CHAPTER – 1
INTRODUCTION
Corrosion in a broad sense signifies the whole range of interactions between metals and their non-metallic environments. Shreir describes corrosion as the reactions of a solid and its environment [1].

Corrosion is defined as the destruction or deterioration of a material / metal because of the interaction with its environment. It is now generally accepted that corrosion is a reversion or a partial reversion from the metastable condition of the metal to the stable condition of the mineral accompanied by a decrease in the free energy of the system. Corrosion is actually the most common electrochemical phenomenon experienced in day-to-day living.

1.1 COST OF CORROSION

Corrosion has a major impact on the economy of a nation. The loss to the world economy due to corrosion is in the billions per year. This loss is due to, galvanic corrosion, direct attack corrosion, and other types of corrosion. The loss due to corrosion has been estimated to be the order of 2 – 5% of the GNP of any country. In India the losses have been estimated approximately Rs. 25000 crores per year due to impact of corrosion [2].

Thus from national economic point of view, it is necessary for scientists and engineers to adopt various ways and means to minimize the losses due to corrosion. With technological and industrial growth, the use of metals and their alloys is increasing very rapidly and any step in the direction of understanding the nature of corrosion, its mechanism and the way to control it, would be of great help to nation’s economy.

1.2 CLASSIFICATION OF CORROSION

Corrosion has been classified into different types such as low temperature and high temperature corrosion, direct oxidation and electrochemical corrosion etc.

The preferred classification is

1. Dry or Chemical Corrosion
2. Wet or Electrochemical Corrosion

Dry corrosion occurs in the absence of a liquid phase. Vapours and gases are usually the corrodants and the corrosion is usually associated with high temperature. An
example of dry corrosion is tarnishing of copper and silver. Wet corrosion occurs when a liquid is present. This involves aqueous solutions or electrolytes. A common example is corrosion of steel in water. A general scheme for the classification of corrosion processes is presented separately in the form of a Table – 1.1. Various important forms of corrosion with definition and examples are summarized in Table – 1.2.

1.3 FACTORS INFLUENCING CORROSION

The nature and the extent of corrosion depend largely on the metal and the environment. Thus factors like structural features of the metal, nature of the environment and the type of reactions that occur at the metal/environment interface have to be considered for the understanding of the corrosion phenomenon.

The important factors, which influence the corrosion process, are

1. nature of the metal
2. nature of the environment
3. electrode potential
4. temperature
5. solution concentration
6. aeration
7. agitation
8. pH of the solution
9. nature of the corrosion products and
10. hydrogen over potential

1.4 THEORIES OF CORROSION

1.4.1 HETEROGENEOUS THEORY

According to this theory corrosion requires the presence of an impurity on metal thus creating a local cell set up between cathodic and anodic part of corroding surface. As a consequence of electrochemical reactions occurring at metal interface and ionically conducting moisture films or solution metal becomes unstable and thus corrosion occurs.
Table - 1.1 Classification of Corrosion Processes

<table>
<thead>
<tr>
<th>Classification</th>
<th>Processes</th>
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<tbody>
<tr>
<td>Electrochemical Corrosion</td>
<td>Room Temperature Corrosion, Elevated Temperature Corrosion</td>
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<td>- Uniform Corrosion, High Temp. Oxidation</td>
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<td>- Localized Corrosion</td>
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<td>- Fused Salt Corrosion</td>
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<td>Chemical Corrosion</td>
<td>- Corrosion Initiated in the Metal, Environment</td>
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<td>- Intergranular Corrosion, Pitting Corrosion, Exfoliation, Dealloying</td>
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<td></td>
<td>- (a) Dezincification, (b) Graphitization, Galvanic Corrosion</td>
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<td></td>
<td>- Crevice Corrosion, Filiform Corrosion, Water Line Attack</td>
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<td>- Metal Ion Concentration, Cell Corrosion, Soil Corrosion</td>
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<td></td>
<td>- Stress Corrosion, Cracking, Hydrogen Embrittlement, Corrosion Fatigue</td>
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<td></td>
<td>- Erosion Corrosion, Cavitation Corrosion</td>
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<td>- Fretting Corrosion</td>
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<td>S. No.</td>
<td>Corrosion type</td>
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</tr>
<tr>
<td>1.</td>
<td>Dry corrosion</td>
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<td>2.</td>
<td>Wet corrosion</td>
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<td>3.</td>
<td>Uniform corrosion</td>
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<td>5.</td>
<td>Crevice corrosion</td>
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<td>6.</td>
<td>Galvanic corrosion</td>
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<td>7.</td>
<td>Integranular corrosion</td>
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<tr>
<td>8.</td>
<td>Stress corrosion cracking</td>
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<tr>
<td>9.</td>
<td>High temperature oxidation</td>
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<tr>
<td>10.</td>
<td>Erosion corrosion</td>
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</tbody>
</table>
1.4.2 HOMOGENEOUS THEORY

According to Wagner and Traud [3] metal instability arises due to different electronic charge transfer reactions occurring simultaneously in opposite directions at metal/environment interface. For this, it is necessary that the potential difference across the interface should be more positive than the equilibrium potential of the metal dissolution reaction and more negative than the equilibrium potential of the electonation reaction.

1.4.3 ELECTROCHEMICAL THEORY OF CORROSION

The electrochemical theory of corrosion is the only theory which is universally accepted and is applicable to most of the corrosion processes. Most of the corrosion reactions can be separated into two or more partial reactions, which can be further divided into two classes, oxidation and reduction.

An oxidation reaction is indicated by production of electrons as given below:

\[ M \xrightarrow{\text{\footnotesize oxidation}} M^{\dagger} + e^{-} \quad (1) \]

This reaction constitutes the basis of corrosion of metals. In a similar fashion, a reduction reaction is indicated by the consumption of electrons. For every oxidation reaction there must be a corresponding reduction reaction. In aqueous solutions, various reduction reactions are possible depending upon the system. Some example of reduction reactions are:

- **Hydrogen evolution**: \[ 2H^{+}+2e^{-} \rightarrow H_{2} \] (in acidic system) (2)
- **Oxygen reduction**: \[ O_{2}+4H^{+}+4e^{-} \rightarrow 2H_{2}O \] (in acidic solution) (3)
  \[ O_{2}+2H_{2}O+4e^{-} \rightarrow 4OH^{-} \] (in neutral and alkaline solution) (4)
- **Metal ion reduction**: \[ M^{n+} + e^{-} \rightarrow M^{(n-1)} \] (5)
- **Metal deposition**: \[ M^{n+} + ne^{-} \rightarrow M \] (6)

Oxidation reactions are known as anodic reactions while reduction reactions as cathodic. During the corrosion more than one anodic and cathodic reaction may occur. Oxidation-reduction (redox) reactions can be understood by the example of corrosion of mild steel in sulphuric acid contaminated by ferric ions. Anodic reaction will occur as follows.
\[ M \underset{\text{M}}{\rightarrow} M^{n+} + n e^- \quad (6a) \]

All the component elements of mild steel (e.g. Fe, Mn, etc.) go into the solution as their respective ions. The electrons produced by these anodic (oxidation) reactions will be consumed by the cathodic (reduction) reactions. In this case, reaction (5) can be represented as follows:

\[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad (7) \]

Removing one of the available cathodic reactions e.g. reaction (7) by removal of the Fe^{3+} ions will reduce the corrosion rate.

When a metal or alloy is immersed in a corrosive environment (conductive) different potential zones are developed on the surface of metal or alloy due to the presence of different metallic phases, grain boundaries, segregates, crystalline imperfections, impurities, etc. This difference in potential leads to the formation of anodic and cathodic areas on the metallic surface where oxidation and reduction reactions occur, respectively. These area result in the formation of local action cells on the metallic surface. Local action cell can also be formed where there are variations in the environment or in temperature. The electrode potential is calculated from the Nernst equation:

\[ E = E_o + \frac{RT}{zF} \ln \frac{[\text{ox}]}{[\text{red}]} \quad (8) \]

Where,

- \( E_o \) = standard electrode potential
- \( R \) = Gas constant (1.98 cal / gm equivalent)
- \( F \) = Faraday constant (96,500 coulombs/gm equivalent)
- \( Z \) = Number of electrons transferred in the reaction
- \([\text{ox}]\) = concentration of oxidized species (mol/l)
- \([\text{red}]\) = concentration of reduced species (mol/l)

1.4.4 THERMODYNAMIC PRINCIPLES OF CORROSION

In most of the cases metallic state represents the state of high energy Therefore, metals have a natural tendency to react with other substances and go back to lower energy state with subsequent release of energy. All metals show decrease in free energy by
undergoing reaction with the environment, (except noble metals, which are found in native state in nature), Thermodynamic stability of chemical compounds is determined by the sign and the change in the free energy (ΔG), when they are formed from simple substances.

Free energy is the thermodynamic property that express the resultant enthalpy of substance and its inherent probability. At constant temperature free energy can be expressed as follows:

\[ \Delta G = \Delta H - T\Delta S \]  \hspace{1cm} (9)

where ΔG is the change in free energy, ΔH is the change in enthalpy, ΔS is the change in entropy and T is absolute temperature.

When the reaction are at equilibrium then:

\[ \Delta G^\circ = -RT \ln K_{eq} \]  \hspace{1cm} (10)

Where ΔG° is standard free energy, R is gas constant and K_eq is equilibrium constant. The potential of a reaction is related to its free energy (ΔG) by:

\[ \Delta G = -zFE \]  \hspace{1cm} (11)

A negative value for the energy corresponds to a spontaneous reaction, whereas a positive value of ΔG indicates that the reaction has no tendency to proceed. The change in free energy accompanying an electrochemical or corrosion reaction can be calculated from a knowledge of the cell potential of the reaction. It is the redox potential by which one can predict whether a metal will corrode in a given environment or not.

1.4.5 POTENTIAL – pH DIAGRAM

To overcome some of the limitations of the 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 or ordinates, 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 1.1. It is necessary to consider the following equilibria before drawing the potential diagram for iron:

\[
\begin{align*}
&\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2 \text{e}^- \quad \text{Corrosion reaction} \\
&\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + 3 \text{e}^- \quad \text{Oxidation reaction} \\
&\text{Fe(OH)}_3 + 3\text{H}^+ + \text{e}^- \rightleftharpoons \text{Fe}^{2+} + 3\text{H}_2\text{O} \quad \text{Precipitation reaction} \\
&\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_2 + 2\text{H}^+ \quad \text{Hydrolysis reaction} \\
&2\text{Fe} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \quad \text{Corrosion reaction} \\
&\text{Fe} + 2\text{H}_2\text{O} \rightleftharpoons \text{HFeO}_2^- + 3\text{H}^+ + 2\text{e}^- \quad \text{Corrosion reaction} \\
&\text{HFeO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + \text{e}^- \quad \text{Precipitation reaction} \\
&\text{Fe}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Fe(OH)}_2 \quad \text{Precipitation reaction}
\end{align*}
\]

Figure 1.1 Pourbaix diagram for Fe – \(\text{H}_2\text{O}\) system at 25 °C.

Reaction (12), (13) and (18) are independent of pH and are represented by straight horizontal lines; while reactions (14), (16) and (17) are dependent upon pH and potential are represented by the \(E_{H}/\text{pH}\) plots by sloping lines. Reaction (15) and (19) which only
depend on pH are represented by vertical lines. Oxygen is evolved above but not below (line “cd”) in accord with the reaction:

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \]  

(20)

Hydrogen is evolved below but to above (line “ab”) in accord with the reaction.

\[ \text{H}^+ \rightarrow \frac{1}{2} \text{H}_2 - e^- \]  

(21)

As can be seen in Figure 1.1 the redox potential of the hydrogen electrode (line “ab”) lines above immunity region along all the pH scale. This means that Fe may be dissolved with evolution of hydrogen in aqueous solutions of all the pH values. In the pH interval (9.4-12.5), however, a passivating layer of Fe (OH)\textsubscript{2} is formed (reaction 20). At higher pH values soluble hypoferrite can form within a restricted active potential range. At a higher redox potential in the corroding medium, the passivating layer consist of Fe (OH)\textsubscript{3} or Fe\textsubscript{2}O\textsubscript{3}, nH\textsubscript{2}O or Fe\textsubscript{2}O\textsubscript{3}, in different situations. Soluble ferrate (Fe O\textsubscript{4}^-\textsuperscript{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:

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 corrosion attack.

1.5 CORROSION CONTROL METHODS

The corrosion reaction takes place at the metal/environment interface, so corrosion can be controlled by

1. Modifying the composition of metal

2. Modifying the metal surface

3. Altering the metal/environmental potential
The account of various methods controlling corrosion is given in the literature [4]. The general classification of various corrosion control methods is summarised in Table 1.3 may be given as follows.

