diagrams kinetic provide information i.e. rate of corrosion reaction as a function of applied potential. The corrosion potential (E_{corr}) is in effect the line that differentiates the corrosion and immunity regions. In general, if the potential held below E_{corr} in Evans diagram, the rate of anodic reactions i.e. rate of iron dissolution decreases and rate of hydrogen evolution, that is, rate of cathodic reaction increases. While, if the potential held above E_{corr} in Evans diagram, the rate of anodic reactions i.e. metallic dissolution increases and rate of hydrogen evolution, i.e. cathodic reactions increases. And therefore, maintaining the potential below that of E_{corr} is adopted in practice ad is known as cathodic protection.

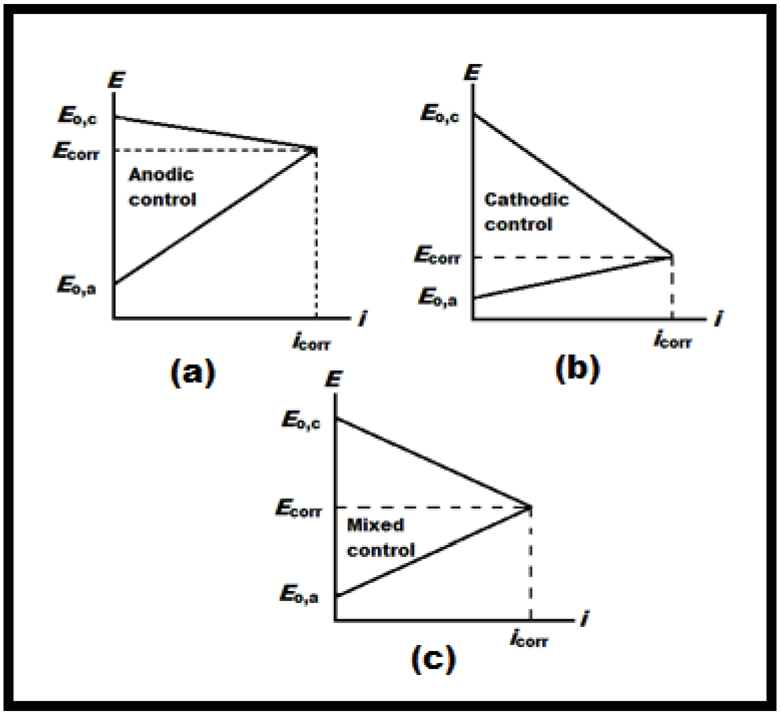


Figure 1.6: (a) Anodic control (b) cathodic control, (c) mixed control of a corrosion process.

Nevertheless,

Evans diagrams are a convenient way of viewing electrochemical reactions as shown in Figure 1.6, which tells us the control of electrochemical reaction in either in anodic, cathodic and mixed direction.

1.9.3. Mixed potential theory

The mixed potential theory is simply based on the simple hypothesizes:

(i) Every electrochemical reaction consists of two or more partial oxidation or reduction reactions

(ii) There can be no net accumulation of electric charge during the electrochemical corrosion of metal. This is simply a restatement of the law of conservation of charge.

On this basis it can be concluded that when a metal immersed in an electrolyte it cannot spontaneously accumulate electric charge. And therefore, during corrosion of an electrically isolated metal species, the total rate of oxidation must equal the total rate of reduction.

1.9.4. Corrosion potential and current density

To understand, what is corrosion potential and current density, consider the following anodic and cathodic reactions:

$$Zn \longrightarrow Zn^{2+} + 2^{e-} \quad \text{(anodic reaction)} \quad (1.43)$$

$$2H^{+} + 2^{e-} \longrightarrow H_2 \quad \text{(cathodic reaction)} \quad (1.44)$$

These two half reactions tales place simultaneously on the metallic surface and each half reaction has its own half-cell electrode potential and exchange current density as shown in Figure 1.7. However, these tow half-cell electrode potential ($E_{Zn2+/Zn}$ and $E_{H+/H2}$) cannot coexist separately on the electro conducting metal surface. And therefore each half cell electrode potential must polarize or change to a common intermediate value which is called as corrosion potential (E_{corr}).

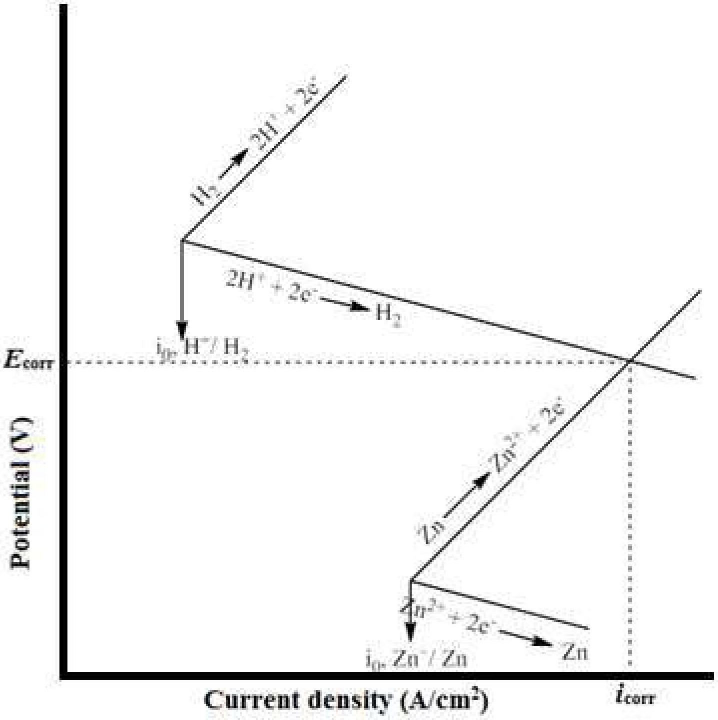


Figure 1.7: Polarization of anodic and cathodic half-cell reactions for zinc in acid solution to give a mixed potential, E_{corr} and a corrosion rate (current density).

The both half-cell reactions polarize on the same metallic surface and during this polarization the half-cell electrode potential changes according to the following relationship until they become equal at E_{corr} as shown in Figure 1.7:

$$\eta_a = \beta_a \log(\frac{i_a}{i_o}) \quad (1.45)$$

$$\eta_c = \beta_c \log(\frac{i_c}{i_o}) \quad (1.46)$$

For mild steel corrosion the *E* vs. *i* graph is shown in the Figure 1.8. At the point of corrosion potential, the rate of Fe dissolution is equal to the rate of hydrogen evolution expressed in terms of current density.

