Chapter 1

Introduction

Corrosion can be defined as the undesirable reactions between materials and the environment which lead to the loss of the functionality of the materials. Each year corrosion of materials and related loss cost us tremendously with the direct loss due to corrosion estimated to be 3-5% of the gross national product. Generation of scientists and engineers have dedicated themselves to the investigation of corrosion mechanism and the development of effective protection techniques.

Corrosion is a complex and it can take on various forms depending on the properties of the material and the corrosive environment. Uniform corrosion refers to homogenous dissolution of materials, such as the corrosion of carbon steels in acidic solutions. The corrosion rate is almost the same everywhere and the corrosion can be mentioned easily. Few accidents occur as a result of the uniform corrosion due to its predictability, although significant amount of materials is lost in the process. Non uniform corrosion, however, concerns the inhomogeneous deterioration due to the heterogeneities of the material or the environment. It consists of various forms of corrosion such as intergranular corrosion, selective corrosion and pitting corrosion.

Steel is produced from iron, the following elements are always present in steel; carbon, manganese, phosphorous, sulfur, silicon and traces of oxygen, nitrogen and aluminum. Various alloying ingredients are frequently added, such as nickel, chromium, copper, molybdenum and vanadium. The most important of these elements in steel is carbon, it forms a compound Fe_3C (iron carbide), which is extremely hard and brittle and known as cementite.

Commercially available steel comes in a wide variety of shapes, forms and chemical composition, depending on the intended use of the material. In the course of its usage the product is subjected to unfavorable environments as is the case of chemical engineering. Under these conditions steel undergoes more or less severe corrosion attacks.

The majority of metal-corroding processes in electrolytes is electrochemical in nature. The rate of any given electrochemical process depends on the rates of two conjugate reaction proceeding at the metal surface: an anodic reaction consisting in the transfer of metal ions from the lattice to the solution, with liberation of electrons, and a cathodic reaction consisting in the assimilation by some depolarization of the electron librated during the anodic reaction.

Inhibitor can vary the rate of a corrosion process by affecting the kinetics of the electrochemical reactions responsible for that process. Thus, they can be used to the greatest advantage for the protection of metals in many different environments.

1.1- Types of Corrosion

1.1.1 General or Uniform Corrosion

Differences in electrical potential occur on the surface of a piece of metal due to small differences in chemical composition, amount of cold work, etc. These differences set up small corrosion cells each with an anode and cathode. Corrosion continues until the metal is consumed or the film of rust formed on the surface sets up a barrier to the electrolyte.

1.1.2 Pitting Corrosion

Pitting corrosion is a complex but an important problem that is at the root of many corrosion failures. In pitting corrosion the surface of the metal is attacked in small localized areas. Organisms in water or breaks in a passive film can initiate corrosion. In pitting corrosion very little metal is removed from the surface but the effect is marked.

In passivated metals, or alloys that are exposed to solutions containing aggressive anions, primarily chloride, pitting corrosion results in local dissolution leading to the formation of cavities or (holes). The shape of the pits or cavities can vary from shallow to cylindrical holes, and the cavity is approximately hemispherical(1). The pit morphology depends on the metallurgy of the alloy chemistry of the environment as well as, on the leading conditions. As observed first by Mc. Adam (1), these pits may cause local increase in stress concentration and cracks may nucleate from them.

Pitting corrosion occurs mostly in solutions containing halides or oxyhalides, chlorides, bromides and hypochlorites are the most aggressive anions(2). Fluoride, iodide and iodine containing anions were thought to be without pitting tendency. However, iodide ions were found to cause pitting corrosion in many cases(3). Solutions of certain oxidizing actions produce the worst pitting reagents. The non - oxidizing metal halides such as Al, Ca and Na cause pitting to a lesser degree.

Electrochemical studies of pitting corrosion have found that there exists characteristic potentials. Stable pits, form at potentials noble to the pitting potential, E_{Pit}, and will grow at potentials noble to the repassivation potential, E_R, which is lower than E_{Pit}. During upward scanning in a cyclic polarization experiment, a stable pit starts growing at E_{Pit} where, the current increases sharply from the passive current level and, upon reversal of the scan direction, repassivates at E_R where the current drops back. It is generally considered that materials exhibiting higher values of E_{Pit} and E_R are more resistant to pitting corrosion, and cyclic-polarization experiments are commonly used for this purpose.

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

1.1.3 Stress Corrosion Cracking

Failure is due to the simultaneous influence of static tensile stresses and a corrosive environment and this is specific to a particular metal. The stresses may be internal such as those caused by cold work, welding, heat treatment or external forces caused by mechanical stresses set up by assembly practices. A good example of this form of corrosion is 316 stainless steel in marine environments. 316 stainless steel was developed to withstand attacks in chloride environments, but if stressed the steel will fail by stress corrosion cracking.

1.1.4 Intergranular Corrosion

Corrosion occurs at the grain boundaries due to a difference in potential between the anodic grain boundaries and the cathodic grains. "Sensitized" stainless steels, where carbides have been precipitated in the grain boundaries during heat treatment or in the heat- affected zone of a weld, are particularly susceptible to intergranular corrosion.

1.1.5 Corrosion Fatigue

Is failure under repeated cycling stresses in a corrosive environment.

1.1.6 Filiform Corrosion

Filiform corrosion appears as a network of corrosion trials, of a worm like structure, particularly beneath thin organic. Salts containing chlorides, which have been left on the surface prior to coating, are suspected.

1.1.7 Crevice Corrosion

Crevice corrosion occurs when there is a difference in ion, or oxygen, concentration between the metal and its surroundings. Oxygen starvation in an electrolyte at the bottom of a sharp V-section will set up an anodic site in the metal that then corrodes rapidly.

1.1.8 Galvanic or bi- Metallic Corrosion

Galvanic corrosion takes place between two different metals, or coatings, which are joined together in the presence of an electrolyte. Each metal has a potential different from any other metal when placed in an electrolyte. A series can be built up of all the metals relative to each other.