1.6 CORROSION CONTROL BY THE APPLICATION OF INHIBITORS

One of the major methods of corrosion control particularly in closed system is the use of corrosion inhibitors.

An inhibitor is a chemical substance which when added in a small concentration to the corrosive environment causes a substantial reduction in the rate of corrosion of metal either by reducing the probability of its occurrence (deterrent) or by reducing the rate of a attack (retardant) or by both. Inhibitors are very specific to the medium for which they are used.

An inhibitor useful for a particular corrosion system may be harmful to another under certain situations. According to NACE, Inhibitor is a substance which retards corrosion when added to an environment in small concentration [5] and the recent ISO definition of an inhibitor is a chemical substance which decreases the corrosion rate when present in the corrosive system at a suitable concentration without significantly changing the concentration of corrosive medium [6]. Inhibitors may also be defined on electrochemical basis as substances that reduce the rates of either or both partial anodic oxidation and cathodic reduction reaction.

In the majority of cases inhibition is achieved through interaction or reaction between the corrosion inhibitor and metal surface, resulting in the formation of an inhibitive surface film, this may occur directly at the metal / environment interface or via precipitation. In other cases the chemistry of the environment may be modified to render it less corrosive, e.g. by chemically scavenging dissolved oxygen, chemically neutralising dissolved acidic gases, adjusting pH to promote stable (inherent) passivation.

Corrosion inhibition was in early times a practical art. Now it has reached sufficient maturity and attained scientific status. Initial empirical approaches to the selection of inhibitors were followed by more scientific approaches in the selection and design of inhibitors [7-8]
Table – 1.3. Methods of Corrosion Control

<table>
<thead>
<tr>
<th>Corrosion Control Methods</th>
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<tbody>
<tr>
<td>Modification of Metal</td>
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<tr>
<td>Modification of Environmental</td>
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<tr>
<td>Change of Metal / Environmental Potential</td>
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<tr>
<td>Modification of Metal Composition (by alloying)</td>
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<tr>
<td>Modification of Metal Surface</td>
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<tr>
<td>Surface Alloying (Ion Implementation)</td>
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<tr>
<td>Coating</td>
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<tr>
<td>Organic</td>
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<tr>
<td>Metallic</td>
</tr>
<tr>
<td>Inorganic (Silicate Coating etc.)</td>
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<tr>
<td>Vapour Phase Inhibitors</td>
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<tr>
<td>Acid Inhibitors</td>
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<tr>
<td>Neutral &amp; Alkaline Inhibitors</td>
</tr>
<tr>
<td>Organic</td>
</tr>
<tr>
<td>Inorganic</td>
</tr>
<tr>
<td>Electrodeposition (Zn, Cd, Ni, Cr etc.)</td>
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<tr>
<td>Hot Dipping (Zn, Al, Sn)</td>
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<tr>
<td>Diffusion Coating (Cr, Al)</td>
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<tr>
<td>Alloying with Noble Metal</td>
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<tr>
<td>Impressed Current</td>
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<tr>
<td>Sacrificial Anodic</td>
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<tr>
<td>Impressed Current</td>
</tr>
<tr>
<td>Cathodic Protection</td>
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<tr>
<td>Anodic Protection</td>
</tr>
<tr>
<td>Impregnation</td>
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<tr>
<td>Dehumidification</td>
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<td>Inhibitors</td>
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The basis action of inhibitors is attributed to an increase in over voltage of the hydrogen ion discharge as the cathodic reaction of the corrosion process [9-10] or an increase in ohmic resistance of an inhibitor film at the metal-electrolyte interface [11] or due to some type of adsorption on the metal surface. Correlations between molecular structure and the extent of inhibition by organic inhibitors have given further support to these theories [12].

Modern instrumental techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) [13-14] coupled with electrochemical techniques which measure the polarization curves, polarization resistance, electrochemical noise and electrochemical impedance have been found to elucidate the corrosion inhibition mechanisms [15-16]. A knowledge of the mechanism of a corrosion inhibition process is highly desirable in the design and proper selection of inhibitors based on structural [17] and theoretical considerations [18].

1.6.1 CLASSIFICATION OF INHIBITORS

Classification of corrosion inhibitors is somewhat a subjective exercise being very much dependent on the method employed. For example one could choose the inhibitors to classify them in terms of mechanism environment to which they are added, metal to be protected or inhibitor chemistry, of which none are mutually exclusive.

Some of the main classification used particularly for inhibitor are as follows.

1. Safe or dangerous inhibitors.
2. Oxidizing or non-oxidizing inhibitors
3. Acid or alkaline or neutral inhibitors
4. Vapour phase inhibitors
5. Anodic or cathodic or mixed inhibitors.

According to Putilova [19] inhibitors are of three types.

Type A Forms a protective film on the metal surface.

Type B reduces the aggressiveness of the corrosive media.

Type AB forms a protective film and also reduces the aggressiveness of the corrosive agent.
1.6.1.1 SAFE OR DANGEROUS INHIBITORS

This classification relates to the type of corrosion that will occur when the concentration is below the minimum or critical value.

Thus any inhibitor present in insufficient amount, it allows only a uniform type of corrosion to proceed at a rate not greater than that obtaining in an uninhibited system is called 'safe' inhibitor such as carbonates, zinc sulphates do not interfere with anodic reaction but inhibit cathodic reaction, whereas 'dangerous' inhibitor leads to enhance the localized attack e.g. pitting when present in below critical concentration, such as some chromates, nitrates, phosphates, molybdates, tungstate etc.

1.6.1.2 OXIDIZING OR NON-OXIDIZING INHIBITORS

These are characterized by their ability to passivate the metal. In general non-oxidizing inhibitor require the presence of dissolved oxygen in the liquid phase for the maintenance of the passive oxide film for e.g. phosphate and molybdate, whereas dissolved oxygen is not necessary with oxidizing inhibitor for e.g. nitrates and nitrites work as anodic oxidizing passivators.

1.6.1.3 ACID INHIBITORS

This may be further classified into inorganic and organic inhibitors

(i) INORGANIC INHIBITORS

In strong acid solutions, Br\(^{-}\), I\(^{-}\) have been found to be effective inhibitors [20]. The oxides like AS\(_2\)O\(_3\), Sb\(_2\)O\(_3\) have been reported as the inhibitors in acid media. These substances get deposited in the form of metal on iron surface and increase the hydrogen over-voltage and subsequently reducing the corrosion [21]. Addition of heavy metal ions such as Pb\(^{2+}\), Mn\(^{2+}\) and Cd\(^{2+}\) inhibit the corrosion of iron in acids. This effect is due to the under potential deposition of metal ions, which leads to complete coverage of metal adsorbate on the iron surface [22].

(ii) ORGANIC INHIBITORS

Various classes of organic compounds such as alcohols, amines, aldehydes, mercaptans, alkaloids, anisidines, aliphatic, aromatic, heterocyclics, fatty acids, polymers, natural products etc. and some condensation products have been extensively used as
corrosion inhibitors in the recent past years. The effectiveness of a large number of organic compounds as inhibitors have been correlated [23-26] to different factors like chemical structure, substituent effect, sterric, Hammett constant, molecular weight, carbon chain length, basicity (pka), dipole moment, magnetic suceptibility, pH of the solution, temperature, nature of metal, NMR shift etc. The study of a variety of organic compounds in relation to their different aspects of inhibition in different environments has been excellently reviewed by Sanyal [27].

An organic compound can be cathodic, anodic or both depending on its reaction at the metal surface and how the potential of the metal is affected [28]. Generally cathodic inhibitors increase cathodic polarization and shift the corrosion potential to more negative values and anodic inhibitors enhance anodic polarization and shift the corrosion potential to more positive values.

The effectiveness of an organic inhibitor depends mainly on (i) size (ii) carbon chain length (iii) Bonding strength to the metal surface (iv) aromaticity and / or conjugated bonding and (v) Nature and number of bonding atoms.

1.6.1.4 ALKALINE AND NEUTRAL INHIBITORS

These inhibitors include cathodic inhibitors (which increase cathodic polarization), anodic inhibitors (which enhance the anodic polarization) and mixed or general inhibitors (which act on both cathodic and anodic areas).

Anodic inhibitors form an oxide or some other insoluble film. Insufficient concentration of anodic inhibitor will lead to severe pitting.

Sodium chromate is one of the most widely used and efficient inhibitors. Sodium silicate is generally used in hot water system. The other compounds used in neutral and alkaline media are borates, molybdates and salts of organic acids, like benzoates and salicylates.

1.6.1.5 VAPOUR PHASE INHIBITORS (VPI)

The substances which protect metallic materials against atmospheric corrosion are called vapour phase inhibitors. These are also called volatile corrosion inhibitors. These are used in boilers to prevent corrosion in condenser tubes by neutralizing the acidic
They are transported to the site of corrosion in a close system by volatilization from a source. Compounds of this type inhibit corrosion by making the environment alkaline.

These inhibitors usually consist of aliphatic and cyclic amines and nitrites with a high vapour pressure. The vapour pressure of these compounds at room temperature is usually between 0.1 and 1.0 mm mercury, so that the inhibitor evaporates sufficiently fast to ensure its adequate availability in the vicinity of the metal surface, but not so fast that it has disappeared in a few hours or days.

Typical examples of VPI include dicyclohexylamine chromate and benzothiazole for protecting copper, phenylthiourea and cyclohexylamine chromate for brass. Dicyclohexylamine nitrite is said to protect both ferrous and non-ferrous parts.

The inhibitors vapour condenses on contacting a metal surface and is hydrolysed by moisture present to liberate nitrite and benzoate ions which in presence of available oxygen are capable of passivating steel as they do in aqueous solution.

1.6.1.6 ANODIC INHIBITORS

The substance which reduce the anode area by acting on the anodic sites and polarize the anodic reaction are called anodic inhibitors. In the presence of anodic inhibitors, displacement in corrosion potential ($E_{corr}$) takes place in positive direction. Supress corrosion current ($I_{corr}$) and reduce the corrosion rate. In aqueous acid media, the corrosion of metals takes place at the anodic area through metal dissolution. The cathodic reaction generally involves the reduction of hydrogen ions or by oxygen reduction to hydroxyl ion. These reactions may be represented schematically as shown in Figure 1.2. The curve $E_a^{corr}$ represents the anodic reaction while $E_c^{corr}$ represents the cathodic reaction and the point B where both anodic and cathodic reactions intersect corresponds to corrosion potential ($E_{corr}$) and corrosion current ($I_{corr}$). The substances which retard the anodic reaction leads to enhancement of anodic polarization. In this situation, anodic curve becomes $E_a^{corr}$ (Figure 1.2a) and the current $I_a^{corr}$ corresponding to O is less than $I_{corr}$ (corrosion current in the absence of the inhibitors) and the rate of corrosion is decreased.

Anodic inhibitors which causes a large shift in the corrosion potential are called passivating inhibitors, if used in insufficient concentrations, they cause pitting and sometimes an increases in corrosion rate. With careful dosage control, anodic inhibitors
Figure 1.2. Mechanism of action of corrosion inhibitors based on polarization effects.
are frequently used because they are very effective in sufficient quantities. Anodic inhibitors cause passivity by speeding up the corrosion reaction to the extent that the anodes are polarized to a passive potential. If a corrosion of a metal or alloy is controlled by the anodic reaction (anodic control), it is obvious that decrease in overall corrosion should be proportional to the portion of the anodic areas being polarized. On the other hand, if corrosion is controlled by the cathodic reaction (cathodic control), the corrosion current and, therefore, the total amount of the corrosion is not affected by decreasing the anodic areas. In this case, the same amount of corrosion must be distributed over a smaller anodic area, resulting in intensified localized attack (pitting type of corrosion).

The inhibitions mechanism of the anodic corrosion inhibitors has been a matter of long dispute and there have been two points of view advance to explain their action. One supports the formation of protective insoluble film on metals in the presence of the inhibitors while the other can be understood in such a way that the inhibitors get adsorbed by specific force interaction or through chemisorption on the surface of metals.

(1) PROTECTIVE FILM MECHANISM

It has been observed that most of the potassium and sodium salts containing anions act as anodic inhibitors by forming a sparingly soluble salt with the metal. Hoar and Evans [29] have shown that chromates react with ferrous ions and precipitate an adherent protective film of hydrated ferric and chromic oxides on the anodic areas. It has been shown that during the inhibition of corrosion by sodium hydroxide [30], orthophosphate [31], nitrite [32], chromate [33] and other anodic inhibitors like sodium carbonate, benzoate and molybdate [34] in aerated solutions, there occurs the formation of an invisible protective thin film by $\gamma$-Fe$_2$O$_3$.