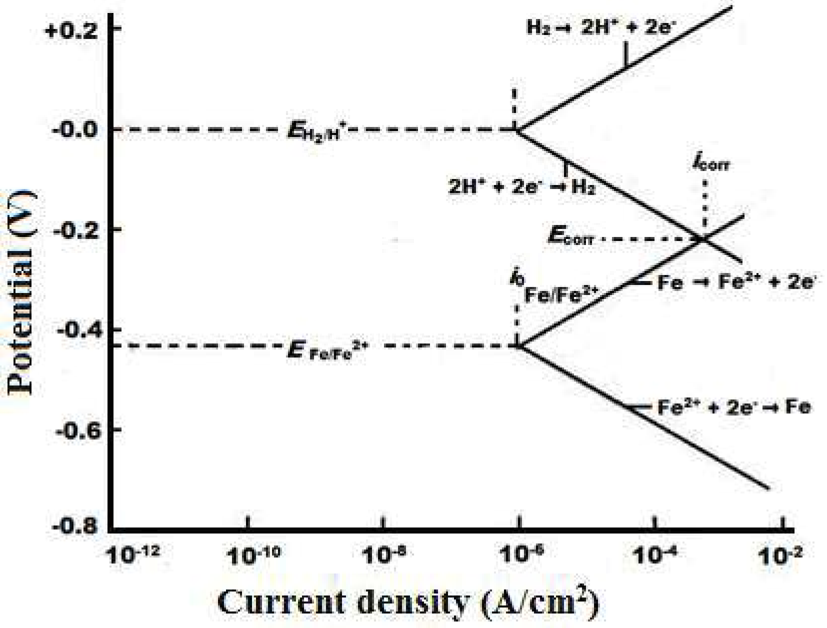


Figure 1.8: "*E vs. i*" for Fe in acid solution.

1.9.5. 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,

$$M \rightarrow M^{n+} + ne^- \tag{1.47}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{1.48}$$

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 1.9.

The Tafel extrapolation technique has some limitations like,

(i) 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.

(ii) A clearly defined anodic and cathodic tafel region should be present (on at least one decade of current).

(iii) Both the anodic and cathodic branches for the polarization curves are activation controlled.

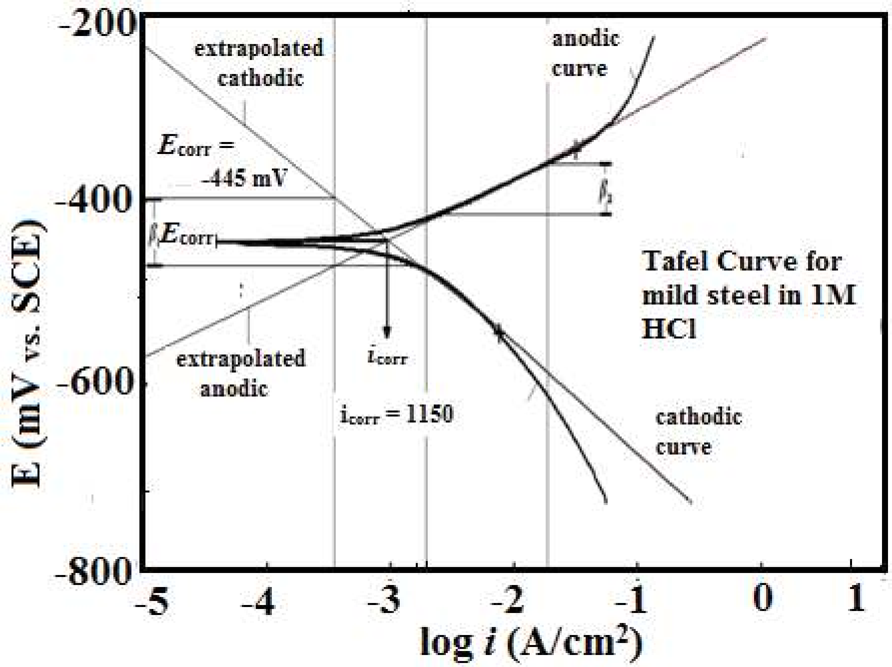


Figure 1.9: Extrapolated Tafel curves.

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. Linear polarization methods:

There is a linear relationship between current density and electrode potential when ‘E’ is not more than 20 mV. The polarization resistance (R_p) is the tangent of a polarization curve at corrosion potential. The slope of the '*E*' versus '*I'* gives 'R_p' which is related to corrosion current i_{corr} respectively by the expression.

$$\frac{\Delta\eta}{\Delta i} = R_p = \frac{b_a \times b_c}{2.3(b_a + b_c)i_{corr}} \qquad (1.49)$$

where β_a and β_c are the anodic and cathodic Tafel slopes. If the cathodic process is diffusion controlled then the equation can be modified as:

$$i_{corr} = \frac{b_a \times b_c}{2.3(b_a + b_c)R_{ct}} \qquad (1.50)$$

Assuming β_a and β_c values to be 0.12 V. The equation can be reduced to $i_{corr} = 0.026/\ R_p$ by which corrosion rate of any system can be calculated without the knowledge of its kinetic parameters.

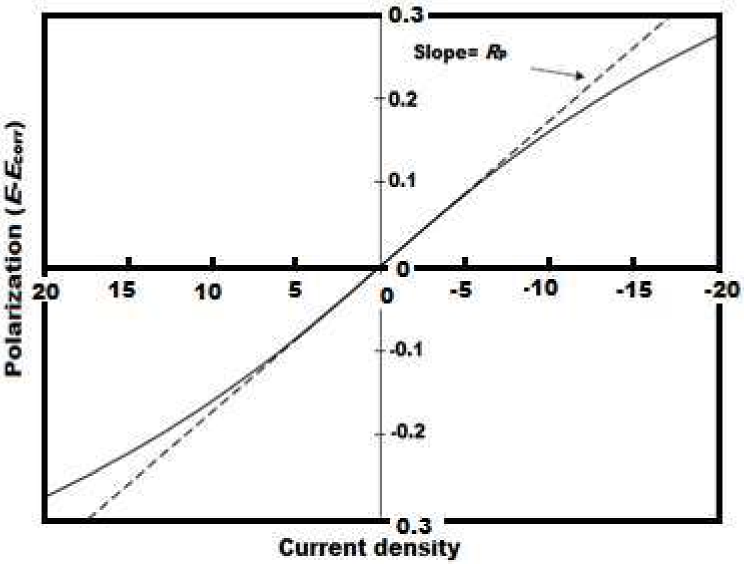


Figure: 1.10: Hypothetical linear polarization plot

1.11. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopy which is also known as dielectric spectroscopy or impedance spectroscopy, measure the dielectric properties of the medium as a function of frequency. In this technique a small amplitude perturbation is applied to the working electrode at a number of discrete frequencies. Further, the EIS technique measure the impedance of the system over a range of frequencies, and therefore the frequency response of the system including the energy storage and dissipation, is revealed. The main advantages of this technique are:

(a) Applicable to low conductivity system

(b) Provide mechanistic information

(c) Solution resistance is totally eliminated

In EIS technique the electrochemical data expressed graphically in the forms of Nyquist and Bode plots. Impedance is the opposition to the flow of alternating current (AC) in a complex system. Electrochemical impedance is the response of an electrochemical system (cell) to an applied potential. The frequency dependence of this impedance can reveal underlying chemical processes. The response of electrochemical systems is very nonlinear as shown in Figure 1.11.

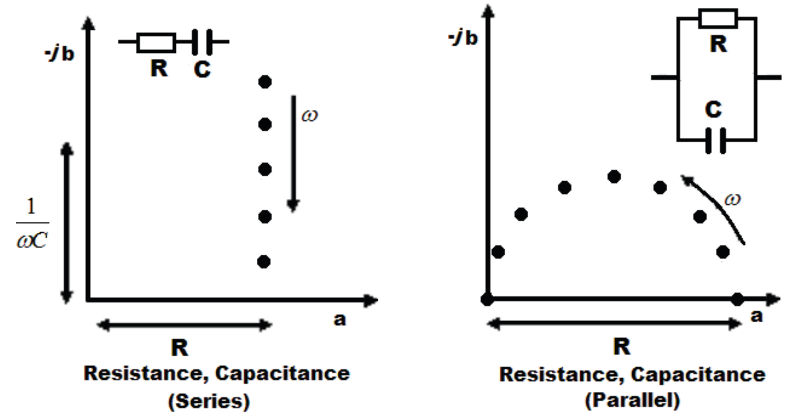


Figure 1.11: Complex plane impedance spectrum.