1.1.9 Fretting Corrosion

Fretting corrosion occurs when two or more parts rub against each other. The rubbing action removes the corrosion products and exposes new metal to the electrolyte.

1.1.10 Erosion Corrosion

Erosion is the removal of metal by the movement of fluids against the surface. The combination of erosion and corrosion can provide a severe rate of corrosion.

1.1.11 Selective Leaching or Demetalification

Demetalification is the removal of one of the alloying elements in an alloy by the electrolyte. This results in a " spongy" metal. Typical example is the removal of zinc in chloride waters form brass (dezincification).

1.2- Corrosion Prevention By Electrochemical Methods

1.2.1- Cathodic Protection :

Cathodic protection is an electrochemical means of corrosion in which the oxidation reaction in a galvanic cell is concentrated at the anode and suppresses corrosion of the cathode in the same cell. For example, the steel pipline is catholically protected by its connection to a sacrificial magnesium anode buried in the same soil electrolyte. Cathodic protection is different from anodic protection. In cathodic protection, the object to be protected is the cathode, but in anodic protection, the object to be protected is the anode. Anodic protection can be used on only a limited number of alloys in certain restricted environment, but cathodic protection can, in principle, be applied to any metal. In practice, cathodic protection is primarily used on carbon steel. The effectiveness of cathodic protection allows carbon steel, which has a little natural corrosion resistance, to be used in such corrosive environments as sea water, acid soils, salt-laden concrete, and many other corrosive environment. Properly designed and maintained cathodic protection system can prevent corrosion indefinitely in these environments.

1.2.2-Anodic Protection

The term anodic protection refers to corrosion protection achieved by maintaining an active- passive metal or alloy in the passive region by an externally applied anodic current. Solution oxidizing power and corrosion potential are equivalent, and therefore it is possible to achieve passivity by altering the potential of the metal by an appropriate external power supply. Since the potential must be maintained within the passive region, it is necessary to use a special device called a potentiostat which is capable of maintaining a constant electrode potential by controlling the anodic current.

1.2.3 Corrosion Inhibitors

An inhibitor is a chemical substance which, when added in small concentrations to corrosive environment effectively decreases or prevents the reaction of the metal with the environment (4). Inhibitors often work by adsorption on the metallic surface and protect it by forming an isolating film. Electrochemically inhibitors slow the corrosion processes by increasing the anodic or cathodic polarization behavior, reducing the movement or diffusion of aggressive ions to the metallic surface or by increasing the electrical resistance of the metallic surface. In oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion.

Inhibitors have been classified differently by various authors. Some authors, for example, prefer to group inhibitors by their chemical functionality. However, by far the most popular organization scheme consists in regrouping corrosion inhibitors in a functionality scheme as passivating, anodic, cathodic, precipitation and organic inhibitors.

Passivating inhibitors (passivators) or anodic inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. There are two types of passivating inhibitors:

i) Oxidizing anions, such as chromate and nitrite that can passivate steel in the absence of oxygen.

ii) Non oxidizing ions such as phosphate, tungstate and molybdate that require the presence of oxygen to passivate steel.

These inhibitors are the most effective and consequently the most widely used. Chromate based inhibitors are the least expensive inhibitors and were used until recently in a variety of applications, e.g. re-circulation cooling systems of internal combustion engines, rectifiers, refrigeration units, and cooling towers. Recent environmental laws in many countries have imposed sever restrictions on chromate use due to its high toxicity (5,6) and consequent environmental hazards(7). Therefore, a variety of passivating inhibitors has been tested. Ions such as MoO_4^{2-}, MnO_4^-, SiO_4^{2-} and WO_4^{2-} have shown efficiencies similar to that of chromate in protecting aluminum alloys (8-9). Other anions, like benzoate or nitrite have been shown to give a high degree of protection to stainless steel exposed to solutions containing chloride (8,10,11).

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by three different mechanisms as cathodic poisons, cathodic precipitates or oxygen scavenger.

Precipitation inducing inhibitors are films forming compounds that have a general action over the metal surface, blocking both anodic and cathodic sites indirectly. Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film. The most common inhibitors of this category are the silicates and the phosphates.

Organic inhibitors, on the other hand, are usually organic compounds which adsorb on the whole metal surface and simultaneously retard both the anodic and cathodic reactions. But, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors usually designated as "film-forming" and protect the metal by forming a hydrophobic film on the metal surface.

The effectiveness of these inhibitors depends on the chemical composition, their molecular structure and their affinities for the metal surface. Because film formation is an adsorption process, the temperature of the system is an important factor.

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines, or anionic inhibitors, such as sulfonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors.

1.3- Type of Adsorption

The adsorption of inhibitors is influenced by the nature and surface change of the metal, by the type of aggressive electrolyte, and by the chemical structure of the inhibitor. The principle types of interaction between an organic inhibitor and a metal surface are physical (electrostatic, coulombic) adsorption and chemisorption (contact adsorption). It is common practice to place each system into one of the two categories mentioned.

1.3.1- Physical Adsorption:

Physical adsorption is the result of electrostatic attractive force between inhibiting organic ions or dipoles and the electrically charged surface of the metal. The surface charge can be defined by the position of the free corrosion potential (E_{corr}) of the metal with respect to its potential of zero charge (PZC) ($E_q=0$)(12).

At the PZC, the net charge on the electrode is zero. At potential more positive than the PZC, the electrode surface has net positive charge; while at potential more negative than the PZC, the electrode surface has negativity net charge. As a consequence, when the difference $E_{corr} - E_{q=0} = \xi$ is negative, the adsorption of cations is favored. On the contrary, the adsorption of anions is favored when ξ becomes positive. This behaviour is related not only to inorganic or organic ions with formal positive or negative charge, but also to dipoles whose orientation is determined by the value of the ξ potential.

