Chapter-II
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CORROSION INHIBITORS

2.1 Introduction

National Association of Corrosion Engineers defines inhibitors, as substances which can retard the rate and extent of corrosion, when added to a corroding environment in small concentrations (sometimes as low as $10^{-5}M$). Hundreds of chemicals-inorganic and organic were studied and recommended as inhibitors of corrosion, for various metals in various environments-aqueous, non-aqueous, molten salt and dry atmospheres. Inhibitor properties are reported at various temperatures-ranging from very low to very high values. Information about inhibitors is scattered throughout corrosion literature.

Since corrosion consumes approximately 10% of the GNP of any country, the process must be prevented or inhibited. The study of corrosion inhibition probably dates back to the thirties, when lime treatment of water was stated to reduce corrosion in desalination plants and water pipes. Large structures, both open and closed exposed to atmospheric and marine corrosion are invariably protected by appropriate thick coatings of paint or by cathodic protection. However, inhibitors find extensive applications. Dr. Ergman estimated that some large installations spend as much as hundred thousand dollars per year on inhibitors. Inhibitor efficiency may be defined as $E=[(I^c-I)/I] \times 100$, where $I^c$ and $I$ are the corrosion currents in the presence and absence of the inhibitor. In the absence of polarization measurements, the corresponding weight loss rates can also be used for calculating efficiency.
Very often, the quantity of inhibitor present is insufficient to form a mono layer and hence inhibition can not be due to the physical adsorption on the metal surface. A more detailed study, using various techniques, has shown that many inhibitors selectively come in the way of either the anodic dissolution process or the cathodic reduction process. This provides evidence for the electrochemical theory of corrosion. Many inhibitors, have effects on both processes associated with corrosion. In a few cases, physical obstruction through the formation of a film or a layer is also inferred. Most inhibitors are developed by trial and experiment. Many of these are proprietary in nature, the compositions are not known.

2.2 Classification of inhibitors

Inhibitors can be roughly classified as,

i. passivating or film forming inhibitors and

ii. adsorption type inhibitors. The latter are mostly organic compounds.

There are long chain organics and polymers (or polymers formed from monomer on the surface) which form films, isolating the corroding solutions. Many inorganic salts such as chromates, nitrites, nitrates etc. (having high oxidizing power) inhibit corrosion by producing passive material on the metal surface particularly on iron, stainless steel and other alloys which show active-passive transition. Adsorption is the primary step in all inhibition processes, other reaction / processes follow. Some are known as vapour phase inhibitors and these are similar to the organic adsorption type inhibitors. They are highly volatile and when placed in the vicinity of the metal to be protected, they are transferred onto the metal surface by sublimation and condensation. These are usually effective in closed space (as in cans and containers). Scavengers inhibit corrosion by removing a
species responsible for corrosion from the solution. \( \text{Na}_2\text{SO}_3 \) and hydrazine remove oxygen from aqueous solutions. Arsenic and antimony retard the hydrogen evolution reaction—the cathodic process of electrochemical corrosion and thus inhibit overall corrosion. But they are ineffective when other processes such as reduction of oxygen, is the cathodic process.

The potential across the electrical double layer of the metal-solution interface or charge present on the metal surface can control this adsorption. Synergistic effects of the solution which promote adsorption of some of the charged inhibitors, is another factor to be considered. Hence there cannot be one adsorption inhibitor universally useful. In face, it is interesting to note, that often an ortho-derivative is an inhibitor for a metal while the para, derivative is not. Many of the inorganic inhibitors retard corrosion by producing passive oxides or thick precipitates.