In present case, we apply small amplitude of ~10 mV) AC ripple on top of the controlled DC polarization potential. The equivalent circuit generally used to explain the complex response of the electrochemical system and display the impedance data in form of Nyquist and bode plots. The Nyquist plots is the most commonly used electrochemical technique which allow easy understanding of the electrochemical behavior of the corroding system. It also offers some easy prediction of the equivalent circuit elements as depicted in the Figure 1.12.

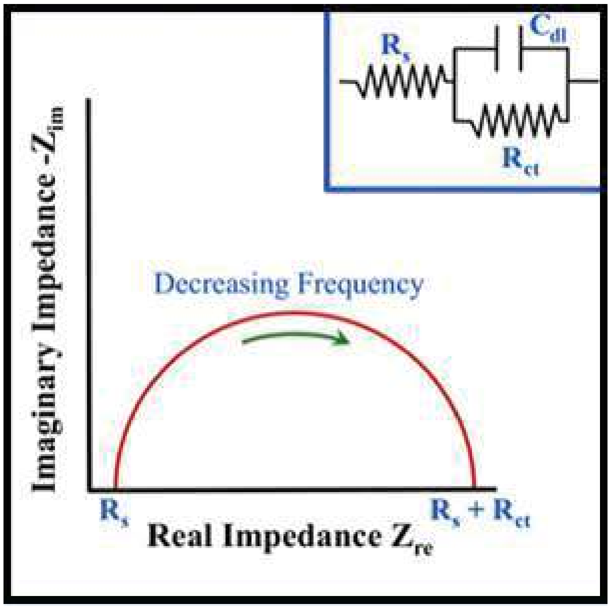


Figure 1.12: Nyquist plot along with constant phase element (CPE).

The response of the electrochemical system as function of small amplitude of perturbation frequency gives information about the internal kinetics of the corroding system. The metal/ electrolyte interface always associate with some capacitance which play very important role while explaining the electrochemical nature of the corroding system. Generally, for a metal corroding in acid solution, the equivalent circuit consists of parallel combination of capacitance and resistance (which represent the corroding interface) in series with the second resistance, as shown in Figure 1.12. The values of various circuit components can be calculated from the series of the equivalent circuit. In the circuit series, the R_Ω represents the resistance of the electrolyte caused in the flow of electric charge. The parallel resistance, R_{ct}, which determine the rate of corrosion, is known as charge transfer resistance. The capacitance occurring at metal/electrolyte interface is generally represented by double layer capacitance, C_{dl}. It is well established that in acid solution the metallic surfaces are charged due to excess corrosion of metals which leads to loss of electrons into the electrolyte and accumulation of metals cations on the exterior part of the metals which is balanced by an equal number of the appositively charged particle of the electrolyte. The extent of the force acting between appositively charged species determine the strength of the interface, which in turn determines the magnitude of ion movement (transfer). Generally, the electrochemical impedance spectroscopy measurements are performed after stabilization of the steady state and therefore EIS is a time taking process. The drift in the corroding system being measured is the common cause of problem in EIS measurements.

The electrochemical nature of cell can change through adsorption of the impurities of solution, growth of oxide layers build on metallic surface, formation of corrosion products in solution, coating degradation, and/ or change in temperature are few perturbing factors due to which steady state is difficult to achieve. The EIS data is commonly analyzed by fitting these data in an equivalent circuit model consisting of few common elements such as resistors, capacitors, and inductors. To be useful, the elements in the model should have a basis in the physical electrochemistry of the system. As an example, most models contain a resistor that models the cell's solution resistance. The aim if EIS analysis is to elucidate the electrode process and to drive its characteristic parameters. It should be noted that the EIS is an important very sensitive technique however does not offer a direct measurement of physical phenomenon [Macdonald (1987)].

1.12 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.

1.13. Corrosion Inhibitors

1.13.1. Definition of Inhibitor

National association of corrosion engineers (NACE) defines corrosion inhibitor as a substance which when added in suitable quantity to corrosive environment lower the corrosion rate [NACE (1965)]. They reduce corrosion by either acting as a barrier by forming an adsorbed layer or retarding the cathodic and/or anodic process [V.S. Sastri (1998)].

Any corrosion retardation process or the reduction in the oxidation rate of the metal by addition of a chemical compound to the system is caused by corrosion inhibitors [N. Hackermann *et al.* (1962)].

Inhibitors are often easy to apply and offer the advantage of in-situ application [P.B. Raja *et al.* (2008)] without causing any significant disruption to the process.

1.13.2. Classification of Inhibitors

Classification of inhibitors is presented below (Figure 1.13) [R. W. Revie (2000)].

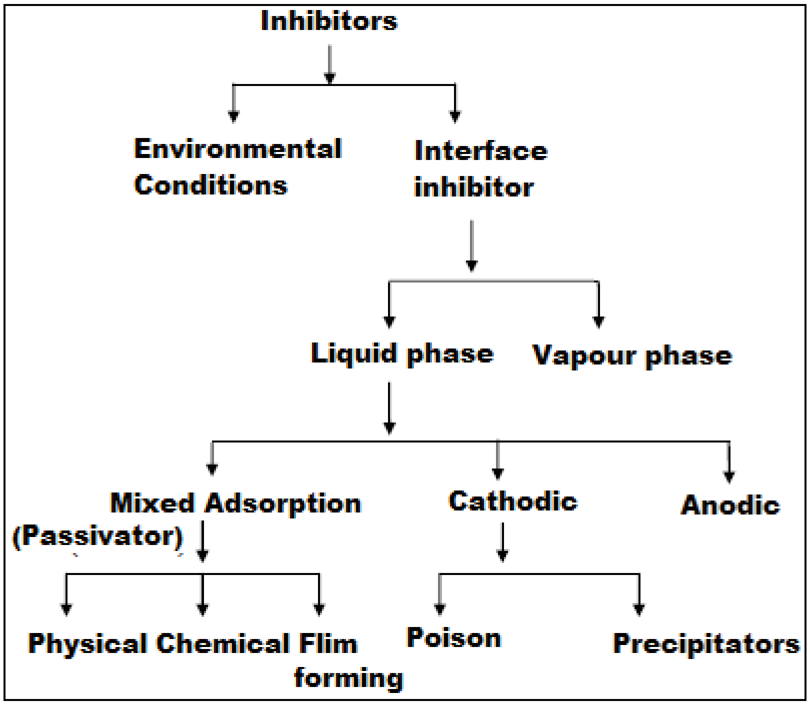


Figure: 1.13: Classifications of Inhibitors

1.13.3. Environmental Conditions

Corrosion can be controlled by removing the corrosive species from the medium. Inhibitors that decrease corrosivity of the medium by scavenging the aggressive substances are called environmental conditioners or scavengers [M. Fanum *et al.* (2014)]. In near-neutral and alkaline solutions, reduction of oxygen is a common cathodic reaction. In such situations, corrosion can be controlled by decreasing the oxygen content using suitable scavengers.