(2) ADSORPTION MECHANISM

According to Uhlig [35], for inhibition, oxide film formation is not necessary, primary inhibition by chromates and other oxidizing inhibitors is due to physical and activated adsorption-chemisorption, through which valence forces of the surface metal atoms are satisfied. These views were confirmed from the measurements of electrode potential as well as the measurement of residual activity of an iron sample immersed in radioactive chromate solution and subsequently washed thoroughly with distilled water.
[36-38]. Later on, Hackerman [38] found that anions adsorbed at the oxide solution interface were responsible for inhibition rather than the formation of metal oxide film.

### 1.6.1.7 CATHODIC INHIBITORS

Those substances which reduce the cathode area by acting on the cathodic sites and polarize the cathodic reaction are called cathodic inhibitors. They displace the corrosion potential \(E_{\text{con}}\) in the negative direction and reduce corrosion current, thereby retard cathodic reaction and suppress the corrosion rate (Figure 1.2b). In this situation, the point of intersection is at \(O\) and corresponding corrosion current \(I_{\text{cor}}\) will be lower than that without inhibitor \(I_{\text{con}}\).

The cathodic inhibitors, with a few exceptions [39] do not lead to intensified or localized attack, since, cathode areas are not attacked during corrosion. If corrosion is controlled by cathodic reactions, the added cathodic inhibitor would decrease cathodic area and hence overall corrosion rate. On the other hand, if the corrosion is controlled by anodic reaction, decrease in cathodic area would increase cathodic current density but will have no effect on the nature of corrosion. The increase in cathodic current density may cause the reduction of substances present which would not otherwise be reduced. Mann et al [40-42] and other investigators [43-46] working on numerous organic inhibitors in acid media have proposed that inhibitors exist in onium structure and get adsorbed on the cathodic area of the surface by force of physical adsorption, and chemisorptions. In contrast, Bockris and Conway [47] have claimed that the action of cathodic inhibitors is due to an increase of the hydrogen over voltage rather than that by an adsorbed inhibitor film on the metal surface. The cathodic inhibition due to the general adsorption of the inhibitors on the metal surface remains, however the most accepted theory [48-49].

Like anodic inhibitors, cathodic inhibitors are not dangerous but safe, when present in solution in sufficient quantities and involve no additional risk of pitting attack.

Cathodic inhibitors may be divided into three categories.
(i) CATHODE POISONS

When the cathodic reaction is the reduction of hydrogen ions to hydrogen gas, several steps are involved. The hydrogen ions are reduced to hydrogen atoms which are adsorbed on the surface of the metals.

\[ 2H^+ + 2e^- \rightarrow 2H^0 \text{ (ads)} \]  \hspace{1cm} (22)

Two hydrogen atoms may be then combine to form a hydrogen molecule which is discharged from the surface:

\[ 2H^0 \text{ (ads)} \rightarrow H_2 \uparrow \]  \hspace{1cm} (23)

Cathodic poisons are substances which interfere with the formation of hydrogen atoms or recombination of hydrogen atoms to hydrogen gas on the surface of corroding metal. The rate of cathodic reaction is slowed and because anodic and cathodic reactions must proceed at the same rate, then the whole corrosion process is slowed. Some cathodic poisons such as sulfides and selenides are adsorbed on the metal surface other compounds of arsenic, bismuth and antimony are reduced at the cathodic to deposit a layer of the respective metals. Sulfides and selenides generally are not useful inhibitors because they are not very soluble in acidic solutions, they precipitate many metal ions and are toxic. A serious drawback in the use of cathodic poisons is that they sometimes cause blistering of steel and increase its susceptibility to hydrogen embrittlement. Since the recombination of hydrogen atoms is inhibited, surface concentration of hydrogen is increased and a greater function of hydrogen produced by the corrosion reaction, is adsorbed \([50]\) by the steel.

(ii) CATHODIC PRECIPITATES

These are filming type of inhibitors for example \(\text{Ca}(\text{HCO}_3)_2\), \(\text{ZnSO}_4\) and some other compounds with cations that migrate towards the surface and react with cathodically formed alkali (mild) to produce insoluble protective film or layer thus lessening corrosion current by making the cathode reaction more difficult.

\[ \text{Ca}^{2+} + 2 \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CaCO}_3 + \text{HCO}_3^- + \text{H}_2\text{O} \]  \hspace{1cm} (24)

\(\text{From hard water}\) \hspace{1cm} \(\text{Cathodic alkali}\) \hspace{1cm} \(\text{Cathodic film}\)

\[ \text{Zn}^{2+} + \text{OH}^- \rightarrow \text{Zn} (\text{OH})_2 \]  \hspace{1cm} (25)

\(\text{From Cathodic Inhibitor}\) \hspace{1cm} \(\text{Cathodic alkali}\) \hspace{1cm} \(\text{Cathodic film}\)
Hard waters are less corrosive to iron than soft or distilled water.

(iii) CATHODIC SCAVENGERS

The most common oxygen scavengers used are sulfite, sulphur dioxide and hydrazine which remove dissolved oxygen from aqueous solution

\[
2 \text{Na}_2\text{SO}_3 + \text{O}_2 \rightarrow 2 \text{Na}_2\text{SO}_4 \tag{26.1}
\]

\[
2 \text{SO}_2 + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{SO}_4 \tag{26.2}
\]

\[
\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O} \tag{26.3}
\]

Such inhibitors will function on very efficiently in close systems where oxygen depolarization (reduction is the controlling cathodic reaction, but will not be effective in strong acid solutions.

The advantage of hydrazine over sulphite in boiler water corrosion control is that the former does not cause an increase in hardness of the water with accompanying danger of boiler scale formation in the presence of free calcium ions. Besides, the liberation of ammonia by reaction

\[
3 \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4 \text{NH}_3 \tag{27}
\]

leads to an alkalinization of water to reduce free carbondioxide concentration. The reaction rate of sulphite, sulphur dioxide and hydrazine with oxygen at low temperature is slow. So catalyst like cobalt, manganese and copper salts are usually added to increase the reaction rate.

1.6.1.8 MIXED INHIBITORS

There are a number of chemicals which inhibit the metallic corrosion by interfering with both the anodic and cathodic reactions are called mixed inhibitors. This type of inhibition can be represented by Figure 1.2c. The anodic and cathodic reactions are represented by $E^{m}_{\text{corr} A}$ and $E^{m}_{\text{corr} C}$ respectively and corrosion current $I^{m}_{\text{corr}}$ in presence of such type of inhibitors is considerably less than that in their absence. Glue Gelatin and other high molecular weight substances fall in this category. It is believed that the action of such type of inhibitors at the metal-liquid interface is due to their concentration or coagulation providing a shield to the metal surface. Machu [51-52]
claims that their action is mainly due to formation of porous layer which increases the electrical resistance of the surface layer.

1.6.1.9 RECENT CLASSIFICATION OF INHIBITORS

A recent classification [53] on the basis of the mechanism of inhibitive action, has divided the corrosion inhibitors into four major categories (Table 1.4)

(i) Barrier Layer Formers
(ii) Neutralizers
(iii) Scavengers
(iv) Miscellaneous

(i) BARRIER LAYER FORMERS

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

(ii) NEUTRALIZERS

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

(iii) SCAVENGERS

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

(iv) MISCELLANEOUS

These inhibitors include material such as scale inhibitors and biological growth inhibitors which reduce corrosion by interfering with other processes.
The above classification of inhibitor types by function appears to give a fairly simple and concise approach, although it has limitations in cases where the mechanism is not known. In general the use of neutralizing and scavenging type inhibitors seems to be the best suited for closed systems where such chemicals are not lost in the system. In open systems however the use of inhibitors is difficult to justify.

**Table 1.4 Recent classification of inhibitors**

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Barrier layer formers</td>
<td>Acetylenic alcohol in HCl</td>
</tr>
<tr>
<td>A. Adsorbed layer formers</td>
<td>NaNO₂ in water</td>
</tr>
<tr>
<td>1. Cathodic Inhibitors</td>
<td></td>
</tr>
<tr>
<td>2. Anodic Inhibitors</td>
<td></td>
</tr>
<tr>
<td>3. Mixed Inhibitors</td>
<td></td>
</tr>
<tr>
<td>B. Oxidizing inhibitors-Passivators</td>
<td></td>
</tr>
<tr>
<td>C. Conversion layer formers</td>
<td></td>
</tr>
<tr>
<td>1. Insoluble Corrosion Products</td>
<td></td>
</tr>
<tr>
<td>2. Cathodic deposits</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>II. Neutralizing inhibitors</td>
<td></td>
</tr>
<tr>
<td>1. Volatile</td>
<td>Cyclohexylamines in boilers</td>
</tr>
<tr>
<td>2. Non-Volatile</td>
<td>Amines, brine</td>
</tr>
<tr>
<td>III. Scavengers</td>
<td></td>
</tr>
<tr>
<td>1. Oxygen scavengers</td>
<td>Na₂SO₃ in boilers</td>
</tr>
<tr>
<td>2. Decomposition inhibitors</td>
<td>Dioxane in CH₃CCl₃⁻</td>
</tr>
<tr>
<td>IV. Miscellaneous</td>
<td></td>
</tr>
<tr>
<td>1. Biological growth inhibitors</td>
<td>Quaternary amines</td>
</tr>
<tr>
<td>2. Scale inhibitors</td>
<td>Phosphate</td>
</tr>
<tr>
<td>3. Other</td>
<td>H₂O in NH₃</td>
</tr>
</tbody>
</table>
1.7 SOME ASPECTS OF CORROSION INHIBITION

1.7.1. APPLICATION OF HAMMETT EQUATION IN CORROSION INHIBITION

Hammett equation has been applied to corrosion inhibition and the corrosion inhibition efficiencies of various substituted organic inhibitors were correlated with Hammett's $\sigma$ parameter which is a measure of the electron donating or withdrawing ability of the substituent [54]. The principle of substituting organic inhibitors with electron donating substituents and thereby increasing the electron density at the donor atom and hence corrosion inhibition efficiency has been applied to aromatic acids, aromatic amines and aromatic nitriles. In thiophene derivatives [55] substituents increased the dipole moment of the molecule thereby causing an increase in adsorption and inhibition efficiency.

Following relation was given [54] as an application of the Hammet equation in corrosion inhibition by a blocking mechanism.

$$\log \left( \frac{1 - \gamma_R}{1 - \gamma_H} \right) = \rho \sigma$$  \hspace{1cm} (28)

$\gamma_R$ and $\gamma_H$ are inhibitors efficiencies in blanks and inhibited solution.

$\rho$ = constant & a measure of the sensitivity of the equilibrium constant.

$\sigma$ = substituent constant, substituents with positive values of $\sigma$ are classified as electron withdrawing groups while negative values as electron donating groups.

Later on it was shown that the linear free energy relationship (LEFR) can be applied to the acid corrosion inhibition. The LEFR principal is applicable to organic reactions in cases of isoentropy ($\Delta S = $ constant), isoenthalpy ($\Delta H = $ constant) and isokinetic ($\Delta H \sim \Delta S$) reaction series.

(i) Corrosion inhibition by blocking the active site without changing $\Delta G''_{\text{corr}}$. e.g the corrosion inhibition of nickel in IN HCl by 2, 4-diphenyl-6-(R-styryl) pyrilium cation [56]. The blocking action is due to the adsorption of the inhibitor through a $\pi$ electronic interaction of inhibitors with nickel.

(ii) Corrosion inhibition due to changes in $\Delta G''_{\text{corr}}$. Following equation is valid [56]

$$\log \gamma_R = \log \gamma_H + \rho \sigma$$  \hspace{1cm} (29)
e.g. corrosion of iron in HCl by substituted anilines

(iii) Corrosion inhibition due to surface blocking as well as due to changes in $\Delta G^{*}_{\text{corr}}$

Following equation is valid [56]

$$\log \gamma_R / \gamma_H = \rho \sigma - \log \theta_R / \theta_H$$  \hspace{1cm} (30)

$\theta$ = surface covered by inhibitors e.g. inhibition of iron in 1N HCl by 2, 4-diphenyl-6-(R-styryl) pyrilium perchlorate.

1.7.2 STUDY OF CORROSION INHIBITION FROM THE ASPECT OF QUANTUM CHEMISTRY

For proper design and selection of corrosion inhibitors quantum chemical calculations provide, qualitative and semi-quantitative information [57-59].

Chakrabarti [58] used the simple Hückel molecular orbital theory in studying the corrosion inhibition of mild steel in 6% HCl by biguanide and biurets compounds. It was found that the inhibition efficiency depends mostly upon the energy of the highest occupied molecular orbital (HOMO) and energy of the lowest unoccupied molecular orbital (LUMO). The inhibitors act as electron donors to the iron atoms, block the corrosion reaction by the formation of a bond [58].