The anodic inhibitors are often called dangerous inhibitors. If all anodic sites are not protected because of insufficient concentration of the inhibitor leading to a partial surface adsorption or partial film formation or if the protective films are non-adherent at a few points, corrosion sets in at such exposed sites. This corrosion, if supported by an adequate cathodic process, can become high, the corrosion current density becomes high, since the area of corrosion is small. This intensive corrosion can become deep-rooted and lead to catastrophic failures. This may also be true, when corrosion protective films are non-adherent at a few points, corrosion sets in at such exposed sites. The corrosion, if supported by an adequate cathodic process, can become high, the corrosion current density becomes high, since the area of corrosion is small. This intensive corrosion can
become deep rooted and lead to catastrophic failures. This may also be true, when corrosion protective paintings are non-uniform and expose a few anodic sites.

By considering the electrochemical nature of corrosion processes, inhibitors may be classified as anodic, cathodic and mixed inhibitors.

a. Anodic inhibitors

Substances which reduce the anode area by acting on the anodic sites and polarise the anodic reaction are called anodic inhibitors.

They cause a large potential shift in corrosion potential to render a metal passive and if present in sufficient concentration are generally the most effective of all inhibitors because they can stifle corrosion almost completely. Anodic inhibitors are primarily inhibitors of oxidising action. As oxidants they have a two fold nature, viz.,

i. they act as good depolarisers and therefore accelerate the cathodic process (corrosion stimulators) and

ii. they also lead to the formation of protective film on the anode (chemical passivators). The oxidising anodic inhibitors are so readily reduced that large local cathodic currents cause the adjacent anodic areas to become passive. The oxidising anodic inhibitors are therefore called passivators. At low concentration the passivators do not form complete protective films on the anodic areas, when the dangerous small anodic-large cathode combination\(^2\) is obtained, which may lead to pitting and therefore often classified as dangerous inhibitors (eg.) phosphates, Silicates and molybdates.
b. Cathodic inhibitors

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 in the negative direction and reduce corrosion current, thereby retard cathodic reaction and suppress the corrosion rate.

Cathodic inhibitors may be divided into three categories viz.,

i. those that absorb oxygen

ii. those that reduce the area of the cathode

iii. those that increase the hydrogen over potential of the cathodic process (hydrogen-evolution poison).

The cathodic inhibitors are perhaps less susceptible than the anodic type to the nature of the metal.

c. Mixed inhibitors

Substances which affect both the cathodic and anodic reactions are called mixed inhibitors. Such mixed inhibitors include the commercially available phosphates. Potential change in such a case is smaller and its direction is determined by the relative size of the anodic and cathodic effects. In general, these are organic compounds which adsorb on the metal surface (adsorption-type inhibitors) and suppress metal dissolution and reduction reactions.

When two or more inhibiting substances are added to a corrosive system, the inhibiting effect is sometimes greater than that which would be achieved by either of the two substances alone. This is referred to as synergistic effect. Inhibitor mixtures often consist of
one oxidizing agent, such as nitrate or chromate, and one non-oxidising but precipitating agent, such as orthophosphate or silicate and

one cathodic with one anodic type of inhibitor eg., Zinc ions and/or polyphosphate with chromate, organic amines with halide ions. Combinations of chromate and phosphate or polyphosphate are found to be more effective than the individual substances in engine cooling systems even in salt water. Nitrate-benzoate combination is the most frequent and effective inhibitor for automobile radiators.

Classification based on industrial application

i. Pickling inhibitors

Most pickling inhibitors function by forming an adsorbed layer on the metal surface, which essentially blocks discharge of H⁺ and dissolution of metal ions. For example, both iodide and quinoline are reported to inhibit corrosion of iron in hydrochloric acid by this mechanism³.

Compounds serving as pickling inhibitors require, a favourable polar group or groups by which the molecule can attach itself to the metal surface. These include the N in amines, S and OH groups. The size, orientation, shape, and electric charge of the molecule play a part in the effectiveness of inhibition. The surface charge of the metal decides the relative strength of the adsorbed bond⁴. In addition, due to specific electrostatic interaction of polar groups with the metal a given compound may act as a good inhibitor.
O-tolylthiourea\(^5\) in 5 % H\(_2\)SO\(_4\) is better inhibitor at elevated temperatures then at room temperature, because adsorption increases or the film structure becomes more favourable at higher temperatures.