1.13.4. Interface inhibitors

(a) Anodic Inhibitors

The substances, which retard the anodic area by acting on the anodic sites and polarize the anodic reaction, are called anodic inhibitors [Bockris et al. (1993)]. In the presence of anodic inhibitors, displacements in corrosion potential (E_{corr}), takes place in positive direction (Figure 1.14a) and suppress corrosion current (I_{corr}) and reduces corrosion rate. Anodic inhibitors which cause a large shift in the corrosion potential are called passivating inhibitors, if used in insufficient concentration, they cause pitting and sometimes increases corrosion rate.

Anodic inhibitors may be oxidizing anodic inhibitors in which they inhibit corrosion by passivating the metal surface. e.g. chromate, nitrite, and non-oxidizing anodic inhibitors, which include inorganic anions such as molybdate, benzoate and phosphate etc. These inhibitors slow down anodic reaction by forming passive film on the metal surface in presence of oxygen.

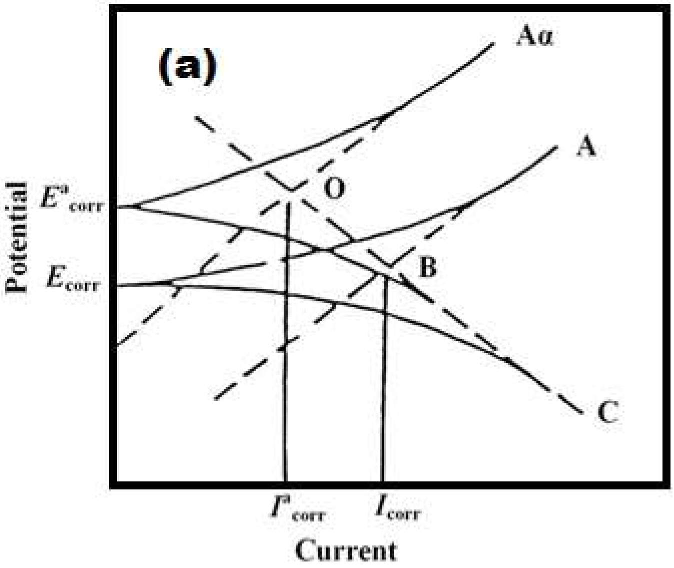


Figure 1.14: (a) Mechanism of action of Anodic corrosion inhibitors based on polarization effects.

(b) Cathodic Inhibitors

Those substances, which reduce the cathodic area by acting on the cathodic sites and polarize the cathodic reactions, are called cathodic inhibitors. They displace the corrosion potential (E_{ccorr}) in the negative direction and reduce corrosion current, thereby retard cathodic reaction and suppress the corrosion rate (Figure 1.14b).

The basic mechanism of cathodic inhibitors is either by acting as cathodic poison i.e. reducing the reduction rate or acting as cathodic precipitators i.e. selectively precipitating on the cathodic areas. There inhibition action occurs either reducing the cathodic area by forming a layer or by adsorbing over the metal surface. In near-neutral and alkaline solutions, these inhibitors inhibit the corrosion by forming a protective films which decrease the cathodic reaction rate by limiting the diffusion of oxygen towards the metal surface [R. W. Revie (2008)].

In acid solution, cathodic inhibitor causes hydrogen blisters and hydrogen embrittlement due to hydrogen evolution. The hydrogen gas instead of leaving the surface diffuses into steel causing hydrogen damage such as hydrogen-induced cracking, sulfide stress cracking etc. The cathodic precipitators increase the alkalinity at cathodic sites and precipitate insoluble compounds on the metal surface. The most widely used cathodic precipitators are the carbonates of calcium and magnesium. This type of inhibitor shifts the corrosion potential in the negative direction. Here cations migrate towards cathode surface, where they are precipitated chemically or electrochemically and thus block the surfaces. For example, the action of As^{3+} and Sb^{3+} on dissolution of iron in acids.

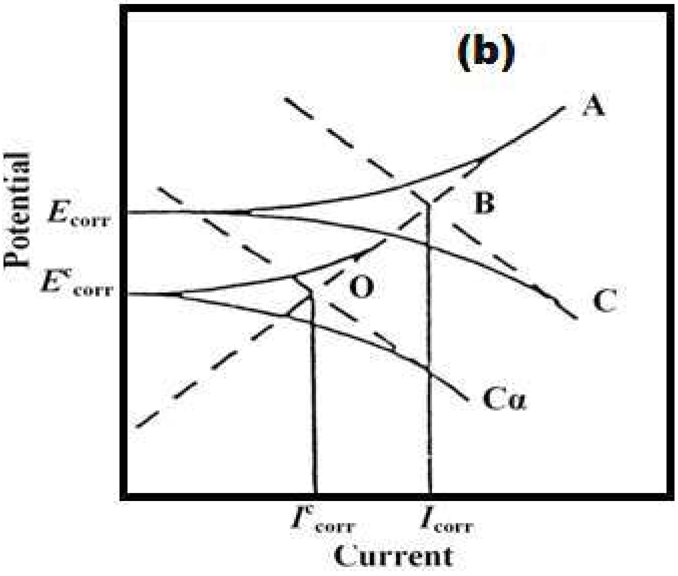


Figure 1.14: (b) Mechanism of action of Cathodic corrosion inhibitors based on polarization effects.

(c) Mixed Inhibitor

The protection power of mixed inhibitors can be divided into three types namely, physical adsorption, chemical adsorption and film formation [R. W. Revie (2011)]. The inhibition action of mixed inhibitor depends on the extent at which they are adsorbing at the metal surface and this adsorption mainly depends upon the type of electrolyte used, charge on the metal surface and the structural properties of inhibitor. This type of inhibitors can retard both the anodic metal oxidation and cathodic metal reduction reactions. These inhibitors dominate the other inhibitors because they can control both the anodic and cathodic corrosion reactions and thus are much safer to apply.

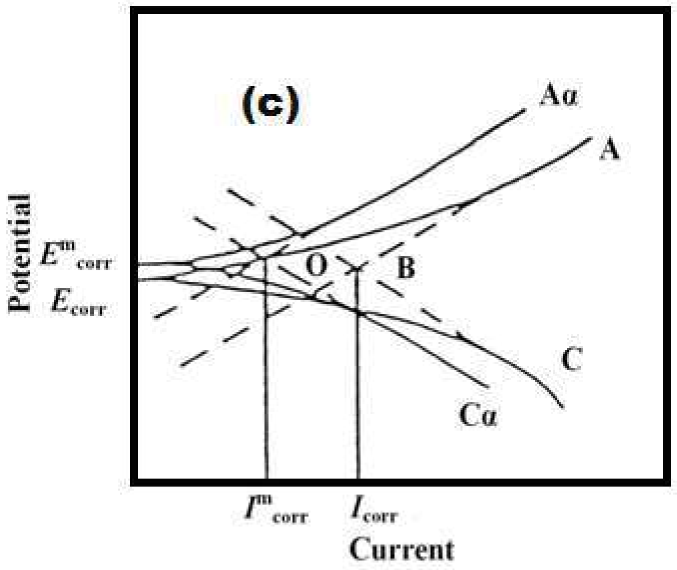


Figure 1.14: (c) Mechanism of action of Mixed corrosion inhibitors based on polarization effects.