The linear combination of atomic orbitals (LCAO) self consistent field (SCF) molecular orbital (MO) semiempirical method was used to study [57] linear chain diols, diamines and aliphatic aminoalcohols. It was observed that the corrosion inhibition is high when the molecule is planar and has a high energy value for HOMO.

1.7.3 HSAB PRINCIPLE IN CORROSION INHIBITION

The hard and soft acid base theory propounded by Pearson [60] was applied to corrosion inhibition phenomena. According to HSAB principle inhibitors have been termed as ‘hard’ ‘soft’ inhibitors [61]. Softness and hardness are associated with high and low polarizability respectively [60]. According to hard and soft base (HSAB) principle, hard acids react with hard bases more readily than with soft bases. Neutral metal atoms are soft acids which tend to react with soft bases such as sulphur – bearing inhibitors. Nitrogen-containing inhibitors are considered to be hard bases and may interact with neutral metal atoms less strongly than sulfur – containing inhibitors [62]. Hence HSAB
Principle has been extensively used in proper designing and selection of inhibitors in environments of interest.

Application of the HSAB principle to the adsorption of inhibitors on the metals has been recently analysed quantitatively for a general reaction [63].

\[ v_a S_L + v_B [M]_L \rightarrow v_c [M]S + v_D L \cdot L \]  

(31)

where \( v_a, v_b, v_c \) stoichiometric coefficients

\( S = \) adsorbing species, \( M = \) Metal, \( L = \) Solvent.

In terms of standard free energy and HSAB equation is modified and given as

\[ -G^o_{(M|S)} = G^o - k_H G^o_{(M|S)(H)} - k_S G^o_{(M|S)(S)} \]  

(32)

\( \Delta G^o \) = Standard free energy of changes transfer from donor to accepter

\( G^o_{(M|S)} \) and \( G^o_{(M|S)(S)} \) standard energies of stabilization due to 'hard' and 'soft' inhibition, \( k_H \) and \( k_S \) are coefficients.

Finally the expression is written as

\[ G^o_{MS} = \alpha \left( W_e + V_{M-L}^0 \ F - Z_i X_{i-v} \ F - F_{eff} + \Phi F \right) + \left( Z_2 - \alpha \right) \left( \Phi + \Delta \psi \right) F \]  

(33)

\( \alpha = \) degree of charge transfer, \( F = \) Farday, \( Z = \) charge

\( V_{M-L}^0 = \) Voltaic potential of metal solvent interface,

\( W_e = \) electronic work function of metal, \( \Phi = \) electrode potential.

The sign and value of \( \Phi \) determines the nature of adsorption, when \( \Phi < 0 \), adsorbents of cation - type (hard) are predominantly adsorbed. When \( \Phi > 0 \) for metals, anion - type adsorbents (hard bases) are adsorbed when \( \Phi = 0 \), metals are biphilic and neutral, dipole adsorbents are adsorbed.

Application of HSAB principle shows that metals such as Hg, Cd, Pb & Zn belong to 'hard' type. The surface complexes formed are due to the 'hard' type interaction e.g. aliphatic alcohols, aromatic amines are readily adsorbed on these metals.

### 1.7.4 HANSCH MODEL (HYDROPHOBICITY)

Hansch equation and hydrophobicity give criteria in the selection of inhibitors. Modified Hansch equation [64] for corrosion inhibition is given as

\[ \log A = -(\log P)^2 + b \log P + c(p) + cte \]  

(34)
A and P are coefficients of distribution, a and b are constants, c is the concentration of the inhibitor, cte is free enthalpy change involved in the active inhibitor to corrosion site interaction process, p is electronic factor.

When corrosion inhibition is achieved by surface active compounds with amphiphatic structure such as hydrocarbon chains, extensive hydrogen bonding in water is affected by the hydrophobic groups of the surface active compounds dissolved in water. The polar functional groups adsorbs on the metal with a hydrophobic tail. The hydrophobic groups of the free inhibitor molecules in solution interact with the hydrophobic groups of the adsorbed molecule at the interface and results in aggregation known as hemi micelle formation [65]. Dupin and co-workers [64] introduced the concept of micellization of corrosion inhibition processes and defined ‘p’ according to thermodynamics of micellization of surface active species [66] and expressed as

\[
p = \frac{RT}{\langle n \rangle_{nc}} \ln \langle n \rangle_{nc} + RT \ln (\text{cmc}) - \Delta G^0_{\langle n \rangle_{nc}} + \text{cte}
\]

\(\langle n \rangle_{nc}\) = average size of micelle obtained from ‘n’ molecules containing \(n_c\) atoms of carbon; \(\Delta G^0\) is the standard free energy change involved.

With an increase in concentration of surface active compounds in solution, the probability of formation of micelles increases. The concentration at which the molecules aggregate and form micelles is known as critical micelles concentration (cmc). The temperature above which micellization occurs is the Kraft point. Studies of corrosion inhibition of steel in a chloride solution containing hydrogen sulfide by imidazoline derivatives showed the dependence of inhibition efficiency on critical micelle concentrations of the inhibitors [64].

In a given homologous series of inhibitors, the degree of inhibition at a fixed concentration of inhibitor was found to increase with the number of carbon atoms in the chain up to 10 – 14 followed by a decrease in inhibition. This observation indicates that the transport of the active inhibitor to the corrosion site plays an important role in the corrosion inhibition process. These results also show the existence of a relationship between the formation of aggregates in solution and the inhibiting behaviour of the inhibitors. This phenomenon can be attributed to structural changes in the adsorption
layer and is in a way comparable to the effects of micellization on the structure of the electrical double layer and the adsorption potential of micelles.

cmc, average size of the micelle and hence ‘p’ depend on the number of carbon atoms in the hydrophobic chain and the coefficient of distributions ‘P’. Hansch method later modified by Nys and Rekker [67]. According to this the overall hydrophobicity, log P, is assumed to be a sum of individual hydrophobicity factors, fi

$$\log P = \sum_i f_i$$

(36)

The equation used for correlations of data for imidazoline, data shows that hydrophobicity is more representative than p. This relationship involves a modification in the electrical double layer of inhibitor concentrations in the region of critical micelle concentrations.

1.7.5. FREE AND WILSON CORRELATIONS

Free and Wilson model was applied by Dupin et al [68] to the corrosion inhibition phenomenon. The model allows one to predict the most favourable structure of an inhibitor. This is a general mathematical approach which does not take into account any specific chemical behavior of the inhibitors.

The equation due to the Free and Wilson model that describes the efficiency of the inhibitor (E) is

$$E = \gamma + \sum e_i x_i$$

(37)

Where γ is the contribution of the skeletal structure to the activity, e_i is the contribution of the i^{th} substituent e_i is the contribution of the i^{th} substituent to the efficacy and x_i is a coefficient which is unity in the presence of a substituent and zero in the absence of a substituent. An analogous equation for the measured corrosion current in the presence of an inhibitor may be written as

$$\text{colog} i_{corr} = \gamma + e_1 x_1 + e_j y_j + e_k Z_k$$

(38)

1.7.6 SYNERGISM IN INHIBITION

Synergism is the term applied to the marked reinforcement of the inhibiting action of one inhibitor by the addition of small amounts of second inhibitor, even though the
second inhibitor is less effective when used alone. The phenomenon of synergism is also supported by the synergistic parameter \( S_i \), which was calculated by using the relationship given by Aramaki and Hackerman [69]

\[
S_i = \frac{(1 - I_{1+2})}{(1 - I'_{1+2})}
\]  

(39)

Where \( I_{1+2} = (I_1 + I_2) - I_1 I_2 \); \( I_1 \) = inhibition efficiency of the anion; \( I_2 \) = inhibition efficiency of the anion; \( I_2 \) = inhibition efficiency of the cation; \( I'_{1+2} \) = measured inhibition efficiency for the cation in combination with anion.

The inhibition efficiency of acetylenic compounds has been greatly improved when combined with amines or thio compounds [70].

It was shown by Foley [71] that tetraisoamyl ammonium sulphate has little influence on the dissolution of iron in 4N sulphuric acid. However, when 0.005N KI was added, the organic cation is adsorbed reducing the double layer capacity and the dissolution of iron is very much decreased.

Halide ions are known both to stimulate and inhibit the corrosion of metals [72]. The synergistic effect takes place due to co-adsorption of ions on the metal surface [73].

1.7.7 ADSORPTION

When a corrosion inhibitors is added to a system, adsorption of the inhibitor molecule at the metal solution interface occurs and this is accompanied by a change in potential difference between the metal electrode and the solution due to the non uniform distribution of electric charges at the interface.

Adsorption of the organic molecule occurs because the interaction energy between the inhibitors and the metal surface is higher than the interaction energy between the water molecules and the metal surface [74].

In the adsorption of organic inhibitors the water molecules adsorbed at the metal surface in contact with the aqueous solution are involved. As a consequence, the adsorption of an organic substance at the metal/solution interface may be written [75-76] according to the following displacement reaction.

\[
\text{Org}_{(\text{sol})} + n\text{H}_2\text{O}_{(\text{ads})} \rightleftharpoons \text{Org}_{(\text{ads})} + n\text{H}_2\text{O}_{(\text{sol})}
\]  

(40)
Where 'n' is the number of water molecules removed from the metal surface for each molecules of inhibitor adsorbed. The adsorption can be classified as:

(i) Electrostatic adsorption
(ii) Chemisorption
(iii) π-bond orbital adsorption

(i) ELECTROSTATIC ADSORPTION (PHYSICAL ADSORPTION)

Physical adsorption is due to the electrostatic attraction between the inhibiting ions or dipoles and the electrically charge surface of the metal. The surface charge on the metal is defined by the potential of metal (E_{corr}) with respect to its potential of zero charge PZC [77]. At PZC the net charge on the electrode is zero. At potentials more positive than PZC, the electrode is positively charged and at potentials more negative than PZC the electrode is negatively charged. When φ = E_{corr} - E_{eq} is negative, cations are adsorbed and when φ is positive, anions are adsorbed. The forces in electrostatic adsorption are generally weak. The inhibiting species adsorbed on the metal surface due to electrostatic forces can also be desorbed easily. A main feature of electrostatic adsorption is that the ions are not in direct physical contact with the metal. A layer of water molecular separates the metal from the ions. The physical adsorption process has a low activation energy and is relatively independent of temperature.

(ii) CHEMISORPTION

It is probably the most important type of interaction between the metal surface and an inhibitor. Chemisorption of an organic molecule involves a bonding between the metal and adsorbed molecules through an atom containing an unshared electron. It depends on the nature of the metal, molecular structure of the inhibitor molecule and the chemical nature of the bonding atom. Chemisorption process is slower than electrostatic sorption and has higher activation energy. It depends on the temperature and higher degree of inhibition should be expected at higher temperature.
(iii) **π - BOND ADSORPTION**

Inhibitor molecule containing aromatic nucleus with double bonds or triple bonds interact with metal by their π - bond orbitals. This type of interaction is independent of potential, but effective principally on the positive branch of electrocapillary maximum (ecm) and is temperature independent. Hackerman and Hurd [78] correlated the inhibitor efficiency with the number of carbon atoms in the ring.

**1.8 MECHANISM OF INHIBITION IN ACIDS**

The inhibitive action of organic compounds occur on the metallic surface due to interaction between the inhibitor and the metal surface by adsorption phenomenon. In this process [79], the molecules are held on to the surface of the adsorbent by valence forces i.e., variation in the charge of the adsorbed substance and a transfer of charge from one phase to the other. Therefore, the molecular structure of the inhibitors assumes special significance [80]. The electron density at atoms of functional group constituting a reaction centre affects the strength of the adsorption bond [81]. It also depends on the properties of the metal, as well as on the polarizability of the functional group [82-84]. Inhibition by adsorption can be explained by LFER correlation [85-86].

**1.8.1 FACTORS AFFECTING ADSORPTION MECHANISM**

Inhibitor adsorption on metals is influenced by the following main factors.

(i) **SURFACE CHARGE ON THE METAL**

The magnitude and sign of the surface charge of the metal play a very important role for the establishment of the adsorption bond. The effects exercised by organic inhibitor on the electrode reactions must be connected with the modifications induced in the structure of the electrochemical double layer because of their adsorption. In solution the charge on a metal can be expressed by its potential with respect to the zero charge potential. This potential often referred to as the Φ potential, is more important than the potential on a hydrogen scale and sign of these potentials are different [87]. As the potentials becomes more positive, the adsorption of anions is favored and as the potential becomes more negative, the adsorption of cations is favoured.
(ii) REACTION OF ADSORBED INHIBITORS

In some cases, the adsorbed corrosion inhibitors may react to form a product by
electrochemical reduction, which may also be inhibitive in nature. Inhibition due to the
added substances has been termed as primary inhibition and that due to the reaction
product, secondary inhibition [88]. In such cases, the inhibitive efficiency may increase or
decrease with time according to whether the secondary inhibition is more or less effective
than the primary inhibition [89].