The position of the PZC can be useful in interpreting the positive synergistic effect observed in the corrosion inhibition of iron in sulfuric acid solution by quaternary ammonium cations in the presence of halide ions, such as chlorides(13). In this case, the degree of inhibition in the presence of both absorbable anion and inhibitor cations is higher than the sum of the individual effect. At the free corrosion potential of iron in sulfuric acid solution, the surface charge of the metal is positive

(E_{corr} about -0.2 V_H ; PZC about -0.37 V_H)(14). In this situation, only very poor adsorption of organic cations can occur. If chloride ions are present in the sulfuric acid solution, they are adsorbed on the metal surface and the creation of dipoles oriented to the surface takes place. As a consequence, the PZC shifts to more positive values. If the PZC is more positive than the free corrosion potential, the adsorption of inhibitor cations will occur. This effect can also explain the higher inhibiting efficiency of various organic cations on iron corrosion in hydrochloric acid solutions compared to sulfuric acid solutions.

Distinction has been made between cooperative and competitive adsorption. In the cooperative adsorption, the organic additive is adsorbed onto the halide, pre-adsorbed at the metal surface. In the competitive adsorption, the organic compound displaces adsorbed water molecules and competes with halide ions in the adsorption process. In this way, the hydrocarbon chains or rings of the adsorbed additive protect the surface from successive attacks by halide ions.

The action of halide ions and organic cations has been interpreted to involve not only electrostatic adsorption but also contact adsorption. The inhibiting species whose cations is attributed to electrostatic adsorption interact rapidly with the electrode surface, but they are also easily removed from the surface. A characteristic of the electrostatic adsorption is that no ions are in direct physical contact with the metal a layer of water molecules remains on the surface and divided the metal from the solution. The electrostatic adsorption process has a low activation energy and it proves to be relatively independent of the temperature.

1.3.2- Chemisorption :

The most important type of interaction between an inhibitor and metal surface is chemisorption. In this type of adsorption, the adsorbed species actually come in contact with the metal surface. It is generally assumed that the chemisorption process involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond(14).

According to Bockris, there is not necessarily a chemical bond between the contact- adsorbed species and the metal(15).

The chemisorption process takes place more slowly than electrostatic adsorption and with a higher activation energy. It depends on the temperature; higher inhibiting should be expected at higher temperature.

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

Concerning inhibitors, electron transfer can be expected with molecules having relatively loosely bound electrons. This situation may arise because of the presence in the inhibitor molecule of multiple bonds or aromatic rings, whose electrons have a π character. Clearly, the presence of heteroatoms with lone- pair electrons in the inhibitor molecule will favor the electron transfer.

Most organic inhibitor are substances with at least one functional group considered as the reaction center for the chemisorption process. In this case, the strength of the adsorption bond is related to the heteroatom electron density and to the function group polarizability. As an example, the inhibiting efficiency of homologues series of organic substances differing only in the heteroatom is usually in the following sequence:

$$Se > S > N > O$$

This has been interpreted on the basis of the easier polarizability and lower electronegativity of the elements on the left on the sequence.

1.3.3- Adsorption Isotherms :

The relationships between concentration of inhibitor and corrosion rate or concentration of inhibitor and degree of inhibition respectively, were investigated(16) and resembled adsorption isotherms. Langmuir showed the classical relationship between the concentration of an adsorbate and the amount of adsorption. The fractional surface θ, covered by adsorption is related to the concentration, C, of the adsorbed species in solution by equation (1.16),

$$\theta = aC/(a + aC) \qquad (1.16)$$

where a is a characteristic constant for the specific adsorbate. In the context of corrosion one can write θ as in equation (1.17),

$$\theta = k(m_o - m)/m_o \qquad (1.17)$$

where m_o = the loss in mass per unit area in unit time in the absence of inhibitor, m= the loss in mass per unit area in unit time in the presence of an inhibitor and C is the concentration of the inhibitor. The above relation may be written as in equation (1.18),

$$m_o/(m_o - m) = A/(1/C) + B \quad (1.18)$$

If the plot of $m_o / (m_o - m)$ versus 1/C gives a straight line, then the Langmuir isotherm is said to apply.

Adsorption isotherm is often shown to demonstrate the performance of organic adsorbent-type inhibitors, and surface coverage rates determined by capacitance measurements give a good correlation with these plots. Three types of adsorption isotherm usually cover all the data relating to adsorption inhibitors. The three isotherm are the Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm. The plots are usually given as :

- Log θ /1-θ versus log C for Langmuir isotherms.
- Log θ versus log C Freundlich isotherms.
- θ versus log C for Temkin isotherms.

1.4- Electrochemical Nature of Steel Corrosion

In iron or steel corrosion, electrochemical reactions may take place as follows: at the anodic area

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad (1.1)$$

This reaction is rapid in most media, as shown by the lack of pronounced polarization when iron is made anode employing an external current. When iron corrodes, the rate is usually controlled by the cathodic reaction, which in general is much slower (cathodic control). In the deaerated solutions, the cathodic reaction is:

$$H^+ + e^- \longrightarrow 1/2\ H_2 \qquad (1.2)$$

This reaction proceeds rapidly in acids, but slowly in alkaline or neutral aqueous media. The rate of hydrogen evolution at specific pH depends on the presence or absence of low hydrogen overpotential and impurities in the metal. For pure iron the metal surface itself may provide sites of hydrogen evolution, hence high purity iron continues to corrode in acids but at a measurable lower rate than does the commercial iron.