These inhibitors are classified into acid, base and neutral depending on the environmental conditions, which may further classified into;

(i) Inorganic inhibitors and (ii) Organic inhibitors

(i) Inorganic inhibitors

To improve the inhibition, one of the methods is to add salts of metals in the corrosive medium. In this case, the protection is due to the reduction of electropositive ions and deposition on the metal surface thus lowering the over voltage of main cathodic depolarization reaction [N.D. Tamashov *et al.* (1967)].

In neutral solutions, inorganic inhibitors interact with the oxide layer which is covering the metal surface and prevent the reduction of oxygen at the cathodic sites. These inhibitors protect the oxide layer of metal from aggressive electrolyte solution. The first step of inhibition mechanism is displacing the pre-adsorbed water molecules, which is followed by electrochemical and chemical reactions over the metal surface. Thus, inhibitors which can reduce the cathodic oxygen reduction are said to be cathodic inhibitors e.g., phosphates, silicates, borates etc and inhibitors which form the passive oxide layer and prevents the anodic metal dissolution are called as anodic inhibitors e.g., chromates and nitrites. A high surface coverage was observed in presence of benzoate anions, favoring the establishment of passive state [D.S. Azambuja *et al.* (1999)].

(ii) Organic inhibitors

Organic compounds having oxygen, nitrogen, sulphur and multiple bonds have been reported as good corrosion inhibitors [G. Moretti *et al.* (2013)], [L. C. Murulana *et al.* (2015)], [S. Pournazari *et al.* (2013)], [V.V. Torres *et al.* (2014)]. Organic inhibitors can be classified as anodic, cathodic or mixed type depending upon their reactions at the metal surface and shift of potential. The effectiveness of these inhibitors depends upon aromaticity, molecular size, length of carbon chain, nature of bonding atoms and conjugation [G. Schmitt *et al.* (1985)].

In alkaline solution, metals which are forming amphoteric oxide layer are very susceptible towards corrosion. The inhibitors used in basic medium are tannin, gelatins, agar-agar etc. Also another class of compounds like thiourea, naphthol β-diketone, and substituted phenols has been tested as effective inhibitors in basic solutions and their action of inhibition is due to forming the metal complexes.

1.13.5. Interface inhibitors (Vapor phase)

Those substances whose vapour pressure is sufficiently high act as vapour phase inhibitors. The vapour pressure of these compounds at room temperature is usually between 0.1 and 1.0 mm mercury, so that the inhibitors become sufficiently fast moving to ensure its adequate availability in the vicinity of the metal surface e.g. dicyclohexyl ammonium nitrite. .). They get readily vaporized and form a protective layer on the metal surface. They are capable of establishing a stable bond with the metal surface in a given environment of a certain range of acidity and pressure. Such inhibitors are specific in nature. Certain vapour phase inhibitors are toxic and cause skin disease on prolonged exposure. Major advantages of vapour phase inhibitors include) Easy to apply as paper coated VPI for temporary protection and ii) Life of inhibitor becomes very long.

1.14. Mechanism of corrosion inhibition in acid solution

The inhibition of metallic corrosion by organic compounds in acid solution is resulted due to their adsorption on the surface. The inhibitor molecules may adsorb on the mild steel surface in acid solution by electrostatic interaction between positively charge inhibitors and already adsorbed counter ions (physisorption), interaction between unshared electron pairs of heteroatoms and vacant d-orbital of surface metal atoms (chemisorption), interaction between π- electrons of aromatic rings and vacant d-orbital of surface Fe atoms(chemisorption) and/or interaction between of d-electron of surface iron atom and vacant antibonding molecular orbitals of the inhibitor molecule (retro donation) [S. K. Shukla *et al.* (2008)]. The addition of inhibitor may alter the corrosion potential resulting into decrease in the rate of anodic process, the cathodic process or both. The shift of the corrosion potential in positive direction indicates mainly the retardation of the anodic process (anodic control) whereas shift in the negative direction indicates retardation of the cathodic process (cathodic control). Little change in the corrosion potential suggests that both anodic and cathodic processes are retarded. In the presence of an inhibitor, a shift of polarization curves without change in the Tafel slope indicates that the adsorbed inhibitor acts by blocking active sites so that reaction cannot occur [Machu (1961)]. A change inthe Tafel slope is the indication of affecting the mechanism of the reaction.

1.15. Theories of inhibition

There are different types of theories related to inhibition and are given below (Figure 1.15):

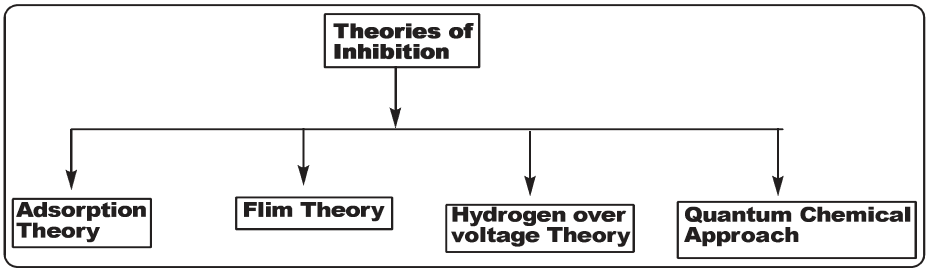


Figure: 1.15: Theories of inhibition

1.15.1. Adsorption Theory

According to adsorption theory, inhibitors are adsorbed on the metal surface forming a protective layer. The mode of adsorption leads to its classification as physical and chemical adsorption [P. Tushar (2004)]. Organic inhibitors have the ability to absorb and impede either anodic or cathodic reaction or both at the metal-electrolyte interface. The different types of adsorptions associated with organic inhibitors are: Electrostatic adsorption or electrosorption, Physical or Van der Waals type adsorption and chemisorption or π-electron adsorption.

(a) Adsorption Isotherms

An adsorption isotherm is a mathematical equation, which is used to relate the bulk concentration of an adsorbing molecule to its surface concentration at a constant temperature. It is a relationship which can be expressed in terms of the surface coverage of an adsorbing species at the interface with that of the concentration of the species in solution. Various adsorption isotherms have been formulated [G. Wranglen (1972)]. The experimental data can be fitted to any one of the adsorption isotherms and the free energy of adsorption can be obtained [N. Hackermann (1948)].

Table1.1. Various types of adsorption isotherms

S. No.	Isotherms	Equations
1.	Freundlisch	$\beta C_{\text{inh}} = \theta$
2.	Langmuir	$\beta C_{\text{inh}} = \frac{\theta}{1-\theta}$
3.	Frumkin	$\beta C_{\text{inh}} = \frac{\theta}{1-\theta}\exp(-2a\theta)$
4.	Temkin	$\beta C_{\text{inh}} = \frac{\exp(a\theta)-1}{1-\exp[-a(1-\theta)]}$
6.	Parsons	$\beta C_{\text{inh}} = \frac{\theta}{1-\theta}\exp\frac{2-\theta}{(1-\theta)^2}\exp(-2a\theta)$
7.	Bockris, Devanathan and Muller	$\log C_{\text{inh}} + \log\frac{\theta}{1-\theta} = C_{\text{inh}} + p\theta^{3/2}$

β = adsorption constant = 1/55.5 (exp-($\Delta G^{\circ}_{\text{ads}}/RT$); $\Delta G^{\circ}_{\text{ads}}$= free energy of adsorption θ = surface coverage; C_{inh}= concentration of inhibitor; a= molecular interaction constant; $a > 0 =>$ attraction and $a < 0 =>$ repulsion; p and q = constants expressed in terms of dipole moments

(b) Adsorption of Inhibitor in acidic solution

(i) The heteroatom present in the inhibitor molecules would get protonated in acidic solution. As the metal is immersed in the acid solution anionic part of the solution will get adsorbed over it and will facilitate the adsorption of protonated inhibitor molecules over the metal surface through electrostatic interaction (physical adsorption).