Inspite of high effectiveness, sulphur containing inhibitors are not favoured because of the incidence of hydrogen embrittlement of steel.

ii. Slushing compound

Slushing compounds are used to protect steel surfaces temporarily from rusting during shipment or storage. They consist of oil, greases, or waxes containing small amounts of organic additives. The mechanism of inhibition by the organic additives is similar to that of inhibition by pickling inhibitors except that these additives must suitably adsorb on the metal surface forming a closely-packed oriented layer in the near neutral range of pH through which water has difficulty in diffusing. Suitable organic additives for use in slushing compounds include organic amines, zinc naphthenate, various oxidation products of petroleum, alkali and alkaline-earth metal salts of sulfornated oils, and various other compounds\(^6\).

iii. Vapour-phase inhibitors

Substances that have high vapour pressures which rapidly spread into the surrounding atmosphere and are then adsorbed on metallic surfaces, protecting them from atmospheric corrosion, are called vapor phase inhibitors.

VPI compounds consist of a volatile organic cation, usually an amine, and an anion which acts as an inhibitor. On the metal surface, the cation produces a thin adsorbed film which has two important functions:
a. it is hydrophobic and

b. it controls the pH of any moisture layer which forms on its surface.

Carbonate and nitrite are the anions in typical VPs. They are carried with the volatile cation to deposit on the metal surface. The component become immersed so that the cation film breaks down, the anion acts as a normal inhibitor to control the rate of corrosion by polarizing the electrode reactions.

Cyclohexylamine carbonate has a somewhat higher vapour pressure of 0.4 mm Hg at 25°C and its vapor also effectively inhibits steel. The higher vapour pressure provides more rapid inhibition of steel surfaces either during packaging or on opening and again closing a package during which time concentration of vapour may fall below that required for protection. Dicyclohexyl ammonium nitrite (DICHAN) is an effective vapour phase inhibitor. Urea with sodium nitrite is used in impregnated paper.

iv. Inhibitor to reduce tarnishing of copper

Benzotriazole (BTA) \( \text{C}_6\text{H}_5\text{N}_3 \) is a corrosion inhibitor widely used for copper and its alloys. Film thickness 0.01/\( \mu \)m in near neutral and mildly basic solutions. 0.5/\( \mu \)m in acidic solutions Inhibitor forms a \( \text{Cu}^+ \) surface complex following its adsorption or \( \text{Cu}_2\text{O} \) present on copper surfaces.

2.3 Practical considerations

The parameters to be considered for the inhibitors are mainly:

i. solubility

ii. compatibility with the corroding system

iii. stability over long time under stationary and flowing conditions at different temperatures and pH of the medium
iv. undesired effects of the effluents containing the inhibitor (pollution)

v. cost.

2.4 Factors affecting the applicability of inhibitors

i. Nature of the metal

Majority of inhibitors are specific in their action towards particular metals. For example, $\text{SO}_4^{2-}$ ion which behaves as aggressive ion towards mild steel in water can inhibit $\text{Cl}^-$ induced pitting of stainless steel and caustic embrittlement in boilers.

If different metals are in the same system then a single inhibitor cannot be applied. A mixture of inhibitors which are useful in preventing corrosion of both the metals can be used. Care must be taken in this case that the inhibitors must be taken in adequate concentrations and correct proportions. Otherwise failures will take place.

ii. Nature of metal surface

Clean, smooth surfaces of metals usually require low concentrations of inhibitors. Presence of oil, grease or other corrosion products may lead to adverse effects. So before the use of inhibitors, surface treatment is necessary. One of the well known surface treatment is phosphate delayed chromate technique.