(iii) INTERACTION OF ADSORBED INHIBITORS SPECIES

Lateral interactions between adsorbed inhibitor species becomes significant with
increase of surface coverage of the adsorbed species. This lateral interaction may be
attractive or repulsive. Attractive interaction occurs between molecules containing large
hydrocarbon components. Repulsive interactions occur between ions or molecules
containing dipoles and lead to weaker adsorption at high coverage [90].

(iv) INTERACTION OF THE INHIBITOR WITH WATER MOLECULES

The surfaces of metals in aqueous solutions are covered with adsorbed water
molecules. Adsorption of inhibitor takes place by the displacement of adsorbed water
molecules from the surface, which involves free energy for adsorption. It is found to
increase with the energy of solvation of the adsorbing species [91].

(v) STRUCTURE OF INHIBITORS AND THEIR ADSORPTION

Inhibitors can bond to metal surface by electron transfer to the metal to form
adsorption bond. Generally the inhibitors are the electron donor and the metal is the
electron acceptor. The strength of this bond depends on the characteristics of both the
adsorbate and adsorbent. Electron transfer from the adsorbed species is favoured by the
presence of relatively loosely bound electrons, such as may be found in anions and
neutral organic molecules containing lone pair electrons or π - electron systems
associated with multiple, especially triple bonds or aromatic rings.

Most organic compounds have at least one polar atom i.e. nitrogen, sulphur,
oxygen and in some cases selenium and phosphorous. In general, the polar atom is
regarded as the reaction center for the establishment of the chemisorption process [82]. In
such cases, the adsorption bond strength is determined by the electron density of the atom
acting as the reaction center and by the polarizability of the polar atoms. The effectiveness of the polar atoms with respect to the adsorption process varies in the following sequence [84].

Selenium > Sulphur > Nitrogen > Oxygen

The importance of electron density in chemisorption of organic substances in relation to inhibition phenomena has been evaluated by Donahue [85]. The idea of electron density acquires particular importance in aromatic or heterocyclic inhibitors whose structure may be affected by the introduction of substituents in different positions of the rings [83]. The availability of electron pairs for the formation of chemisorption bonds can thus be altered by regular and systematic variations of the molecular structure. The molecular area, molecular weight and the molecular configuration have been found to have a profound effect on corrosion inhibition efficiency effect on corrosion inhibitors [92].

1.8.2 INFLUENCE OF INHIBITOR ON CORROSION REACTION

An inhibitor may decrease the rate of anodic process, the cathodic process or both processes. The change in the corrosion potential on addition of the inhibitor is the indication of a retarded process [93-94]. Displacement of the corrosion potential in the positive direction indicates mainly retardation of the anodic process (anodic control), whereas displacement in the negative direction indicates mainly retardation of the cathodic process (cathodic control). Little change in the corrosion potential suggests that both anodic and cathodic process are retarded.

In the presence of inhibitor, a displacement of polarization curve without a change in the Tafel slope indicates that the adsorbed inhibitors acts by blocking active sites so that reaction cannot occur, rather than by affecting the mechanism of the reaction [95]. A change in the Tafel slope is the indication of affecting the mechanism of the reaction.

Inhibitors in acid solutions affect the corrosion reactions of metals in the following ways.

(i) FORMATION OF A DIFFUSION BARRIER

The adsorbed inhibitor which forms a surface film on the metal surface, can act as a physical barrier to restrict the diffusion of ions or molecules to or from the metal surface
and so retard the corrosion reactions. This type of behaviour occurs in inhibitors containing large molecules [96].

(ii) **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 reactions corrosion. This blocking process reduces the surface metal atoms at which these reactions can occur, and hence the rates of these reactions. The mechanism of the reactions are not affected and the Tafel slopes of the polarization curves remain unchanged. The anodic and cathodic processes may be inhibited to different extents [93]. 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.

(iii) **PARTICIPATION IN THE ELECTRODE REACTIONS**

The electrode reactions involve the formation of adsorbed intermediate species with surface metal atoms. The presence of adsorbed inhibitors will interfere 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 and the inhibitor remain unchanged with a change in the Tafel slope [97]. 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 curves. This effect has been observed on iron in the presence of inhibitors such as phenylthioureas [98 – 99].

(iv) **ALTERATION OF THE ELECTRICAL DOUBLE LAYER**

The adsorption of ions or species which can form ions on metal surfaces will change the electrical double layer at the metal solution interface, and this in turn will affect the rates of the electrochemical reactions [87, 97].

(v) ** ADSORPTION ISOTHERMS**

An adsorption isotherm give the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in
solution [100]. Various adsorption isotherms have been formulated. Table 1.5 gives the list of isotherms and their corresponding equations [101].

Interpretation of the inhibition characteristics of organic molecules can be made by fitting the data to one of the adsorption isotherm.

1.9 MECHANISMS IN NEUTRAL SOLUTIONS

Inhibition in neutral solution is due to compounds which can form or stabilize protective surface film. The inhibitor may form a surface film of an insoluble salt by precipitation or reaction. Inhibitors forming films of this type include [102 – 103].

(a) Salts of metals such as zinc, magnesium, manganese and nickel
(b) Soluble calcium salts
(c) Polyphosphates in the presence of zinc or calcium.

Another class of inhibitors in neutral solutions act by stabilizing oxide films on metals to form thin protective passivating films e.g. chromate, nitrite, benzoate, silicate, phosphate and borate. Passivating oxide films on metals offer high resistance to the diffusion of metal ions and the anodic reaction of metal dissolution is inhibited.

The mechanisms of action of inhibitors which form salt films on metal have been reviewed [104]. Regarding inhibition of corrosion of iron and steel by anions, further evidence for anion incorporation into oxide films has been obtained using radiotracers [105] and Auger electron spectroscopy [106].

Support for the poreplugging mechanism has been given by autoradiography studies [105].

The anodic passivation of iron has been shown [107-108] to involve the formation of an oxide of lower valency state.

1.10 MECHANISMS IN ALKALINE SOLUTIONS

Metals which form amphoteric oxide are subject to dissolution attack by alkalis are prone to corrosion in basic solutions. Naturally occurring organic compounds such as tannins, gelatin, saponin and agar-agar are often used as inhibitors for metal in basic solutions. The inhibitors extend the pH stability range of the amphoteric oxide and hydroxide layers, as well as repairing the defective oxide and hydroxide films, decreasing
### Table 1.5. Adsorption Isotherms

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Isotherms</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Freundlich</td>
<td>$\beta C = \theta$</td>
</tr>
<tr>
<td>2.</td>
<td>Langmuir</td>
<td>$\beta C = \frac{\theta}{1 - \theta}$</td>
</tr>
<tr>
<td>3.</td>
<td>Frumkin</td>
<td>$\beta C = \frac{\theta}{(1 - \theta)} \exp(-2a\theta)$</td>
</tr>
<tr>
<td>4.</td>
<td>Temkin</td>
<td>$\beta C = \frac{\exp(a\theta) - 1}{1 - \exp[-a(1 - \theta)]}$</td>
</tr>
<tr>
<td>5.</td>
<td>Blomgren-Blockris</td>
<td>$\beta C = \frac{\theta}{1 - \theta} \exp(p\theta^{3/2} - q\theta^3)$</td>
</tr>
<tr>
<td>6.</td>
<td>Parsons</td>
<td>$\beta C = \frac{\theta}{1 - \theta} \exp\frac{2 - \theta}{(1 - \theta)^2} \exp(-2a\theta)$</td>
</tr>
<tr>
<td>7.</td>
<td>Bockris, Devanathan and Muller</td>
<td>$\log C \pm \log \frac{\theta}{1 - \theta} = C + p\theta^{3/2}$</td>
</tr>
</tbody>
</table>

where,

- $\beta = 1/55.5 \left(\exp - (\Delta G_{\text{ads}} / RT)\right) = $ adsorption constant
- $G_{\text{ads}} = $ free energy of adsorption
- $\theta = $ surface coverage
- $C = $ concentration of inhibitor
- $a = $ molecular interaction constant
- $a > 0 = >$ attraction and $a < 0 = >$ repulsion,
- $p$ and $q = $ constants expressed in terms of dipole moments.
the diffusion rate of reactant to the surface and removing corrosion products from the surface.

Compounds such as urea, substituted phenols and naphthols, \(\beta\)-diketones, 8-hydroxyquinoline have been found to be efficient inhibitors in basic solution probably because of their capability in forming metal complexes of exceptional stability. The inhibition action of these compounds involve adsorption, increase in over voltage and formation of metal chelate complexes covering the surface of the metal [109].

### 1.11 TECHNIQUES FOR CORROSION INHIBITION MONITORING

The various techniques employed for corrosion monitoring have been classified as

i. Non-Electrochemical Methods

ii. Electrochemical Methods

i. NON-ELECTROCHEMICAL METHODS

These include techniques like weight-loss measurement and gasometric methods. The main disadvantage of these methods is that these require relatively long exposure times of the corroding system. Also the non electrochemical methods are in general restricted to systems which do not form adherent layers of corrosion products.

a. WEIGHT LOSS MEASUREMENTS

This method is the most reliable method. The electrochemical measurement result are usually compared with weight loss data. Here the change in weight of the specimen is determined by immersing the specimen in the corrosive medium for a fixed time. The rate of metal removal due to corrosion is calculated from:

\[
R = \frac{KW}{ATD}
\]

Where \(R\) is the corrosion rate, \(K\) is a constant, \(W\) is the weight loss to the nearest 0.0001 g, \(A\) is the area of the specimen to the nearest 0.01 sq cm., \(T\) is the time exposure to the nearest 0.01 hour and \(D\) is the density in g/cu.

A variety of units have been used in the literature to express the corrosion rate. Using the units for \(T\), \(A\), \(W\) and \(D\) in the above equation corrosion rate can be calculated in different units with the appropriate value of \(K\) (Table 1.6). If desired, these constants may also be used to convert corrosion rates from one set of units to another [110]. To
convert corrosion expressed in units \( x \) to a rate in units \( y \), multiply by \( K_y / K_x \), e.g., if \( R \) is 10 mpy the rate in mm/yr would be:

\[
10 \left( \frac{8.76 \times 10^4}{3.45 \times 10^6} \right) = 0.254 \text{ mm/yr}
\]

**Table 1.6**: Value of constant K, for determining corrosion rate in different units using weight loss measurements

<table>
<thead>
<tr>
<th>S. No.</th>
<th>EXPRESSION</th>
<th>DIMENSION</th>
<th>CONSTANT K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Inches per month, imp</td>
<td>in/mo</td>
<td>2.87 \times 10^2</td>
</tr>
<tr>
<td>2.</td>
<td>Inches per year, ipy</td>
<td>in/yr</td>
<td>3.45 \times 10^3</td>
</tr>
<tr>
<td>3.</td>
<td>Miles per year, mpy</td>
<td>mils/yr</td>
<td>3.45 \times 10^6</td>
</tr>
<tr>
<td>4.</td>
<td>Millimetres per years, mm/yr</td>
<td>mm/yr</td>
<td>8.76 \times 10^6</td>
</tr>
<tr>
<td>5.</td>
<td>Micrometre per year, mm/yr</td>
<td>\mu m/yr</td>
<td>8.76 \times 10^7</td>
</tr>
<tr>
<td>6.</td>
<td>Picometre per second, pm/sec</td>
<td>pm/sec</td>
<td>2.78 \times 10^6</td>
</tr>
<tr>
<td>7.</td>
<td>Micrograms per square metre per sec., mg/(sq m)(sec)</td>
<td>\mu g/(sq m)(sec)</td>
<td>2.78 \times 10^6 D</td>
</tr>
<tr>
<td>8.</td>
<td>Miligrams per square decimetre per day, mdd</td>
<td>mg/(sq dm)(day)</td>
<td>2.40 \times 10^6 D</td>
</tr>
<tr>
<td>9.</td>
<td>Grams per square metre per hour, g/(sq m)(hr)</td>
<td>g/(sq m)(hr)</td>
<td>1.00 \times 10^4 D</td>
</tr>
</tbody>
</table>

**b. GASOMETRIC METHODS**

This method yields reliable and accurate results with a high degree of reproducitvity. In this method the volume of hydrogen gas (in acid corrosion) evolved during a corrosion reaction is directly measured at a constant temperature. The corresponding metal loss can be calculated. This technique has been used for the inhibitor studies by Nathan [111] and Hackerman [112]. Mathur et al [113] have designed a gasometric unit with which corrosion rates could be monitored under controlled conditions of temperature and pressure without any aqueous tension correction. Singh et al [114] have designed apparatus for measuring adsorbed hydrogen gas and hydrogen diffusion. Also this technique has been successfully applied for the determination of corrosion kinetic parameters by them [113].
However this techniques has certain limitations such as it cannot be applied to a strong oxidising medium like nitric acid, to systems where the inhibitor used undergoes reduction with the hydrogen gas evolution, etc.

ii. ELECTROCHEMICAL METHODS

The electrochemical methods are mostly widely used for the study of inhibitors. Electrochemical methods are finding increased use in corrosion research and in engineering applications. Such methods are practical because the corrosion behaviour of material-electrolyte combinations is a direct function of the mechanism as well as kinetics of the electrochemical methods can be used, in field or in laboratory, to measure corrosion rates without removing the specimen from the environment or altering the sample itself.

a. POLARIZATION METHODS

The electrochemical polarization of metallic sample is accomplished with a power supply known as potentiostat. An auxiliary electrode supplies the current to the working electrode (test specimen) in order to polarize it. The potential between the working electrode and reference electrode is monitored or set at a fixed value. Figure 1.3 illustrates schematically a typical experimental arrangement.