(ii) In the acid solution the protonated inhibitor molecules start competing with the H^+ ions for electrons which are present on metal surface. The protonated inhibitor molecule, upon accepting electron, release H_2 gas and will become neutral. These neutral inhibitor molecules have free lone pair electrons on the heteroatoms and promote chemical adsorption [S. K. Shukla *et al.* (2008)].

1.15.2. Film Theory

This theory reveals that the effective protection of metals by inhibitors is due to the formation of a layer of insoluble or slightly soluble corrosion products on the metal surface [I.N. Putilova *et al.* (1960), R.H. Husler (1985)].

1.15.3. Hydrogen Overvoltage

This theory postulates that the inhibitors which are adsorbed on the metal, retard either anodic or cathodic or in some case both the reactions. This leads to rapid polarization of anodic or cathodic sites and thus overall corrosion rate is retarded.

1.16. Application of Theoretical methods in Corrosion Inhibition Studies

1.16.1. Quantum chemical calculations

Recently computational studies using DFT based quantum chemical calculations have gained the substantial advances in determining the molecular structure as well as predicting the electronic structure and reactivity of any given series of compounds. Therefore, it is a common practice to perform quantum chemical calculation in the field of corrosion inhibition. The quantum chemical calculations furnished some important parameters which can be used to predict the reactivity of the inhibitor molecules toward metallic surface and therefore relative affinity of any chemical species can be determine on the basis of these calculations. One’s a series of compounds synthesized, their chemical reactivity can be predicted by simply performing the quantum chemical calculation without doing any experiment and thereby polluting the environment. And thus quantum chemical calculation is a ‘green tool’ which allows the prediction of chemical reactivity of any molecule without performing the experiment [Karelson and Lobanov (1996)].

The quantum chemical calculations give some vital parameters which are derived by employing mathematical equations on the basis of which chemical reactivity of molecule is determined [Bouayed *et al.* (1999)]. Nowadays, the quantum chemical calculation in the field of the corrosion inhibition by organic inhibitors is a very active research. The corrosion inhibition property of the several heterocyclic compounds have been studied by a number of investigators on the basis of quantum chemical calculations which allow the prediction of physiochemical properties of the organic molecules such as presence of functional group, steric effect, electron density of donor atoms and orbital character of donating electrons, and so on towards the metallic surface [Stupnisek-Lisac *et al.* (1994)]. Since, it has been well established that organic inhibitors inhibit metallic corrosion by becoming adsorbate at metals surface; therefore it is essential to correlate their experimental inhibition property with the well-established quantum chemical calculations.

1.16.2. DFT based Quantum Chemical Parameters

The DFT based quantum chemical calculations have been immersed as most powerful theoretical techniques in the last three decades. DFT provided a sound basis for the development of computational strategies for obtaining information about the energetics, structure, and properties of (atoms and) molecules at much lower costs than traditional ab initio wave function techniques. The quantum chemical calculations through DFT method can be successfully applied for atoms, molecules and classical fluids. The DFT based calculation gives the information about properties of ground state of any studding system in which electron density plays an important role. Moreover, DFT method successfully used to study the electronic structures of molecules, ground state of many-body-system with special emphasis of atoms, molecules and the condensed phases. The objective of DFT based calculations is to substitute the wave function of many-body electronic with the electronic density as the basic quantity. For example, the notation BLYP/6-31G* denotes a density functional calculation done with the Becke 1988 exchange functional and the Lee-Yang-Parr correlation functional, with the orbitals expanded in a 6-31G* basis set [Levine (1991)].Although there is some natural overlap, the derived quantum chemical parameters are fundamentally deferent from the experimentally determined quantities. Unlike experimental measurements, the quantum chemical calculations are devoid of any statistical error. The common quantum chemical parameters which can be used to predict the chemical reactivity of inhibitor molecules are listed bellows:

(a) Atomic charges:

Electrostatic interaction between the inhibitor molecule and the metallic surface is the first step of adsorption process. The determination of atomic charges of the molecules is important. For this purpose the Milliken population analysis is mostly used to calculate the charge distribution in a molecule which in turns can be used as descriptor of the molecular polarizability [Murrell *et al.* (1985)].

(b) Molecular orbital energies and related parameters

The E_{HOMO} (energy of highest occupied molecular orbital) and E_{LUMO} (energy of lowest unoccupied molecular orbital) are two most important quantum chemical parameters which can be used to study the interaction between metal and inhibitors. The E_{HOMO} is a measure of the tendency of a molecule to donate its HOMO (highest occupied molecular orbital) electrons to the vacant antibonding molecular orbital of an acceptor molecule during the donor–acceptor interactions. E_{HOMO} generally related with electron donating ability and its high value for any molecule indicates that that particular molecule is susceptible for high electron donation [Murrell *et al.* (1985)].The E_{LUMO} on the other hand is a measure of the tendency of a molecule to accept electrons into its LUMO (lowest unoccupied molecular orbital) from the appropriate occupied orbital of an electron donor[Fukui (1975)].The energy gap (E_{LUMO}-E_{HOMO}), ΔE is another index of reactivity of molecules for which a molecule with lower ΔE is usually more reactive and possesses higher inhibition efficiency[Lewis *et al.* (1994)]. Similarly, few other parameters such as global softness (σ), global hardness (η), absolute electronegativity (χ), and fraction of electron transfer (ΔN) can be derive from the values of E_{HOMO} and E_{LUMO}. Generally, corrosion inhibition efficiency of organic molecules increases with increasing the value of global softness and decreases with increasing the value of hardness. The electronegativity is a measure of tendency to trap of electrons from any inhibitor molecule. A higher value of electronegativity for any organic molecule indicates that it has low tendency to donate its electron to the metal surface, while a lower value of electronegativity suggests the strong interaction between metal and inhibitor molecule and therefore exhibit high inhibition performance. The fraction of electron transfer is other important quantum chemical calculation parameter which inform about the extent of electron transfer from inhibitor to metal surface. Generally, the magnitude of inhibition efficiency increases with increasing values of fraction of electron transfer.

(c) Dipole moment

Dipole moment is the most widely used quantity to describe the polarity of molecule. This is measure of polarity of polar covalent bond which can be defined as the product of charge on the atoms and the distance between the bonded atoms. In general on increasing polarity of molecule, the global polarization increases resulting into an increase in the effective surface area. Thus, a molecule with high dipole moment will cover larger metallic surface area and therefore will exhibit high inhibition efficiency. However, the negative trends of inhibition efficiency are also reported by few authors where the increases in the polarity decrease the inhibition performance of the inhibitor molecule [Kikuchi (1987)].