iii. Nature of the environment

In all circumstances, it is important to ensure that the inhibitor is compatible with the environment. For example, chromates cannot be used in glycols antifreeze solutions, since oxidation of glycol by chromate will reduce this to trivalent state which has no inhibitive property.
iv. Composition of the liquid environment

Ionic composition arising from the dissolved salts and gases has a considerable effect on the performance of inhibitors. In near-neutral pH, the presence of certain ions tends to oppose the action of inhibitors. Cl\(^-\) and SO\(_4\)\(^{2-}\) are the most common aggressive ions. So concentration of inhibitor required depends on the concentration of aggressive ion present.

v. pH of the system

All inhibitors have a pH range in which they are most effective and even in nominally neutral solutions. pH control is often necessary to ensure continuous efficiency of inhibitive treatments.

vi. Temperature of the system

At higher temperatures, the inhibitor is required in larger concentrations or the inhibitor loss its efficiency. For example, polyphosphate can inhibit around 40\(^\circ\)C above this its inhibitive property is lost because of the formation of orthophosphate. If Ca\(^{2+}\) ion is also present precipitation of calcium phosphate takes place.

vii. Inhibitor concentration

To be fully effective, the inhibitor is required above a certain minimum concentration. Insufficient quantities of inhibitor used may result in localised corrosion, if it is a dangerous inhibitor.

viii. Mechanical effects

Corrosion can also be initiated by conjoint action of mechanical factors like stress, fatigue or fretting etc. with corrosive environment. Inhibitors which are effective
in their absence may not be so in their presence. So other methods of prevention are needed.

ix. Aeration and movement of liquid

For majority of inhibitors in near-neutral pH, adequate supply of oxygen is necessary for proper function of inhibitor. In de-aerated system, the non-oxidising type inhibitor will not have effect. In such cases higher concentrations are required.

Excessive aeration also has adverse effect. Tannins lose their ability on excessive aeration. Their inhibitive action is due to their capacity to remove dissolved oxygen.

x. Effect of micro organism

Micro organisms enhance the rate of corrosion by three modes.

(i) By direct bacterial participation in metal corrosion leading to accumulation of large amounts of corrosion products and pitting of the metal. Example is sulphate reducing bacteria.

(ii) Accumulation of flocculent fungal growths that reduces the rate of mass transfer and heat transfer.

(iii) Bacterial attack results in the breakdown and hence depletion of inhibitor at the metal surface.

In addition, inhibitors may act as nutrients to microbes. So we have to incorporate bactericides in such cases.

xi. Scale formation

Scale formation on metal surfaces screens the metal surface and hence contact between metal and inhibitor is lost. Inhibitor is also incorporated in the scale resulting in
the reduction of heat transfer in cooling systems. In some cases scale formation results due to the reaction of inhibitor with the metal surface.

**xii. Toxicity, disposal and effluent problems**

With increasing awareness of environmental pollution problems, the use and disposal of all the types of inhibitors is receiving greater attention than even before. Taking into consideration the disposal of phosphate-chromate inhibitors, formulations containing bio-degradable chemicals are being introduced.

**2.5 Mechanism of inhibitor action in acidic solutions**

The retardation of corrosion reaction is by the reduction of anodic reaction rate or cathodic reaction rate or both. This action may occur by any of the following mechanisms.

i. Changes in the double layer

ii. Formation of physical barrier

iii. Reduction of metal reactivity and

iv. Participation of the inhibitor in partial electro-chemical reactions.

Modern instrumental techniques and surface analysis methods can contribute to the understanding of the inhibition mechanism involved in the system, metal/acid/inhibitor. In particular, the recording of the electrochemical characteristics such as anodic and cathodic polarisation curves, electrochemical impedance *etc.*, in the presence and in the absence of the inhibitor may contribute to the identification of the prevailing mechanism of inhibitor action. Different mechanisms of inhibitor action are discussed below.
i. Changes in the electrical double layer

Corrosion inhibition is related to changes in the structure of electrical double layer at the metal/solution interface. This change takes place as a result of electrostatic adsorption of ionised inhibiting species. The modification of the electrical double layer is shown by the appearance of adsorption potential jump.