Figure 1.3: Instrumental setup for electrochemical polarisation experiments.
The system is designed so that only an extremely small current can pass between the reference electrode and the working electrode. The current needed to polarize the working electrode is supplied for the auxiliary electrode [115]. Several American Society for Testing and Materials (ASTM) standards discuss methods for performing these experiments [116–117].

In this method the behaviour of inhibitor is understood by drawing a Tafel plot (Figure 1.4) in absence and presence of inhibitor. The percentage inhibition is calculated from the formula:

\[
IE\% = \frac{I_0 - I_{corr}}{I_0} \times 100
\]

(41)

\(I_0\) = Corrosion current density (corrosion rate) in absence of inhibitor,

\(I\) = Corrosion current density (corrosion rate) in presence of inhibitor.

Figure 1.4: Polarisation curves for a corroding electrode

- \(E_{corr}\) = Corrosion Potential
- \(i_{corr}\) = Corrosion Current

The corrosion rate is determined from the polarization data in two way:

1. Tafel extrapolation method
2. Linear polarization method.

In Tafel extrapolation method the linear portion of the Tafel curve is extrapolated. The point of intersection is referred to as $I_{corr}$.

Linear polarization method provides the value of absolute corrosion rate from the following relation.

$$I_{corr} = \frac{\beta_a \times \beta_c}{2.3(\beta_a + \beta_c)} \times \frac{1}{R_p} \quad (42)$$

where $\beta_a$ and $\beta_c$ are Tafel constants, $1/R_p = \Delta I / \Delta E =$ polarization conductance.

b. IMPEDANCE METHOD

The impedance technique [118 - 123] has become a popular tool for the measurement of corrosion rate in recent years. In this technique a small amplitude perturbation is applied to the working electrode at a number of discrete frequencies. At each of these frequencies the resulting current waveform will exhibit a sinusoidal response that is out of phase with the applied potential signal by certain amount.

The main advantages of this method are:

i. applicable to low conductivity systems,
ii. provides mechanistic information,
iii. solution resistance is completely eliminated.

The electrical equivalent circuit for the corroding system is given below:

\[ \begin{align*}
R_s &= \text{Solution resistance}, \\
R_t &= \text{charge transfer resistance}, \\
C_{dl} &= \text{double layer capacitance}
\end{align*} \]
W = Warburg impedance,
C_{di} = Double layer capacitance.

The inhibition efficiency of the inhibitors can be determined from AC impedance method [124 - 125] by the following formula:

\[ IE\% = \frac{1/R_o - 1/R_t}{1/R_{to}} \times 100 \quad (43) \]

R_t and R_{to} are the charge transfer resistance with and without inhibitor.

For determination of R_t, very small potential is applied as a function of frequency (usually 60 KHz - 1 mHz). The impedance of the corroding system for various frequencies can be measured using lock-in-amplifier. A plot of Z (real) vs Z'' (imaginary) for various frequencies gives a semicircle (Nyquist plot; Fig. 1.5)) which cuts the real axis at higher and lower frequencies. At higher frequency it corresponds to R_s and at lower frequency it corresponds to (R_s + R_i). The difference between the two values gives R_i. From R_t the corrosion current can be calculated using Stern – Geary equation:

\[ I_{corr} = \frac{\beta_s \times \beta_c}{2.3(\beta_s + \beta_c)} \times \frac{1}{R_i} \quad (44) \]

The double layer capacitance can be determined from the frequency at which Z'' is maximum from the relation:

\[ C_{di, max} = \frac{1}{2\pi C_{di} \times R_i} \quad (45) \]

Figure 1.6 is a Bode plot for the same data as in Figure 1.5. The Bode plot is a useful alternative to the Nyquist plot to avoid the longer measurement times associated with low frequency R_p determination. The Bode format is also desirable when data scatter precludes adequate fitting of the Nyquist semicircle. In general, Bode plot provides a clear description of the electrochemical system's frequency dependent behaviour than does the Nyquist plot, where frequency values are implicit.
Figure 1.5 AC impedance profile for a simple electrochemical system

Figure 1.6 Bode Plots

1.11.1 OTHER METHODS

The methods such as Radio tracer technique, Spectroscopic methods, X-ray photoelectron spectroscopy, Auger electron spectroscopy, Ellipsometry, Hydrogen permeation, Quartz crystal method, Electrochemical noise method have also been used for study the inhibition phenomenon.

i. RADIO TRACER TECHNIQUE

A better knowledge of inhibition phenomena can be obtained by Radio tracer method [126] with labeled inhibitor. It is possible to detect traces of substance adsorbed even under extreme dilution.

The method consist of bringing about the adsorption of the compound under examination on the metal (electrode) by putting the electrode in the electrode in the electrolyte containing the radio active organic substance. The electrode in taken out and washed. It is subjected to a count determination to measure the activity. It is compared with a standard and the amount of substance adsorbed is found. Also the decrease in the
concentration of the labelled additive in the solution as a result of adsorption can be measured. Bockris [127] developed a special type of cell which permits the study of adsorption under definite conditions of applied potential.

ii. SPECTROSCOPIC TECHNIQUE

The results of I.R. and U.V. spectra of the adsorbed products are very useful in the interpretation of inhibition phenomena. I.R. studies help to predict the functions of the adsorption bonds and the arrangement of the inhibitor molecules on the surface of the metal. Schwabe [128] using I.R. studies found that in the case of corrosion inhibition with dibenzylsulfoxide, the product adsorbed on the electrode was dibenzylsulphide.

U.V. spectroscopy has been used to determine the amounts of inhibitor adsorbed on the electrode by evaluating the decrease in concentration in solution under condition of free corrosion [129]. Banerjee et al [130] studied the effect of aniline in 5% HCl containing mild steel at different electrode potentials. They found three kinds of species were adsorbed on mild steel surface.

Suetaka [131] developed a technique to determine directly the amount of inhibitor adsorbed on metallic electrode by spectra recorded.

Riggs et al [132] obtained NMR spectra of anilines and substituted anilines. They have observed a good correlation between chemical shift and coefficient of inhibition of steel corrosion.

X-Ray photoelectron spectroscopy and FTIR spectroscopic techniques have been employed to study the films formed on the metal surface by the inhibitors [133].

Some other surface techniques in understanding the corrosion phenomena and mechanisms are summarized in Table 1.7 [134].

iii. AUGER ELECTRON SPECTROSCOPY

The Auger electron spectroscopy technique for chemical analysis of surface is based on the Auger radiationless process. When a core level of a surface atom is ionized by an impinging electron beam, the atom may decay to a lower energy state through an electronic rearrangement which leaves the atom in a doubly ionized state. The energy
difference between these two states is given to the ejected Auger electrons which will have a kinetic energy characteristic of the parent atom. When the Auger transitions occur within a few angstroms of the surface, the Auger electrons may be ejected from the surface without loss of energy and give rise to peaks in the secondary electron energy distribution function. The energy and shape of these Auger features can be used to unambiguously identify the composition of the solid surface.

An "Auger Spectrum" is obtained by plotting the derivative of the electron energy distribution versus energy. Because the Auger peaks are superimposed on a rather large continuous background, they are more easily detected by differentiating the energy distribution function \( N(E) \). Thus, the conventional Auger spectrum is the function \( dN(E)/dE \). The typical depth analysis with AES is of the order of 10 Å or less and elemental concentrations as low as 0.1 % of monolayer can be detected. Both qualitative and quantitative information can be obtained for all elements above helium.

The inner core vacancy is created by electron bombardment of the surface with electrons having energies in the range of 1-5 KeV. The depth profiles of the surface films are obtained by sputtering the surface away slowly by \( \text{Ar}^+ \) ions. With a 3 kV, 50 μA beam and a high sensitivity cylindrical mirror analyzer, the limit of detection for the elements varies between approximately 0.02 and 0.2 atomic percent with spectrum scanning rates of 1 eV per second. All elements above helium produce Auger peaks in the 0-2000 eV range.

iv. POLAROGRAPHIC TECHNIQUE

The polarographic method is employed for the study of corrosion and has the practical utility in the detection of minute changes in the corrosive system. In this method, the potential is gradually increased in the direction of reducing the substance present in the aqueous solutions. At the reduction potential of the substance, current suddenly increases. The height of the peak in the current versus time curve indicates the concentration of the substance present.
v. ELECTROCAPILLARY TECHNIQUE

The concept of the electro-capillarity has recently been introduced for the study of corrosion inhibitors [135-136]. It consists of measuring the interfacial tension of the electrode-electrolyte interface as a function of applied potential. The shift of electro-capillary curve, i.e. potential and surface tension curve, in the negative region after the addition of the inhibitor shows that adsorbed species are anionic in nature. In the presence of cationic type of inhibitors, the curve shifts towards anodic potential.

vi. NUCLEAR MAGNETIC RESONANCE

This method has been applied to study the electronic structure of organic compounds. Using this method, it has been verified that the electron density on the nitrogen of anilines determines the ability of these compounds as inhibitor of corrosion for steel in acids [132].

vii. HYDROGEN PERMEATION TECHNIQUE

When a metal comes in contact with acid, atomic hydrogen is produced. Before these combine to produce hydrogen molecules, a fraction may diffuse into the metal. Inside the metal, the hydrogen atoms may combine to form molecular hydrogen. Thus, a very high internal pressure is built up. This leads to heavy damage of the metal. This is known as “Hydrogen embrittlement”.

This phenomenon of hydrogen entry into the metals can occur in industrial process like pickling, plating, phosphating etc. Hydrogen permeation depends on the nature of the acid used and it has been shown [137] that hydrogen permeation decreases in the order HCl > H₂SO₄ > HClO₄ for concentration greater than 0.5 N.

A typical cell for permeation studies was introduced by Devanathan et al [138] in which the penetrated hydrogen is ionised and recorded as permeation current.

The effect of inhibitors on the permeation of hydrogen has assumed remarkable importance in the pickling processes. Thus, not only the loss of metal must be protected but also the entry of hydrogen into the metal must be restricted by the application of inhibitor.
An inhibitor can be considered as completely effective only if it inhibits metal dissolution and hydrogen penetration into the metal, simultaneously.

Bockris et al. [139] showed that naphthalene increases the rate of hydrogen penetration into iron. Also, it has been shown [140-141] that thiourea and derivatives act as good inhibitors for iron and steel but stimulate hydrogen penetration. This has been interpreted as due to the formation of hydrogen sulphide. Antropov et al. [142] studied extensively the effects of numerous inhibitors on the corrosion of iron and on the diffusion of hydrogen through the metal. They showed that pyridine derivatives eliminate the diffusion of hydrogen through iron membranes.

The behaviour of the inhibitors with regard to hydrogen permeation can be understood by measuring the permeation current with and without inhibitors. Those inhibitors which reduce the permeation current are good for inhibiting the entry of hydrogen into the metal concerned.

Other methods of evaluating hydrogen penetration [143] consist in the determination of brittleness of the metal previously subjected to acid attack in inhibited solution or charged cathodically with hydrogen in acid solutions containing the inhibitors under study.