The cathodic reaction can be accelerated by dissolved oxygen in accordance with the following reactions (a process called depolarization) (17).

$$2H^+ + 1/2\,O_2 + 2\,e^- \longrightarrow H_2O \qquad (1.3)$$

$$H_2O + 1/2O_2 + 2\,e^- \longrightarrow 2\,OH^- \qquad (1.4)$$

Although the overall anodic and cathodic reactions are those given in equations (1.1-1.4), it is usually considered that the equations take place in a series of steps, one of which is the rate determining step (RDS). The most widely accepted anodic scheme is that proposed by Kelly(18) and is practically applicable in acid solutions. The reaction steps are as follows:

$$Fe + H_2O \longrightarrow Fe(H_2O)_{ads} \qquad (1.5)$$

$$Fe(H_2O)_{ads} \longrightarrow Fe\,(OH^-)_{ads} + H^+ \qquad (1.6\ )$$

$$Fe\,(OH^-)_{ads} \longrightarrow (FeOH)_{ads} + e^- \qquad (1.7)$$

$$(FeOH)_{ads} \longrightarrow (FeOH)^+ + e^-\ (RDS) \qquad (1.8)$$

$$(FeOH)^+ + H^+ \longrightarrow Fe^{2+} + H_2O \qquad (1.9\ )$$

This mechanism postulates that the electron transfer steps takes place in two stages with the oxidation of $Fe(OH)_{ads}$ being the rate determining step.

The final concentration of $FeOH^+$ and Fe^{2+} is strongly pH dependent. The two ions will only be stable in acid or oxygen- free systems. In the presence of oxidants the Fe^{2+} will be oxidized to various insoluble ferric compounds such as Fe_3O_4, Fe_2O_3 and the hydrated oxides α, β and γ $Fe(OH)_2$.

The two cathodic reactions involved in dissolution and corrosion reactions are the reduction of H^+ to H_2 and the reduction of dissolved O_2 to OH^-. The following scheme are the ones which have been postulated.

i) Hydrogen Ion Reduction

$$H_{aq}^{+} + e^- \longrightarrow H_{ads} \qquad (1.10)$$

$$H_2O + e^- \longrightarrow H_{ads} + OH_{aq}^- \qquad (1.11)$$

$$H_{ads} + H_{ads} \longrightarrow H_2 \qquad (1.12)$$

$$H_{aq}^{+} + H_{ads} + e^- \longrightarrow H_2 \qquad (1.13)$$

$$H_2O + H_{ads} + e^- \longrightarrow H_2 + OH_{aq}^- \qquad (1.14)$$

At low pH's reactions (1.10) and (1.13) will predominate over (1.12) and (1.14). The rate determining step, depends in part on the catalytic properties of the surface. This is particularly true for the recombination reactions (1.12) and (1.13) or (1.14). In some cases, the recombination reaction is more difficult than dissolution of atomic hydrogen into the metal and the following alternative reaction.

$$H_{ads} \longrightarrow H_{metal} \qquad (1.15)$$

becomes the predominate one. If catalytic sites for hydrogen atom recombination exist within the metal, such as inclusions, then H_2 gas is formed in the metal, therefore, both blistering and rupture can occur.

ii) Oxygen Reduction

$O_2 + e \longrightarrow O_2^{-}{}_{ads}$

$O_2^{-}{}_{ads} + H^+ \longrightarrow HO_{2ads}$

$HO_{2ads} + e \longrightarrow HO_2^-$ $\quad O_2+2H^++2e^- \longrightarrow H_2O_2$

$HO_2^- + H^+ \longrightarrow H_2O_{2aq}$

$H_2O_{2aq} + e \longrightarrow OH + OH^-$

$OH + e^- \longrightarrow OH^-$

$2\,OH^- + 2H^+ \longrightarrow 2H_2O$ $\quad H_2O_2 + 2H^+ + 2\,e^- \longrightarrow 2H_2O$

$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$

These reactions are all quite rapid in comparison to the hydrogen evolution reaction and hence the oxygen is a better cathodic than hydrogen ion.

1.5-Literature Survey of Corrosion of Carbon Steel in aqueous Solutions:

The inhibition of mild steel corrosion in 0.5M H_2SO_4 by simple amines (cyclohexylamine, pyridine, triethylamine) was investigated by polarization, electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy (18). The results indicate a strong dependence of the inhibition performance on the nature of the metal surface, in addition to the structure effects of amine. Inhibition is accomplished by amine adsorption on the metal surface without detectable changes in the chemistry of corrosion. Adsorption is predominantly chemisorptive in the active region. Amine molecules with delocalized π-electrons or high electron densities at their nitrogen atoms are effective inhibitors in the active region. The effectiveness for corrosion control in the passive region, however, is proportional to the number of NH linkages in the amine molecules.

The synergistic influence caused by iodide ions on the inhibition of corrosion of mild steel in 0.5M H_2SO_4 in the presence of n-hexylamine (n-HA) has been studied using potentiodynamic polarization, linear polarization and ac impedance techniques(19). n-HA accelerates the corrosion at higher concentrations. The addition of iodide ions enhances the inhibition efficiency to a considerable extent. The adsorption of this compound is found to obey Temkin's adsorption isotherm. The increase in surface coverage in the presence of iodide ions indicates that the iodide ions enhance the adsorption of n-HA on the metal surface. The values of the synergism parameter (S_I) of more than unity indicate the fact that the enhanced inhibition efficiency in the presence of iodide ions is only due to synergism and there is a definite contribution from the inhibitor molecule. n-HA is adsorbed by coulombic interaction on the metal surface, where iodide ions are already adsorbed and thus reduces the corrosion rate.

The corrosion of carbon steel in 1M H_2SO_4 solution containing hexadecyl trimethyl ammonium bromide (HTABr) was studied over the temperatures range 30-60°C at different inhibitor concentrations of 0.5×10^{-3} to 2.5×10^{-3}M, the by mass-loss method (20). The inhibition efficiency was found to increase with an increase in inhibitor concentration. Thermodynamic activation parameters of the dissolution of steel in H_2SO_4 e.g. free energy of activation E_a, enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated and their values showed that, the dissolution process becomes very difficult. The adsorption of HTABr on a steel surface obeys Langmuir isotherm. The thermodynamic parameters of the adsorption of HTABr on steel was calculated. From these parameters it was concluded that the adsorption layer formed on the used steel is stable.