As most of the electrochemical reactions in aqueous solutions are electrochemical in nature, organic molecules adsorb at metal-solution interface obeying laws of electrostatics.

Two kinds of adsorptions in electrochemical situation may be realised. They are coulombic adsorption (similar to physical adsorption) and specific adsorption.

a. Coulombic adsorption

No ions or molecules are in direct contact with the metal. A layer of solvent molecules at the surface of the electrode divides the metallic electrode from the solution.

b. Specific adsorption

Compounds with polar functional groups are adsorbed through chemisorption. There is a strong metal-inhibitor binding energy involved in this process. $\pi$ electrons, organic compounds play a vital role in this process.

ii. Formation of physical barrier

Inhibitors such as sulfoxides, acetylene derivatives or substances with number of carbon atoms in the hydrocarbon chain are able to form multi molecular layers on the metal surface. The resulting barrier action is quite independent of the nature of adsorption forces between the inhibitor molecule and the metal surface. The hindering of mass
transport causes inhibition of corrosion reaction. Analysis of corresponding polarisation curves shows concentration polarisation and resistance polarisation on the cathodic branches.

Inhibitors involve in the cathodic polarization or anodic polarisation or both so as to reduce the rate of corrosion. Evan's diagrams explain the anodic, cathodic and mixed polarisations by inhibitors. The effectiveness of an inhibitor increases with its ability to induce anodic polarisation at relatively low current values. Inhibitors inducing anodic polarisation were designated as 'anodic inhibitors' by Evans$^{10}$.

If the corrosion current is proportional to anodic reaction, the decrease in corrosion should be proportional to the anodic area being polarised. On the other hand, if the corrosion is controlled by cathodic reactions, the corrosion current and therefore the total amount of corrosion is not affected by decrease in anodic areas. In this case same amount of corrosion must be distributed over smaller anodic areas, resulting in intensified local attacks.

A number of substances are known to be anodic inhibitors such as alkali metal salts of chromates, phosphates, carbonates, silicates etc., some of these can cause localized attacks when used in small concentrations. Some other inhibitors also cause stimulation of corrosion without causing localised attacks when used in small concentrations. Therefore, anodic inhibitors are in general known as 'dangerous inhibitors'.

It has been reported that sodium chromate and potassium permanganate when present in small quantities accelerate the corrosion of aluminum in NaOH whereas at
higher concentrations they are effective inhibitors for the same system. In these cases, inhibitors act as cathodic depolarisers when present in small concentrations and as anodic polarisers at higher concentrations.

The cathodic reaction in acidic solution is usually hydrogen evolution. The inhibitor which interfere in this reaction shift the potential of local cathodes towards local anodes. The cathodic areas are not affected by the corrosive environment because the metal itself does not participate chemically or electrochemically in the cathodic reaction. Hence cathodic inhibitors do not lead to localised attack. As cathodic inhibitors have no adverse effect on the corroding systems even if employed in small concentrations, they are usually referred to as 'safe inhibitors'.

Some of the substances inhibit corrosion by interfering with both anodic and cathodic reactions thus simultaneously causing anodic and cathodic polarisations. Gelatin, glue and other high molecular weight substances fall in this category and are commonly classified as general or mixed inhibitors. These concentrate at the metal solution interface and because of their high viscosity cause a decrease in the rate of diffusion of corrosive environment towards the metal surface and thus provide a shield for the metal.

iii. Reduction of metal reactivity

This mechanism does not necessarily involve complete coverage of the metal surface by the adsorbed inhibitor. The type of interacting forces are important and higher efficiencies are to be expected when stronger bonds such as chemisorption bonds are established.
According to this mechanism the inhibitor adsorbs on the site, active with respect to the partial electrochemical reactions. A reduction in the rate of anodic and cathodic reaction or both arises from the blockage of corresponding active sites. Clearly, the reaction rate will be reduced in proportion to the extent to which the active sites are covered by the inhibitor. This type of surface coverage does not change the mechanism. The polarisation curves are shifted towards lower current densities without modification in Tafel slope values.