The percentage inhibition of hydrogen penetration is given by:

$$\text{I.E.\%} = \frac{N_{\text{nhb}} - N_o}{N_{\text{nhb}} - N_{\text{i}} \times 100}$$  \hspace{1cm} (46)

where $N_{\text{ini}}$ is the fracture data determined on the metal specimen in the absence of adsorbed hydrogen. $N_o$ is the after cathodic charging with hydrogen in the absence of inhibitor and $N_{\text{nhb}}$ is the fracture data after cathodic charging in the presence of the inhibitor.

viii. GRAY RELATION ANALYSIS

Gray relation analysis is based on geometrical mathematics, which is in compliance with the principles of normality, symmetry, entirety and proximity [144]. The purpose of Grey relation analysis is to search for primarily relationships among the
factors and to determine the important factors that significantly influence some defined objectives. The measure of relevancy between two systems or two factors is known as the relational grade, which describes the trend relationship between an objective sequence (a collection of measurements) and a reference sequence in the system. If both tends towards concordance, the relational grade is regarded as great, or otherwise as small. Li et al [145] used this analysis to investigate the relation between inhibitor structure and inhibitor performance for a series of amines in the corrosion of mild steel in 0.5 M H₂SO₄.

ix. ELECTROCHEMICAL NOISE MEASUREMENT

This technique is a recent development in corrosion monitoring, the noise signal arising from random events such as rupture of the protective film and dissolution of metal at local sites. These random functions of corrosion potential and corrosion current are particularly obvious with localized corrosion monitoring.

In this technique, current noise and the mean current flow between two identical electrodes are monitored and this is correlated with the corrosion potential noise measured via a third electrodes. This technique has been found to be useful for the investigation of pitting corrosion. Meszaros and coworkers [146] studied the corrosion of pure iron by electrochemical noise in 0.5 mol/L H₂SO₄ containing dibenzylsulphoxide and phenylthiourea respectively as the inhibitor.

x. QUARTZ CRYSTAL MICROBALANCE METHOD

This method is used to monitor mass change as well as electrochemical change during corrosion process. The sensitivity of such a device is sufficient to detect submonolayer coverage of a surface with organic molecules. Pickering et al have studied the inhibiting action of benzotriazole and related compounds on corrosion of copper alloy in sulphuric acid solution using this method [147].

xi. SECOND HARMONIC GENERATION

Second harmonic generation (SHG) at surfaces is an optical laser technique by which molecular adsorption from solution on the a solid surface can be probed. The second harmonic response, where by fraction of the incident fundamental beam is
converted into a spatially coincident beam at twice the original frequency, depends on the
texture of the surface and any species adsorbed at it. Second harmonic generation is
extremely surface specific because it is governed by symmetry selection rule such that it
only occurs in non-centrosymmetric media. This condition is met at the interface between
two centrosymmetric media, such as metal immersed in an electrolyte. Consequently, the
second harmonic signal is generated by only the top few atomic layers of the metal and
any overlayer present. This technique is sub-monolayer sensitive. However, the
conversion efficiency is very low, so a high peak power, short pulse laser is required
[148].

1.12 INHIBITION OF CORROSION STEEL IN ACIDS

Inhibitors play an important role in controlling the corrosion of steels [149-150].
The major use of inhibitors in acid solution is in pickling processes [151-152], industrial
acid cleaning, oil and gas well acidizing and for removal of rust, scale and corrosion
products. The chief requirements of the inhibitors are that it should neither decomposer
during the life of the pickle nor increase hydrogen adsorption [153] by the metal. It
should also not lead to the formation of surface films with electrically insulting properties
that might interfere with subsequent electroplating or other surface treatments. Pickling
inhibitors require a favour polar group by which the molecule can attach itself to the
metal surface. These include organic N, amine, S and OH groups. The size, orientation
and shape of the molecule play a part in the effectiveness of inhibition [154]. The surface
charge of the metal and its constituents effect the relative strength of the adsorbed bond
and corrosion inhibition [153]. Granese and Rosales [155] elucidated the mechanism of
corrosion by N-containing organic compounds like acridine hexamethylene, quaternary
ammonium sulphate etc.

The anion of the pickling acid may also take part in the adsorbed film accounting
for differing efficiencies of inhibition for the same compound in HCl as compared to
H₂SO₄. This was supported by Hanna et al [156] for the use of ethoxylated unsaturated
fatty acid. Pickling inhibitors may acts as a good inhibitor for iron but not for other metals
or vice versa due to specific electronic interactions of polar groups with the metal.
Sometimes temperature plays a significant role in affecting the inhibition efficiency [157-158] e.g., o-tolythiourea in 5% H₂SO₄ acts as a good inhibitor at elevated temperatures than at room temperature due to increased adsorption.

In the USSR acid inhibitors are made by the use of industrial by products. Katapan A which is alkylbenzyl pyridine chloride [159] and its analogues are efficient in preventing the corrosion of high C-steel.

Compounds containing N of S have shown vast applications as corrosion inhibitors [160-161]. Machu [160] has shown the use of S-containing compounds for H₂SO₄ and N-containing compounds for HCl solutions. Hackerman [162] gave the idea that higher percentage of π orbitals of the free electrons on the N-atom leads to inhibitive action. N-containing compounds used as acid inhibitors include heterocyclic bases such as pyridine, quinoline and various amines [163-164]. S-containing compounds like thiourea and its derivatives, mercaptans and sulphides in concentrations 0.003 – 0.01 % gave 90 % protection [165-166]. According to Every and Riggs [167], a mixture of N and S-compounds was better than either type alone. Highly substituted N-atoms may increase the inhibition efficiency due to increase of electron density. Alkyl substitution on N-atom or para-position of aromatic nucleus improve inhibition efficiency in contrast to meta-position derivatives. Effects of anions such as I⁻ ad SH⁻, in the promotion of pronounced inhibiting action by organic cations in acid solutions are well known [168-169].

1.13 HETEROCYCLICS AS CORROSION INHIBITORS

The influence of some heterocyclic compounds containing more than one nitrogen atoms in their molecules on corrosion of carbon steel in 1N HCl was investigated by Trabanelli and co-workers [170] with a view to establish correlation between molecular structure and inhibition efficiency of the various compounds. Among the examined substances 2, 2'-Bis-quinoline (1), Quinoxaline (2), Quinozoline (3) and 2-mercaptopyrimidine (4) showed good inhibiting efficiencies (80 – 90 %) at 25 – 60 °C temperature.
The inhibition efficiencies of 1, 1'-alkylene bis-pyridinium compounds (5) have been studied for the corrosion of mild steel in 1N H₂SO₄. The inhibitors namely 1, 1'-ethylene 3,3'-dimethyl bispyridinium iodide and 1, 1'-ethylene bispyridinium iodide showed 87.8% and 86.7% efficiencies in concentration ranges of 250 and 1500 ppm respectively at 30 °C.

The author's have found that substitution in the pyridine ring has a pronounced effect on the inhibition efficiencies [171].

Stupnisek et al [172] investigated the inhibiting action of various substituted N-aryl pyrroles (6, 7) on corrosion of iron in strong acid solutions (5 mol. dm⁻² HCl) using electrochemical methods, with a view of studying the relationship existing between the molecular structure and inhibition efficiencies of pyrroles are significantly influenced by the type and the position of functional groups. Thus N-aryl pyrrole bearing fluorine at ortho position gave better performance than other pyrrole derivatives.
Raicheva and co-workers [173] investigated several diazoles (8, 9) such as imidazole and their derivatives as acid corrosion inhibitors of iron and steel. They have found a very good relationship between the structure of diazoles and inhibition efficiency.

The inhibiting action of substituted pyridine derivatives such as 2-methyl pyridine (10), 3-methyl pyridine, 4-methyl pyridine and 2, 6-dimethyl pyridine (11) and 2, 4, 6-trimethyl pyridine (12) were studied by Sastri et al [174]. They found that substitution of methyl group in the pyridine molecules produced an increase in present inhibition.
Starchack et al [175] investigated the electrochemical behaviour of steel in 0.1 N HCl and 1N H₂SO₄ using some 2-mercapto-benzimidazole (13). The results were discussed with consideration of the resonance and induction effects of polar substituents in the imidazole and benzene ring.

![Image of 2-mercapto-benzimidazole](13)

2-hydrazino-6-methylbenzothiazole was investigated (14) as corrosion inhibitor of mild steel in 1M HCl and 1M H₂SO₄ by Ajmal et al [176]. It showed > 90 % inhibition efficiency in 1M HCl. It behaved predominantly as cathodic inhibitor in HCl and mixed inhibitor in H₂SO₄.

![Image of 2-hydrazino-6-methylbenzothiazole](14)

The effects of 4-amino-3-thio-1, 2, 4-triazolidine (15) and 2-amino-5-thio-1, 2, 4-thiadiazole (16) on the inhibition of corrosion of steel in 3M H₂SO₄ were studied by Osman and co-workers [177]. They found that compound (16) was more efficient than compound (15) as the (16) contains an extra sulphur atom.

![Image of 4-amino-3-thio-1, 2, 4-triazolidine](15)

![Image of 2-amino-5-thio-1, 2, 4-thiadiazole](16)

Polarization and weight loss studies showed that polyvinylpyrrolidone (17) is an effective for the inhibition of low carbon steel over a wide concentration range of aqueous phosphoric acid (H₃PO₄) solution, [178].
The inhibition efficiency of some heterocyclic organic compounds viz 3-methyl-5-aminoiso-oxazole (18), 3, 4-dimethyl-5-aminoiso-oxazole (19), 4-methyl-5-oxazolecarboxamide (20), 2-acetylamino-5-sulphamoyal-1, 3, 4-thiadiazole (21), 2-acetylamino-5-mercapto-1, 3, 4-thiadiazole (22), 4-methyl-5-imidazole carbaldehyde (23) was investigated on iron in hydrochloric acid at 20 °C and in sulfuric acid at 20 – 60 °C [179]. Among these 4-methyl-5-imidazole carbaldehyde showed best inhibiting effect on iron in 5N HCl solutions.

The corrosion inhibition performance of a polymer polyamino-benzoquinone (24) was studied in 1N HCl and H2SO4 by UV, EIS, polarization and hydrogen permeation studies wt. loss studies for 2 hrs duration at room temperature. The polymer exhibited 94.7% IE in H2SO4 whereas 83.4% in HCl at 500 ppm. Polarization studies show that it is a mixed inhibitor. The compound also brought about significant reduction in hydrogen permeation current in H2SO4 [180].
The efficiency of Napthyl-methyl quinolinium chloride (25) was evaluated for oil field tubular steel corroding in HCl at 60 °C and 125 °C [181].

The inhibition and adsorption behaviour of 8-hydroxyquinoline (26) on iron in 1N sulphuric acid solution was studied at 20 °C. It exhibited 99% inhibition efficiency at a bulk inhibitor concentration of 0.1 – 10 mmol/l [182].

The adsorption behaviour of N-p-tolyl-phenylmaleimide (27, 28) on inhibition of iron corrosion was studied by an impedance technique in 0.1 M H₂SO₄ and 0.005 M Na₂SO₄. The compounds were found to obey Frumkin type adsorption isotherm [183].
Muralidharan et al [184] have further synthesized a few anils (29) by condensing 3-alkyl-4-amino-5-mercapto-1, 2, 4-triazoles with salicyldedehyde with a view to investigate the inhibitive action of these compounds on the corrosion of mild steel in acidic medium. They have found that all the compounds show better performance than the corresponding amines. The values of inhibition efficiency followed the order: C₃H₇ > CH₃ > H

The effectiveness of 2-amino-4-phenyl-thiazole and its three anils (30) were evaluated for the corrosion of mild steel in HCl and H₂SO₄ by weight loss potentiodynamic polarization and auger electron spectroscopic methods [185 – 186]. Their inhibition efficiencies followed the order:

2 – cinnamylidene amino-4-phenylthiazole >
2 – vanillidene amino-4-phenylthiazole >
2 – salicylidene amino-4-phenylthiazole >
2 – amino-4-phenylthiazole.
The inhibitive effect of 1(Benzyl) 1-H-4, 5, dibenzoyl-1, 2, 3-triazole (31) on the corrosion of mild steel in acid medium was investigated by Tafel polarization technique, AC impedance measurement and continuous linear polarization resistance method. The corrosion rate of mild steel in 1% HCl was reduced by more than 95% in presence of 50 ppm of this compound. This inhibitor showed mixed inhibition effect with a significant shift in the free corrosion potential to cathodic direction [187].

The inhibitive action of thiouracil derivatives (32, 33) on corrosion of steel in 2M H₂SO₄ was studied by Andis et al [188]. The thiouracil derivative bearing bromine atom at position-5-exhibited the best performance [189].

Various derivatives of indole (34) and quinoline (35) was studied as inhibitor for corrosion of mild steel in 0.5 M H₂SO₄ by Li et al [190] respectively.
The influence of imidazole (36) and 2-methyl-imidazole (37) and benzimidazole (38) on the corrosion and hydrogen permeation through mild steel in 1N HCl and 1N H₂SO₄ was studied by Muralidharan et al [191]. The inhibitors were more effective in 1N H₂SO₄. Benzimidazole gave > 84% inhibition efficiency in 1N H₂SO₄. They found that methyl imidazole accelerated the corrosion in 1N HCl.