Abd El Haleem and Killa(21) studied the inhibition of pitting corrosion of mild steel by organic amines under potentiostatic polarization conditions. They found that, aliphatic amines shift the pitting potential into the noble direction indicating increased resistance towards pitting corrosion. The pitting potential varies with the inhibitor concentration according to the following equation:

$$E_{pitt.} = a + b \ \log \ C_{inh} \qquad (1.19)$$

where a and b are constants. Hydrazine, urea and thiourea behave similarly but to a lesser extent. The following equation was deduced by the authors to explain the relationship between the concentration of amines that can withstand the corroding action of certain concentration of Cl ions:

$$\log C_{inh.} = k + n \ \log \ C_{Cl^-} \qquad (1.20)$$

where k and n are constants.

The inhibition efficiency of n-decylamine on the corrosion of low carbon steel in 1N sulphuric acid at different temperatures was investigated potentiokinetically(22). Various parameters such as corrosion potential, corrosion current, polarization resistance, transfer coefficient, standard free energy of adsorption, enthalpy and entropy as well as the activation energy were calculated. It has been found that n-decylamine is absorbed according to Langmuir isotherm. The mechanism of low carbon steel dissolution and the hydrogen evolution reaction do not change in the presence of the inhibitor used.

The influence of N-heterocyclic compounds, such as, imidazole, benzimidazole and 2-methylimidazole on the corrosion and hydrogen permeation through mild steel in 1M HCl was studied using weight loss and various corrosion monitoring techniques(23). Imidazole and benzimidazole inhibit the corrosion of steel but methylimidazole accelerate the corrosion. They behave as cathodic inhibitor by influencing the cathodic polarization reaction. Except methylimidazole, the other two compounds reduce the hydrogen permeation current in the acid solution. The adsorption of these compounds obeys Temkin's adsorption isotherm. Trends in the increase of charge transfer resistance and decrease of the capacitance values also showed the adsorption of the inhibitor on the metal surface.

Abd El-Nabey et al.(24), studied the corrosion inhibition of carbon steel (0.34%C) in sulfuric acid by four selected S-alkylisothiouronium halides. It was found that, the inhibition of corrosion of carbon steel depends upon the concentration and the nature of the inhibitor. The order of increasing inhibition efficiency was correlated with changes in molecular structure of the inhibitor. The inhibitor character of the additives depends upon the length of the hydrocarbon chain in the alkyl moiety of the S-alkylisothiouronium compound and on the type of the halide ions. Results from potentiodynamic polarization measurements indicated that all compounds studied were of mixed type inhibitors affecting both the anodic and cathodic processes by simple blocking of active sites of the metal.

The influence of azathiones as corrosion inhibitors for the corrosion of carbon steel (0.14%C) in 1N H_2SO_4 and 1N HCl was investigated by weight loss and potentiostatic polarization techniques (25). Potentiostatic data showed that these inhibitors are of mixed type. Azathiones can exist as cationic species like other amino compounds (26). These cationic species are adsorbed on the cathodic sites of the steel and decrease the evolution of hydrogen. The adsorption of azathione molecules on the anodic sites takes place through lone pair of electrons of nitrogen and sulphur atoms which decreases the anodic dissolution of steel. Azathiones give better inhibition in 1N HCl than that of 1N H_2SO_4. This is explained on the basis of synergistic mechanism, according to which Cl^- ions and azathiones molecules can jointly be adsorbed on the steel surface giving higher efficiency.

Gomma and Wahdan (27) studied the inhibition of the dissolution of mild steel in 0.5M sulphuric acid by adenine at different temperatures. Adsorption of adenine on metal surfaces was found to follows the Langmuir adsorption isotherm over a wide concentrations range (10^{-5}-10^{-3}M). The corrosion potential, corrosion current, corrosion rate, polarization resistance as well as activation energy and thermodynamic parameters were calculated at different temperatures. From a comparison between the activation energies of uninhibited and inhibited corrosion reactions, the heat of adsorption of adenine was obtained. The temperature coefficient for corrosion inhibition has a negative value, which may be explained by assuming that the corrosion reaction is no longer the simple metal/acid reaction, but involves the adsorbed species directly.

Hanguo et al.(28), studied the effect of both polyvinylpyrrolidone and polyethylenemine as inhibitors for the corrosion of a low carbon steel in phosphoric acid. Polarization and weight loss studies showed that both polyvinylpyrrolidone and polyethylenimine are effective for the inhibition of low carbon steel over a wide concentration range of aqueous phosphoric acid solutions. Both polymers related the anodic and cathodic corrosion reactions with emphasis on the former.

The effect of mixtures of vinyl triphenyl phosphonium bromide containing various anions on the corrosion rate of steel in 0.5M H_2SO_4 was investigated (29). The inhibitor acted by covering the cathodic area of the metal surface through adsorption of the phosphorous atom. Synergistic effect has been observed by addition of KBr, KI, and KSCN with vinyl triphenyl phosphonium bromide. Thus, an improvement in inhibition was obtained by using mixture compared with that given by individual components. A probable mechanism for this process is suggested. Degree of surface coverage of iron in acid solution containing 10^{-5}M inhibitor was determined for various concentrations of Br^-, I^- and SCN^-. The inhibiting effectiveness was in the order KI > KSCN > KBr. Protection of 93.8% was given by a mixture of 10^{-5}M inhibitor + 10^{-2}M KI. The protection efficiency was sharply enhanced in the presence of 10^{-3}M KI with very low concentrations (10^{-5}M – 10^{-4}M) of the inhibitor.