(d) Fukui indices

The Fukui function is named after Kenichi Fukui, who investigated the frontier orbitals described by the function, specifically the HOMO and LUMO. Fukui functions are related in part to the Frontier Orbital Theory (also known as The Fukui Theory of Reactivity and Selection, also developed by Kenichi Fukui) which discusses how nucleophiles attack the HOMO while at the same time placing their surplus electrons into the LUMO. Basically fukuii functions are the local reactivity indices f^+ and f that are often used to analyze the relative susceptibility of the active atomic sites of an inhibitor molecule to electrophilic and nucleophilic attacks respectively [Gomez *et al.* (2006)], [Yan *et al.* (2013)]. The atom condensed Fukui functions using the Mullikan population analysis (MPA) and the finite difference (FD) approximations approach introduced by Yang and Mortier [Yang and Mortier (1986)] are being used to calculate the Fukui indices. The Fukui indices, f^+ and f are calculated to predict the most probable atomic sites for nucleophilic and electrophilic attacks, respectively. The regions of the molecules with higher values of f^+ are more susceptible to attack by electron rich species, while the sites of the molecules with higher values of f are more disposed to interactions with electron deficient species.

1.17. Molecular dynamics simulations

Molecular dynamics (MD) is a computer simulation technique for using the determination of the physical movements of atoms and molecules. In it, atoms and the molecules are allowed to interact for a fixed time interval, giving a view of the dynamic evolution of the system. In the most common version, the trajectories of atoms and molecules are determined by numerically solving Newton's equations of motion for a system of interacting particles, where forces between the particles and their potential energies are calculated using interatomic potentials or molecular mechanics force fields. The method was originally developed within the field of theoretical physics in the late 1950s [Alder and Wainwright (1959)] but is applied today mostly in chemical physics, materials science and the modelling of biomolecules. The heart of any molecular dynamics scheme is the force model used to analytically describe the atomistic interactions. Regardless of the merits of the other algorithms in the simulation code (integrators, pressure and temperature controls etc.), whether or not the simulation produces realistic results depends ultimately on the force model [Alder and Wainwright (1957)]. 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)].

1.18. Effect of inhibitors on corrosion processes

Electrochemical studies have shown that inhibitors in acid solution may affect corrosion reactions of metal in the following ways.

(a) Formation of diffusion layer

The adsorbed inhibitor forms a surface film on the metal surface and acts as a physical barrier to restrict the diffusion of ions or molecules to or from the metal surface and thus retard the corrosion reaction.

(b) Blocking of reaction sites

The inhibitors may adsorb on the metal surface to prevent the surface metal atoms from participating in either the anodic or cathodic reaction of corrosion. The mechanisms of such reactions are not affected and the Tafel slopes of the polarization curves remain unchanged. Adsorption of inhibitors at low surface coverage tends to occur at anodic sites, causing retardation of the anodic reaction. At high surface coverage, adsorption occurs on both anodic and cathodic sites, and both reactions are inhibited.

(c) Precipitation in the electrode reactions

The electrode reactions may involve the formation of adsorbed intermediate species with the surface of metal atoms. The presence of adsorbed inhibitor interferes with the adsorbed intermediate but the electrode processes may then proceed by alternative paths through intermediates containing the inhibitor. In these processes, the inhibitor affects the reaction rate and remains unchanged with a change in the Tafel slope. Inhibitors may retard the rate of hydrogen evolution on metals by affecting the mechanism of the reaction with the increase in Tafel slopes of cathodic polarization curve.

1.19. Organic Compounds as Corrosion Inhibitors: Literature survey

The use of corrosion inhibitors is considered as the most effective and economic method to mitigate corrosion in acidic media. Most acid-pickling inhibitors consist of a hydrocarbon part attached to a polar group. They are organic compounds containing heteroatom’s (P, S, O, and N), unsaturated compounds containing double and triple bonds in conjugation, aromatic rings, etc. Nitrogen, Oxygen or Sulfur containing compounds have been traditionally used as corrosion inhibitors for metals in acid media [A.S. Fouda *et al.* (2015), L. Bai *et al.* (2015), M. S. Nooshabadi *et al.* (2015)]. The available literature on the use of N, S and O containing heterocyclic compounds as corrosion inhibitors in acid media has been surveyed.

Table: 1.2. Literature survey: DFT methods in corrosion inhibition

Inhibitors/Metal Alloy/Medium	**Remark**	**Reference**
Pyranopyrazole derivatives/ Mild steel/ HCl	Inhibition efficiency increases with concentration. Results obtained from both potentiodynamic and weight loss techniques reveal that these compounds are good inhibitors. These compounds exhibited 88 to 98% inhibition efficiency at 300 mg/L	M. Yadav et al (2015)
Pyranopyrazoles derivatives / Mild steel/ HCl	Inhibition efficiency increases with increasing inhibitor concentration and reached at maximum 94% at 500 ppm. Adsorption of inhibitor molecules on the surface of aluminium followed Langmuir adsorption isotherm. Studied compound is mixed type inhibitor.These compounds exhibited 88 to 98% inhibition efficiency at 300 mg/L	D. K. Yadav et al 2012

Schiff bases of amine/ Mild steel/ HCl	Amine based Schiff base derivatives tested as corrosion inhibitors and found that on addition of these compounds the inhibition efficiency increases. Tha maximum inhibition efficiency found 90% at 400 ppm.	Negm et al 2012
Schiff base derived from 2 amino pyridine/ Mild steel/ HCl	Schiff base derived from 2 amino pyridine tested as corrosion inhibitors.These compounds exhibited maximum IE of 85-95% at 200 mg L^{-1}	Sorkhabi et al 2016
2-phenyl-benzothiazole derivatives as corrosion inhibitors/ Mild Steel/ IM HCl	The inhibition performance of 2-(2_-hydroxylphenyl)benzothiazole, (1), 2-(2_,5_-dihydroxyphenyl)benzothiazole, (2), and (4-benzothiazole-2-yl-phenyl)-dimethyl-amine, (3), hasbeen investigated for mild steel in 1 M HCl. Thease compound shows 95% inhibition efficiency at 50 ppm.	Salarvand et al 2017
pyrimidine derivatives namely 5-styryl-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-d] pyrimidin-4(1H) one (PP-1) and 5-(2-hydroxyphenyl)-2,7-dithioxo-2,3,5,6,7,8-hexahydropyrimido[4,5-d]-pyrimidin-4(1H) one (PP-2) on N80 steel corrosion in	The corrosion inhibition efficiencies at optimum concentration (250 mg/L) are 89.1% (PP-1) and 73.1% (PP-2) respectively at 308 K. PPs obeyed Langmuir adsorption isotherm	Haque et al 2017