Influence of 2-aminobenzothiazole and its substituted derivatives (39) was studied on mild steel corrosion in H₂SO₄ at 35 - 60 °C temperature. Among these chloroderivatives showed best performance at 55 ppm concentration by reducing the hydrogen permeation current as well as inhibiting the corrosion of mild steel (97% IE) [192].

1. R = H,
2. R = CH₃,
3. R = OCH₃,
4. R = Cl

The heterocyclic anils 2-salicylidene-aminobenzothiazole and its derivatives (40) were investigated to evaluate their efficiency as corrosion inhibitors for mild steel in HCl at 100 - 500 ppm concentration at 35 - 60 °C temperature. Among them chloro derivatives exhibited highest inhibition efficiency of 98%. The analysis of inhibited mild steel coupons by auger electron spectroscopy revealed that these compounds are adsorbed on mild steel surface through hetero atoms like N, S or Cl and inhibit corrosion [193].
The inhibitive performance of Benzotriazole (41) on the corrosion of stainless steel (18 Cr - 9Ni - Ti) was studied in acidic chloride solution using potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electron microscopy. The inhibitive action of this compound was observed due to the blocking of anodic and cathodic areas [194].

\[
\begin{align*}
(41)
\end{align*}
\]

The inhibitive effects of 1(benzyl) 1-H-4, 5-dibenzoyl-1, 2, 3-triazole (42) on mild steel in 1% HCl were investigated by Abdennabi et al [195]. The corrosion rate of mild steel was reduced by > 95% in the presence of 50 ppm inhibitor. The authors have also studied the substitution field effect at para position (43) of the inhibitor [196]. The inhibition efficiency at para position followed the order:

H > Br > CH₃ > NO₂

\[
\begin{align*}
(42)
(43)
\end{align*}
\]

The corrosion inhibitive behaviour of 3, 5-bis (n-pyridyl)-4-amino-1, 2, 4-triazoles (44) on mild steel in 1M HCl medium was studied by Mernari et al [197].
The inhibitive effect of 3, 5-bis (2-thienyl)-4-amino-1,2,4-triazole (45) on mild steel in 1M HCl and 0.5 M H₂SO₄ were investigated by Bentiss et al [198] using various techniques, such as wt.loss and electrochemical impedance spectroscopy. The electrochemical study revealed that this compound was an anodic inhibitor. They observed that these molecules were strongly adsorbed on the metal surface and suppress the dissolution reaction and adsorption which led to the formation of a protective film which grow with increasing exposure time. It was found to be as non-cytotoxic substance.

Daxi Wang and co-workers [199] investigated imidazoline derivatives (46) with different electron releasing substituents as acid corrosion inhibitors of iron and steel. They have found a very good relationship between the structure and inhibition efficiency. They found that the electron donar substituents particularly the substituent group with conjugated system, introduced to imidazoline ring will improve IE because it strengthen chemical adsorption of the N atom on the metal surface.

Some bipyrazolic compounds were synthesised and tested as a corrosion inhibitor for Armco Iron in 1M HCl by Touhami et al [200]. It was found that 1, 3-bis (3, 5-dimethyl pyrazolyl) propane (47) showed best inhibition efficiency of 93% at
concentration $10^{-3}$ M. They observed that the IE of the compounds decreases with the carbonic chain length joining the pyrazolic cycles. They also found that the hydrogen evolution reaction at the metal surface occurs through a pure mechanism of activation.

(47)

Elkadi et al [201] investigated the inhibiting action of 3, 6-bis (2-methoxyphenyl)-1, 2-dihydro-1, 2, 4, 5-tetrazine (48) on corrosion of mild steel in acidic media by weight loss and various electrochemical techniques. A better performance was noted in case of 1M HCl. Polarization studied showed that it acts as a mixed inhibitor in 1M HCl and a cathodic inhibitor in 0.5 M H₂SO₄. It was found that the inhibition efficiency increases with increasing value of the adsorption coefficient and inhibition efficiency is temperature independent.

(48)

Substituted 1, 3, 4-oxadiazoles (49, 50) such as 2, 5-bis (2-pyridyl)-1, 3, 4-oxadiazole (49) and 2, 5-bis (2-pyridyl)-1, 3, 4-oxadiazole (50) were synthesized and their inhibitive action on the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ was evaluated by Bentiss et al [202] (50) gave more efficiency than (49) due to the introduction of an electron releasing –OH group in the aromatic ring at ortho position. These oxadiazoles were found to perform well in both acids, but the better performance was seen in the case of HCl, due to synergistic inhibition.
Azhar et al [203] evaluated the effectiveness of 2, 5-bis (n-pyridyl)-1, 3, 4-thiadiazoles (51) on the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ by wt.loss and electrochemical impedance spectroscopy. Results obtained revealed that these compounds are mixed type inhibitors and behave better in 1M HCl than 0.5 M H₂SO₄. The adsorption of these compounds on the mild steel surface in both acidic media followed Langmuir isotherm.

The influence of some azathiones namely, dimethyl-tetrahydro-azathione (52), ethyl-methyl-tetrahydro-azathione (53), cyclopentyl-tetrahydro-azathione (54) on mild steel corrosion in 20% formic acid was studied. All the compounds showed mixed type of inhibiting action. The values of activation energy and free energy of adsorption indicated physical adsorption of these compounds on the steel surface [204].
The influence of some substituted fatty acid triazoles (55) on the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ was studied by Quraishi et al [205]. The values of activation energy and free energy of adsorption were calculated to investigate the mechanism of corrosion inhibition.

![Diagram of chemical structure](55)

R = CH₃(CH₂)₁₀
CH₃ - (CH₂)₇ - CH = CH - (CH₂)₇
CH₂ = CH(CH₂)₈

Chaudhary et al [206] studied the effect if 2-mercaptobenzothiazole (56) and 2-amino-5-mercapto-1, 3, 4-thiadiazole (57) on corrosion of 304 stainless steel in 10 M H₂SO₄ by using wt.loss, polarization resistance, SEM and Auger electron spectroscopy, techniques. Inhibition efficiency increases with the increase in concentration and decreases with the rise in temperature from 20 - 40°.

![Diagram of chemical structure](56)  ![Diagram of chemical structure](57)

Bis-derivatives of 2-mercapto-5-methyl-benzimidazole (58) was studied as the corrosion inhibitor of the steel in two-phase system and in the acids by Kyazimov et al [207].
Inhibitive action of rhodamine B (59) on corrosion of mild steel in 1.0M perchloric and phosphoric acid solution has been studied by Chaudhary et al [208].

\[
\text{CH}_3\text{CH}_2\text{N}^+\text{CH}_2\text{CH}_3
\]
\[
\text{Cl}^-
\]
\[
\text{CH}_3\text{CH}_2\text{N}^+\text{CH}_2\text{CH}_3
\]

Sulphamethoxazole (60) was investigated as corrosion inhibitor for mild steel in 1.0 M HCl solution. It was found to be an effective inhibitor in this medium [209].

\[
\text{H}_2\text{N}^\text{-S-N}^\text{O}
\]
\[
\text{H}_3\text{C}
\]

4-Aminoantipyrine (61) was tested as a corrosion inhibitor for mild steel in 2M HCl solution using different techniques [210]. In the temperature range 20 - 60° adsorption followed the Flory-Huggins isotherm.
The effect of addition of some triazine compounds on the corrosion behaviour of steel in 2M H₃PO₄ has been studied by Bekkouch et al [211]. It was found that 6-azathymine (62) was the best inhibitor. It showed 86% inhibition efficiency at 10⁻³ M.

![Image of compound 62]

The inhibiting effect of indole (63) indole HOAc (64) indole butyric acid (65), 3-acetyl indole (66) on the corrosion of 3C steels in 10% HCl was studied by Ismail et al using galvanostatic polarization method and open circuit potential measurements. The best inhibiting effect was observed at the highest concentration (2 × 10⁻⁴ g/L) of the inhibitors for the 3C steels [212].

![Images of compounds 63, 64, 65, 66]

Ita et al [213] studied the inhibitory effect of Green S and erythrosine (67) for mild steel in HCl solutions. They found that both inhibitors slow down the corrosion reaction by being physically adsorbed. Green S showed better performance due to higher solubility in the acid media compared to erythrosine.
Khaled et al. [214] observed that potassium dihydrobis (1-pyrazolyl)-borate has a significant effect on the corrosion of Fe in HCl medium by using potentiodynamic polarization and electrochemical impedance spectroscopy techniques.

Hajjaji et al. [215] studied a new class of organic molecules containing heteroatoms such as nitrogen and sulfur. The effect of addition of these molecules on iron dissolution and surface blistering in 1M HCl was studied through electrochemical impedance spectroscopy, polarization curves and SEM methods. They observed that corrosion resistance was greatly enhanced in the presence of these compounds.

Wang et al. [216] synthesized N-substituted alkoxyalkyl benzotriazoles (68) as corrosion preventive compounds.

Touham et al. [217] studied some pyrazolic compounds as corrosion inhibitors for Iron Armco in HCl media. 3, 5-Dimethyl pyrazol (69) was found to be the best inhibitor and its inhibition efficiency reaches 83% at $10^{-3}$ M.
Bentiss and Co-workers [218] synthesized a new class of corrosion inhibitors, namely 2, 5-bis (4-dimethyl aminophenyl)-1, 3, 4-thiadiazole (70) and its inhibiting action on the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄ was studied. Potentiostatic polarization studies showed that it is a mixed type inhibitor. The negative free energy of adsorption suggests chemisorption of thiadiazole molecules on the steel surface.

\[
\begin{align*}
\text{(70)}
\end{align*}
\]

The effect of 2-cyanomethyl benzothiazole (71) on the inhibition of corrosion of steel in 1M HCl was investigated at different temperatures (25 – 50 °C) by El-Rehim and co-workers [219]. They found that inhibition efficiencies increased with increase in their concentration but decrease with increase in temperature. Free energies of activation, enthalpies and entropies for the inhibition processes were determined from rate constant data measurement.

\[
\begin{align*}
\text{(71)}
\end{align*}
\]

Jianqiao et al [220] developed a corrosion inhibitor containing imidazoline, non-ionic surfactant, cationic surfactant, ammonium citrate and water. The inhibitor capable of acid mist resistance and etching promotion was used in an HCl solution. The inhibition efficiency was found to be 99.6% at 20°.
Abdallah et al [221] studied the inhibition effect of [Cu\(^{2+}\) cation + 3, 5-dimethyl pyrazole] mixture of different molar ratio on the corrosion of carbon steel in a 0.5 M H\(_2\)SO\(_4\) solution using wt.loss and galvanostatic polarization techniques. They analyzed the solutions by U. V - visible spectrophotometric technique before and after polarization measurements. They found a complex formation between two components which was much more effective than the inhibiting action of each additive separately.

The effect of 2-(acetoacetamido) pyridine aryl hydrazone derivatives on the dissolution of iron in nitric acid was measured using galvanostatic polarization, wt.loss and impedance measurements [222]. Polarization curves indicated that these compounds act as mixed type inhibitors and the cathodic is more preferentially polarized under the influence of an external current. Thermodynamic parameters for adsorption process were calculated using the Langmuir’s adsorption isotherm.

Wang et al [223] showed that 2-mercaptothiazole (72) and cetylpyridinium chloride (73) were effective corrosion inhibitors for low carbon steel over a wide concentration range of aq.phosphoric acid solution.

\[
\begin{align*}
\text{(72)} & \quad \begin{array}{c}
\text{N} \\
\text{S} \\
\text{H}
\end{array} \\
\text{(73)} & \quad \begin{array}{c}
\text{N} \\
\text{CH}_2 (\text{CH}_2)_{14} \text{CH}_3 \\
\text{Cl}^{-}
\end{array}
\end{align*}
\]

Corrosion inhibition efficiencies of heterocyclic compounds (pyrimidines, benzothiazole derivatives, amino acids containing an aromatic part, pyridines and quinolines) were correlated by using quantum chemical calculations [224].

Influence of poly (4-vinyl pyridine) (74) on the corrosion of Armco iron in molar sulfuric acid was studied by wt.loss potentiodynamic polarization and a.c. impedance measurements. The inhibitor adsorbed on the iron surface according to the Furmkin adsorption isotherm [225].
AIMS AND OBJECTIVES

The aim of the present investigation was

(a) To synthesize some new heterocyclic compounds as corrosion inhibitors.
(b) To study the inhibitive action of the synthesized heterocyclic compounds on corrosion of mild steel in acidic environments.
(c) To investigate the mechanism of corrosion inhibition using potentiodynamic polarization and ac impedance technique.
(d) To study the influence of molecular structure on corrosion inhibition.
(e) To analyse the nature and composition of the adsorbed film of inhibitor through auger electron spectroscopy and scanning electron microscopy.
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