The inhibition effects of 3,5 bis (2-pyridil) 4-aminol, 2,4 triazole (NBTA) and 1,10-phenanthroline (PHEN), on the corrosion of mild steel in acidic solutions, (sulphuric acid and hydrochloric acid) were studied (30). The Tafel polarization and ac impedance techniques were employed. Results obtained reveal that both compounds are relatively good inhibitors. The inhibition efficiencies of NBTA are higher in hydrochloric acid than in sulphuric acid. This has been attributed to the synergistic effect of chloride ions present in hydrochloric acid. The adsorption of

NBTA is believed to occur through the formation of an iron-nitrogen coordination bond. The adsorption isotherm was also determined, and found to be of the Langmuir type.

The efficiency of benzylidene-pyrimidin-2-yl-amine, 4-methyl-benzylidene pyrimidine-2-yl-amine and 4-chloro-benzylidene pyrimidine-2-yl-amine, as corrosion inhibitors for mild steel in 1 M HCl has been determined by weight loss measurements and electrochemical polarization method(31). The results, showed that these inhibitors revealed a good corrosion inhibition even at very low concentrations. Polarization curves indicate that all compounds are mixed type inhibitors. The effect of various parameters such as temperature and inhibitor concentration on the efficiency of the inhibitors has been studied. Activation energies of corrosion reaction in the presence and absence of inhibitors have been calculated. The adsorption of used compounds on the steel surface obeys Langmuir isotherm. It appears that an efficient inhibition is characterized by a relatively greater decrease in free energy of adsorption. Significant correlations are obtained between inhibition efficiency and quantum chemical parameters using quantitatives structure-activity relationship (QSAR) method

Corrosion inhibition efficiencies of 3-amino-1,2,4-triazole (3-ATA), 2-amino-1,3,4-thiadiazole (2-ATDA), 5-(p-tolyl)-1,3,4-triazole (TTA), 3-amino-5-methylmercapto-1,2,4-triazole (3-AMTA) and 2-aminobenzimidazole (2-ABA) on steel in sodium chloride media were investigated using Tafel extrapolation method(32). Potentiostatic current-potential curves were utilized to derive corrosion potentials (E_{corr}), corrosion current densities (I_{corr}), surface coverage degrees (θ) and corrosion inhibition efficiencies (η, %). 2-ABA was found to have the highest inhibition efficiency in both, 2.5 and 3.5% aqueous NaCl media. For all the inhibitors studied, surface coverage and inhibition efficiency values were found to increase with increasing concentration of the compound concerned. Inspection of the θ values indicate that the adsorption process obeys the Temkin isotherm for

TTA and 2-ABA, but the Langmuir isotherm is followed by 3-ATA, 2-ATDA and 3-AMTA.

The synergistic influence caused by iodide ions on the inhibition of corrosion of C-steel in 1M H_2SO_4 in the presence of some aliphatic amines(33) has been studied using weight loss, potentiodynamic polarization, linear polarization and a.c. impedance techniques. Aliphatic amines used to inhibit the corrosion of C-steel and the inhibition efficiency increases by increasing the concentration of the additives and also by addition of iodide ions. The adsorption of these compounds is found to obey Frumkin's adsorption isotherm. The increase in surface coverage in the presence of iodide ions indicates that iodide ions enhance the adsorption of these aliphatic amines on the metal surface. Defines and evaluates synergism parameter (S_0). Values of the parameter which are more than unity indicate the fact that the enhanced inhibition efficiency in the presence of iodide ions is only due to synergism and there is a definite contribution from the inhibitors molecules, which are adsorbed by coulombic interaction on the metal surface, where iodide ions are already adsorbed and thus reduces the corrosion rate.

The corrosion inhibition of cold rolled steel in 0.5M sulphuric acid in the presence of o-phenanthroline and sodium chloride (NaCl) has been investigated by using weight loss and electrochemical techniques(34). The experimental data suggest that the inhibition efficiency increases with increasing NaCl concentration in the presence of 0.0002M o-phenanthroline, but decreases with increasing temperature. A synergistic effect is observed when o-phenanthroline and chloride ions are used together to prevent cold rolled steel corrosion in 0.5M sulphuric acid. The polarization curves showed that the complex of o-phenanthroline and NaCl acts as a mixed type inhibitor. The experimental results suggested that the presence of chloride ions in the solution stabilized the adsorption of o-phenanthroline molecules on the metal surface and improved the inhibition efficiency of o-phenanthroline. The adsorption of the complex obeys the Langmuir adsorption isotherm. Some thermodynamic adsorption parameters were calculated by employing thermodynamic equations. Kinetic parameters such as apparent activation energy and pre-exponential factor have been calculated and discussed.

The inhibiton effect of 3,5-diphenyl-4-H-1,2,4-triazole (DHT) on the corrosion of mild steel in hydrochloric acid solution was investigated at 30°C using electrochemical and weight loss measurements(35). Polarization curves revealed that DHT acts as mixed-type inhibitor and inhibition efficiency up to 98% can be obtained. The inhibition efficiency calculated from these techniques are in reasonably good agreement. X-ray photoelectron spectroscopy (XPS) spectra of the steel surface treated with 1M HCl solution containing the DHT molecule revealed their adsorption on the surface. DHT appears to function through the general adsorption mode following the Langmuir adsorption isotherm model.

Three heterocyclic compounds namely 3-anilino-5-imino-4-phenyl-1,2,4-thiadiazoline (AIPT), 3-anilino-5-imino-4-tolyl-1,2,4-thiadiazoline (AITT), and 3-anilino-5-imino-4-chlorophenyl-1, 2,4-thiadiazoline (AICT) were synthesized and their influence on the inhibition of corrosion of mild steel in 1M HCl and 0.5 M H_2SO_4 was investigated by weight loss and potentiodynamic polarization techniques(36). The values of activation energy and free energy of adsorption of these compounds were also calculated. Potentiodynamic polarization studies were carried out at room temperature, and showed that all the compounds were mixed type inhibitors caused by blocking the active sites on the metal. The inhibition efficiency of these compounds was found to vary with concentration, temperature and immersion time. Good inhibition efficiency was evidenced in both acid solutions. The adsorption of the compounds on mild steel for both acids was found to obey the Langmuir adsorption isotherm. Electrochemical impedance spectroscopy was also used to investigate the mechanism of corrosion inhibition.