15% HCl solution		
N, N'- bis (salicylidene)-4-phenyl methanediamine (SBn) derivatives/ Mild steel/ HCl	The IE increases with inhibitor concentration and reached maximum up to 98% at 1mM. The ΔGads suggest chemical and physical adsorption.	Soltani *et al.*(2010)
Schiff base derived from pyridin-2- ylmethyl-N,N-diethylaniline (BPMA) / Mild steel/ HCl	The addition of BPMA induces a decrease in both anodic and cathodic currents. The corrosion potential (E_{corr}) of BPMA 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. The maximum IE of BPMA 88% at 450 ppm	Yan Ji et al 2016
Schiff bases from benzylidene thiourea/ Mild steel/ HCl	Schiff base derived from thiourea gives 80- 90% inhibition efficiency at concentration range (150mgL^{-1})	Hegazy et al 2009
Six amino acids were evaluated as corrosion inhibitors for carbon steel and copper in 0.5mol L^{-1}H_2SO_4solution.	The corrosion inhibitor rankings were:Arg > Gln > Asn > Met > Cys > Ser, for copper, and Met > Cys > Ser > Arg > Gln > Asn, for carbon steel. The DFTapproach failed to explain the corrosion inhibition rating based on the HOMO and LUMO energies	Mendonca et al 2017

	of theisolated amino acid molecules,	
Clozapine (CZP) was used to investigate the mild steel (MS) corrosion inhibition process in 1 M HCl	CZP is a good inhibitor and inhibition efficiency (IE%) reach 96% at an optimum concentration of 10^{-3} M	Lgaz et al 2017
2-(2-trifluromethyl-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 *et al.* (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 *et al.* (2015) (b)]
imidazole based ionic liquids/ Mild steel/ HCl	A series of imidazole based ionic liquids tested as corrosion inhibitor and found that, These compounds having maximum inhibition efficiency 92% at 500 ppm	Yesudass et al, 2016

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 derivates 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 *et al*. (2013)]
Imidazole and methyl substituted imidazoles/Mild steel/ HCl	Potentiodynamic polarization measurements indicated that the presence of imidazoles significantly decreases the cathodic, anodic, and corrosion currents showing that IMs is amixed-type corrosion inhibitor for copper in a 1M HCl and showed 70-77% IE at 150 ppm	El-Haddad et al, 2015
3,5-bis(4-methoxyphenyl)-4-amino-1,2,4-triazole (4-MAT) /Mild steel/1 M HCl	24-MAT) shows excellent inhibition 98% at optimum conc. $4x10^{-4}$ 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	[Bentiss *et al.* (2009)]

	adsorption model obeys to the Langmuir adsorption isotherm and the negative value of the Gibbs free energy of adsorption (ΔG_{ads}) indicates that the adsorption of the 4-MAT molecules is a spontaneous process.	
Several imidazole derivatives/ Mild steel/ HCl	The IE increases with inhibitor concentration and reached maximum up to 70% at 200 ppm in 1M. The ΔG_{ads} suggest chemical and physical adsorption.	[Gutierrez et al, (2016)]
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 *et al.* (2003)]
2-mesit yl-1*H*-imidazo [4,5 -*f*] [1,10] phenanthroline (MEIP) / Mild steel/ H_2SO_4	Inhibition efficiency values increase (from 52 to 87%) with the inhibitor concentration (from 2 to10μM) but decrease with rise in temperature suggesting physical adsorption mechanism.	[Obot *et al.* (2011)]
pyrazole fused with pyridine/ Mild steel/ HCl	Pyrazole-pyridine compounds exhibited maximum inhibition efficiency 92% at 150 mgL^{-1}.	[Mhammedi *et al,* (2007)]

Pyrazolo- pyridine derivatives on mild in 1M HCl	These compounds exhibited maximum IE 85-95% at 200mg L^{-1}.	Singh et al, 2016
Pyridine derivatives/carbon steel/HCl	Inhibition efficiency increases with concentration. Results obtained from both potentiodynamic and weight loss techniques reveal that these compounds are good inhibitors.	S.A.Abd El-Maksud *et al.* (2005)
2-(4-pyridyl)-benzimidazole (PBI); Benzimidazole (BI); Pyridine (Py)/ Mild steel/ HCl	Showed maximum IE (90.8%) at 2 mM at 25°C. Act as a mixed-type inhibitor with predominant cathodic effectiveness. The values of the binding energy reveal the sequence of PBI > BI > Py.	[Zhang *et al.* (2012)]
Pyridine derivatives/N80 steel/HCl	Inhibition efficiency increases and decreases with increase in concentration and temperature. SEM and AFM images reveal inhibitor adsorption on metal.	[M.Yadav *et al.* (2014)]
Pyrazolopyridine derivatives/ Mild steel/ H_2SO_4	Inhibitors show 93-98% IE at 1M of their concentration. The corrosion rate (*i*corr) and hydrogen evolution increases with either increasing temperature or decreasing the inhibitor concentration.	[Fekry *et al.* (2010)]
Glycine derivative/ Mild steel/ H_2SO_4	The inhibition efficiency increases with the increase in inhibitor concentration, while it decreases with temperature, suggesting the occurrence of physical adsorption.	Amin *et al.* (2011)

	Tafel polarization plots indicated that the three tested compounds act as mixed-type inhibitors. Adsorption of the tested inhibitors follow Temkin isotherm.	
2-amino-6-methoxy-4-(4-methoxylphenyl) 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 *et al*. (2015)]
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	[Kosari *et al.* (2014)]

	will severely corrode if inhibitors are not used.	
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)]
2-amino-3,5-dicarbonitrile-4-(4-methoxyphenyl)-6-(phenylthio)pyridine (ADTP I), 2-amino-3,5 dicarbonitrile-4phenyl-6-(phenylthio) pyridine (ADTP II), 2-amino-3,5-dicarbonitrile-4-(4 nitrophenyl)-6-(phenylthio) pyridine (ADTP III)) /Mild steel/1 M HCl	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 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	[Sudheer and Quraishi (2014)]

	Langmuir adsorption.	
3,5-bis (2-thienyl)-4-amino-1,2,4-triazoles (2-TAT)/Mild steel/1 M HCl, 0.5 M H_2SO_4	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 *et al.* (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 *et al.* (1999) (b)]
4-amino-3-butyl-5-mercapto-1,2,4-triazole (ABMT)/ Mild steel/1 N H_2SO_4	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. $4x10^{-4}$ 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 (ΔG_{ads})	[Bentiss *et al.* (2009)]

	indicates that the adsorption of the 4-MAT molecules is a spontaneous process.	
4,4-dimethyl-3-oxo-2 (1,2,4)triazol-1-yl-pentanethioic acid phenylamide (DTP) / Mild steel/0.5M H_2SO_4	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 equilibrium constant (K_{ads}) decreased with the temperature.	[Tao *et al.* (2009)]
4-hydroxy-*N'*-[(*E*)-(1*H*-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 *et al.* (2014)]

1.20. The scope and importance of corrosion inhibition technology

Organic compounds are widely used in various industries as corrosion inhibitors for preventing corrosion in acidic environments. The major industries using corrosion inhibitors are oil and gas exploration and production industry, petroleum refining industry, chemical industry, heavy industrial manufacturing industry, water treatment industry and additive product industry. Corrosion inhibitors are also used in many systems including cleaning pads, cooling systems, pipelines, chemical operations, steam generators, ballast tanks and many products that are marketed to the general public. One of the salient features of the corrosion inhibitor is non-disruption of the process. Inhibitors are mainly used for their effectiveness in protecting the specific metal or combination of metals in a closed or recirculation system.

1.21. Objective of present study

The proposed research work will focus on the following points:

1. Synthesis of efficient organic corrosion inhibitors.
2. Corrosion inhibition study of the inhibitors for Mild steel, N80 steel J55 steel and others alloys in I M HCl, solution by using gravimetric measurements, electrochemical impedance spectroscopy, and potentiodynamic polarization.
3. Surface analysis of uninhibited and inhibited steel samples by using SEM, AFM techniques.
4. Quantum chemical calculations using density functional theory (DFT) and molecular dynamic simulation to correlate the experimental data.
5. Study of the mechanism of corrosion inhibition on the basis of the above studies.