For example, if organic compounds with double and triple bonds or compounds with aromatic nucleus are used as inhibitors, then adsorption may result from $\pi$-orbital interaction with the metal.

iv. Participation of the inhibitor in partial electrochemical reactions

Both anodic reaction of metal dissolution and cathodic reaction of hydrogen evolution proceed by steps with the formation of adsorbed intermediates on the metal surface. According to this mechanism of action the adsorbed additive may participate in the intermediate formation promoting either decrease or stimulation of electrode reaction depending on the stability of the adsorbed surface complex. As a consequence, a variation in Tafel slope can be observed.

For example, Bockris$^{11}$ suggested the following mechanism for iron dissolution.

\[
\begin{align*}
\text{Fe} + \text{OH}^- & \rightleftharpoons (\text{FeOH})_{\text{ads}} + e^- \quad (1) \\
(\text{FeOH})_{\text{ads}} & \xrightarrow{\text{Slow}} \text{FeOH}^+ + e^- \quad (2) \\
\text{FeOH}^+ & \xrightarrow{\text{Fast}} \text{Fe}^{2+} + \text{OH} \quad (3)
\end{align*}
\]
Where step (1) is in quasi-equilibrium, step (2) is the rate determining and step (3) is the fast. Ken Nobe et al.\textsuperscript{12-14} have suggested a sort of chelation mechanism for organic inhibitors. According to them the following steps are probable.

\[ (\text{Fe OH})_{\text{ads}} + n \text{In} \rightleftharpoons (\text{Fe (OH) (In)}_n)_{\text{ads}} \]  \hspace{1cm} (4)

\[ (\text{Fe (OH) (In)}_n)_{\text{ads}} \rightarrow (\text{Fe (OH) (In)}_n^+ + e^-) \] \hspace{1cm} (5)

In step (4) the adsorbed intermediate interacts with ‘n’ molecules of inhibitor to form a complex which is adsorbed on the surface, to the extent that the above complex can undergo charge transfer i.e., as in step (5) and then adsorb as complex ion.

Likewise the value of the equilibrium constant of step (4) is expected to determine the extent of inhibition provided the rate equation (5) is much slower than that of (2).

### 2.6 Adsorption and its influence on inhibition of corrosion

Organic inhibitors inhibit by adsorption\textsuperscript{15} at metal–solution interface. Adsorption of organic inhibitors mainly depends upon the following factors:

i. electrochemical potential at the interface

ii. structure of inhibitors

iii. nature of metal surface.

Since corrosion reactions are heterogeneous reactions taking place at the surface of the metal, it is necessary that they are not capable of oxidizing or precipitating the metal ion and must have the ability to impede either cathodic or anodic or both the reactions.
2.7 Classification of adsorption

It is classified into two types

i. Physical adsorption and Potential at zero charge (PZC)

ii. Chemical adsorption or chemisorption

i. Physical adsorption and potential at zero charge

The electrostatic attraction between the ions or dipole of the inhibiting species and the electrically charged surface of the metal gives physical adsorption. The charge on the metal surface depends on the free corrosion potential $E_{corr}$ and potential with respect to zero charge (PZC).

Potential at zero charge

The potential of the metal measured against a reference electrode is known as zero-charge potential, which is carried out under the condition that metal is in zero charge. At zero-charge potential, the electrodes adsorb the substances dissolved in the electrolyte. At PZC, the net charge on the electrode is zero.

At potential more positive and negative than PZC, the electrode is positively and negatively charged respectively.