Selected triazole derivatives have been synthesized and evaluated as corrosion inhibitors for mild steel in natural aqueous environment by weight loss, potentiodynamic polarization and ac impedance methods. All the condensed products showed good inhibition efficiency (37). The effect of changing functional groups of some triazole derivatives on their inhibition efficiency was also reported. 3-Salicylalidene amino-1,2,4-triazole phosphonate (SATP) was found to be the best corrosion inhibitor compare to the other compounds. Surface analysis was carried out to establish the mechanism of corrosion inhibition of mild steel in neutral aqueous media.

The effect of a new class of corrosion inhibitors namely, arylazobenzoyl acetonitrile derivatives on the corrosion of carbon steel in 2M HCl and 1M H_2SO_4 solutions was studied by electrochemical polarization methods(38) (potentiodynamic, Tafel extrapolation and the determination of polarization resistance). Generally, inhibition efficiency of the investigated compounds was found to increases with increasing concentration. Results obtained from both potentiodynamic and polarization resistance techniques reveal that these compounds are good inhibitors and behave better in 2 M HCl than 1 M H_2SO_4. The adsorption of the compounds on the carbon steel in both acidic media follows Langmuir adsorption isotherm.

The inhibition effect of three amino acids against steel corrosion in HCl solutions has been investigated by potentiodynamic polarization method(39). Corrosion data such as corrosion rate, corrosion potential and corrosion resistance (R_p) were determined by extrapolation of the cathodic and anodic Tafel region. Adsorption isotherm was investigated by weight-loss measurement. The used amino acids were alanine, glycine and leucine. The effect of inhibitor concentration and acid concentration against inhibitor action were investigated. The inhibition efficiency depended on the type of amino acid and its concentration. The inhibition effect ranged from 28 to 91%. The amino acids act as a corrosion inhibitor in HCl solution through adsorption on the steel surface and adsorption follows Langmuir isotherm.

The effect of the concentrations of four types of inhibiting heterocyclic molecules on the corrosion susceptibility of steel pipeline samples grade 5LX-52 in 1M H_2SO_4 was studied by electrochemical testing and SEM analysis(40). The compounds used were: 2-mercaptobenzoimidazole (MBI), 5-mercapto-1-tetrazoleacetic sodium salt (MTAc), 1-hydroxybenzotriazole (HBT) and benzimidazole (BIA). The results showed that there was an optimum inhibitor concentration at which the maximum inhibiting efficiency, IE, was reached. Further, the MBI displayed the best inhibiting characteristics for this system, with a maximum IE of approximately 99% having added only 25 ppm. It is shown that this compound can affect both the anodic and cathodic processes, thus it can be classified as a mixed-type inhibitor for API 5LX-52 steel corrosion in sulphuric acid. Moreover, this compound follows an adsorption mechanism, which can be adequately described by the Langmuir isotherm with an adsorption standard free energy difference ($\Delta G°$) of -28.5 kJ mol^{-1}.

The effects of thiourea (TU), methylthiourea (MTU) and phenylthiourea (PTU) on the corrosion behaviour of mild steel in 0.1 M solution of H_2SO_4 was investigated in relation to the concentration of thioamides(41). These compounds are all similar on one side of the thiocarbonyl group and different on the other. The experimental data were obtained using the techniques of R_p (polarization resistance) and EIS (electrochemical impedance spectroscopy). The results showed that these compounds revaled a good corrosion inhibitor, phenylthiourea being the most efficient and thiourea the least.

The effect of molecular structure on the inhibition efficiency on corrosion was investigated by Abinitio quantum chemical calculations. The electronic properties such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, LUMO-HOMO energy gap and molecular orbital densities were calculated. The relations between the inhibition efficiency and some quantum parameters have been discussed and obvious correlations were found. The highest values of the HOMO densities were found in the vicinity of the sulphur atom indicating it, as the most probable adsorption centre.

The effect of some mercapto-triazole derivatives synthesized in the laboratory containing different hetero atoms and substituents in the organic structures on the corrosion and hydrogen permeation of mild steel in 1.0 M HCl(42) investigated by weight loss and various electrochemical techniques. Results obtained reveal that all the mercapto-triazole derivatives perform excellently as corrosion inhibitors for mild steel in 1.0 M HCl. Potentiodynamic polarization studies have shown that all these compounds suppress both the anodic and cathodic process and they behave as mixed-type inhibitors. Double layer capacitance and charge transfer resistance values were derived from Nyquist plots obtained from AC impedance studies. Changes in impedance parameters are indicative of the adsorption of these compounds on the metal surface. The inhibition efficiency mainly depends on the nature of the investigated compounds. The values of the inhibition efficiency calculated from these techniques are in reasonably good agreement. The extent of reduction of hydrogen permeation current through mild steel surface was studied by the hydrogen electropermeation technique. The adsorption of these compounds on mild steel surface is found to obey Langmuir adsorption isotherm. The free energy of adsorption for inhibiting process was determined on the basis of Langmuir adsorption isotherm.

The corrosion inhibition of mild steel in hydrochloric acid solution by methylene blue dye (MB) was investigated by gravimetric technique(43) at 30 and 60°C as well as thermometric technique. MB was shown to be an inhibitor in the acidic solution. Inhibition efficiency increased with MB concentration but decreased with rise in temperature, with maximum value of 94-95% obtained for 5.0 mM MB at 30°C. Corrosion inhibition is attributed to the adsorption of MB on the mild steel surface via a physical adsorption mechanism. These results were further corroborated by kinetic and activation parameters for corrosion and adsorption processes evaluated from experimental data.