The concept of PZC can also be explained by means of synergistic effect of iron in $\text{H}_2\text{SO}_4$ by means of chloride ion$^{16,17}$.

ii. Chemical adsorption or chemisorption

It is due to the interaction between the metal surface and an inhibitor molecule. The adsorbed molecule is in contact with the surface of the metal. In this, a co-ordinate bond is involved in the electron transfer from metal inhibitors to metal.
Chemisorption is slower compared to electrostatic adsorption process and it has higher activation energy. It depends upon temperature and inhibitor efficiency.

Chemisorption is specific to certain metals. Electron transfer from inhibitor to metal is facilitated by the presence of unshared lone pair of electrons, \( \pi \) electrons due to multiple bonds and aromaticity.

The strength of the adsorption bond depends upon

- The electron density of donar atom of functional group.
- Polarizability of the group.

### 2.8 Adsorption isotherm

The bulk concentration of an adsorbing species to its surface concentration at constant temperature is related by a mathematical expression called adsorption isotherm.

It gives the relationship between the coverage of an interface with the adsorbed species and the concentration of species in solution.

Various adsorption isotherms have been formulated and are given in the following table

<table>
<thead>
<tr>
<th>S.No</th>
<th>Isotherms</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Henry</td>
<td>( \beta c = 0 )</td>
</tr>
<tr>
<td>2.</td>
<td>Freundlich</td>
<td>( \beta c \ n = 0 )</td>
</tr>
<tr>
<td>3.</td>
<td>Langmuir</td>
<td>( \beta c = \theta / (1-\theta) )</td>
</tr>
<tr>
<td>4.</td>
<td>Frumkin</td>
<td>( \beta c = \theta \exp (-2a\theta) / (1-\theta) )</td>
</tr>
<tr>
<td>5.</td>
<td>Temkin</td>
<td>( \beta c = \exp (a\theta) - 1 / \exp (-a(1-\theta)) )</td>
</tr>
</tbody>
</table>
Where,

\[ \beta = e^{-\Delta G_{ads}/RT} \]

\[ a = \text{Interaction parameter} \]

\[ a>0, \text{ Attraction} \]

\[ a<0, \text{ Repulsion} \]

Most of the organic inhibitors obey Langmuir or Temkin adsorption isotherm

A plot of \( \log \theta/1-\theta \) vs \( \log C \) is linear then it is called Langmuir plot.

A plot of \( \theta \) vs \( \log C \) is linear, and then it is Temkin’s plot.

2.9 Effect of inhibitors on corrosion processes

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

i. Formation of diffusion barrier

The adsorbed inhibitors may form a surface film which acts 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 effect occurs particularly when the inhibitor species are large molecules. eg. proteins such as gelatin, agar-agar etc. Similar effect also occurs when the inhibitor can undergo reaction to form a multi molecular surface film eg. acetylene compounds and sulfoxides.

ii. Blocking of reaction sites

The interaction of absorbed inhibitors with surface metal atoms may prevent these metal atoms from participating in either the anodic or cathodic reactions of corrosion. The simple blocking effect decreases the number of surface metal atoms at which these
reactions can occur, and hence the rates of these reactions are proportional to the extent of adsorption. The mechanisms of the reactions are not affected and the Tafel slopes of the polarization curve remain unchanged. Behaviour of this type has been observed for iron in sulphuric acid solutions containing 2,6-dimethyl quinoline, β-naphthaquinoline or aliphatic sulfides.

iii. Participation in the electrode reaction

The electrode reactions of corrosion involve the formation of adsorbed intermediate species with surface metal atoms (e.g.) adsorbed hydrogen atoms in the hydrogen evolution reaction, adsorbed (FeOH) in the hydrogen evolution reaction, adsorbed (FeOH) in the anodic dissolution of iron. The presence of adsorbed inhibitors will interfere with the formation of these adsorbed intermediates but the electrode process may then proceed via alternative paths through intermediates containing the inhibitor. In this process the inhibitor species act in a catalytic manner and remain unchanged, since participation by the inhibitor is generally characterised.
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