Inhibition of the corrosion of carbon steel in hydrochloric acid solution by some mono-and bis-azo dyes based on 1.5 dihydroxynaphthalene was studied in relation to the concentration of inhibitors using weight loss and potentiostatic polarization techniques (44). The percentrage inhibition efficiency calculated from two methods is in a good agreement with each other. The inhibition mechanism of the additives was ascribed to the information of complex compound adsorbed on the metal surface. The adsorption process follows Freundlich adsorption isotherm. The formation of the complex compound was studied by conductometric and potentiometric titrations. The stability constants of the Fe-complexes were determined using the latter technique and related to the inhibition efficiency.

The corrosion inhibition of steel with Schiff base compounds in 2M HCl(45) was studied. The inhibitor effect of N, N-bis(salicylidene)-2-hydroxyl,3-propanediamine (LOH) and N,N- bis(2-hydroxyacetophenylidene)-2-hydroxy-1,3-propanediamine(LACOH) in 2 mol dm^{-3} HCl medium on mild steel with known compound has been investigated at 303 K. It has been determined using weight loss, polarization and electrochemical impedance spectroscopy (EIS) methods. It has been found that the corrosion rates decrease, percentage inhibition efficiencies and surface coverage degrees increase with increasing additive concentration. The inhibitors appear to function through the Langmuir adsorption isotherm. Results show LACOH to have the highest inhibition efficiency among the two compounds studied.

The inhibition action of commercial fatty acid sulphonate in the corrosion of mild steel in 1 M HCl solution was evaluated by weight loss and cathodic Tafel polarization techniques(46). Some corrosion parameters were calculated, such as corrosion potential, corrosion current density, surface coverage and inhibition efficiency. The inhibition efficiency was found to increase with increasing inhibitor concentration. Inhibition was explained by adsorption via π- electron of double bond. The adsorption process was found to follow Langmuir adsorption isotherm.

A pyrazine derivative as corrosion inhibitor for steel in sulphuric acid solution(47). The influence of diethyl pyrazine-2,3-dicarboxylate (P1) on the corrosion of steel in 0.5 M H_2SO_4 solution has been studied by weight loss measurements, potentiodynamic polarization, linear polarization resistance (Rp) and electrochemical impedance spectroscopy (EIS) methods. The inhibiting action increases with the concentration of pyrazine compound to attain 82% at 10^{-2} M. We note good agreement between gravimetric and electrochemical methods. Polarization measurements also show that the pyrazine acts essentially as a cathodic inhibitor. The cathodic curve indicate that the reduction of proton at the steel surface happens with an activating mechanism. They yellow deposit on the steel surface was analyzed by infrared method. P1 adsorbs on the steel surface according to Langmuir adsorption model.

The effect of some pyridine derivatives on the corrosion of carbon steel in 2M HCl solutions was studied using electrochemical polarization method (potentiodynamic, Tafel extrapolation) as well as weight loss method(48). Generally, inhibition efficiency of the investigated compounds was found to depend on the concentration and the nature of the inhibitor. Results obtained from both potentiodynamic and weight loss techniques reveals that, these compounds are good inhibitors. The presence of substitution in pyridine ring plays an important role in the percentage inhibition of the compounds under investigation. The adsorption of these compounds on the carbon steel follows a Langmuir adsorption isotherm.

The effect of concentration of sodium gluconate (SG), triethanolamine (TEA) and mixture of them on the corrosion of carbon steel in 3.5% NaCl solution were studied using weight loss and potentiostatic polarization measurement(49). The inhibition efficiency of these compounds was found to increase with increasing concentrations, but in case of SG, the inhibition efficiency reached a critical value and decreased at higher concentrations. This was attributed to the formation of soluble Fe- gluconate complex. The mixture of SG and TEA improved the inhibition efficiency of steel to 92.48% in presence of 1×10^{-5} M SG+ $1\mathrm{X}10^{-2}$ M TEA .

1,2-bis(1,2,4-triazolyl)dodecane (dTC12) is an excellent corrosion inhibitor for carbon steel in deaerated 1 M HCl solution(50). Electrochemical and analytical techniques were used to study the inhibition of corrosion on carbon steel in acidic medium. The carbon steel corrosion inhibition of dTC12 was attributed to the synergistic effect between chloride anion and quaternary ammonium ion. The protective efficiency of the film was higher than 90%, indicating that corrosion of carbon steel in 1 M HCl is reduced by dTC12. The effect of dissolved oxygen on the inhibition efficiency was also investigated. The results show that the inhibition efficiency increases in early stage and decreases for a long immersion time.

The corrosion inhibition of colled rolled steel in 0.5M sulfuric acid in the presence of 8-hydroxyquinoline and sodium chloride was investigated using weight loss and electrochemical techniques(51). The inhibition efficiency increases with increasing concentration of 8-hydroxyquinoline at the same temperature, but decreases with increasing temperature studied. A synergistic effect exists when 8-hydroxyquinoline and chloride ions are used together to prevent cold rolled steel corrosion in 0.5M sulfuric acid at every experimental temperature. The polarization curves show that 8-hydroxyquinoline is a cathodic inhibitor, while the complex of 8-hydroxyquinoline and NaCl is a mixed type inhibitor. The experimental results suggested that the presence of chloride ions in the solution stabilizes the adsorption of 8-hydroxyquinoline molecules on the metal surface and improved the inhibition efficiency of 8-hydroxyquinoline. The adsorption of 8-hydroxyquinoline follows the Temkin adsorption isotherm, but the complex accords with the Langmuir adsorption isotherm.

The ability of new synthesized non ionic surfactants to protect carbon steel in acid chloride solution was investigated using potentiostatic polarization, open circuit potential, weight loss and surface tension measurements(52). The experimental results showed that these inhibitors revealed a very good corrosion inhibition even at low concentrations. The percentage inhibition efficiency increases by increasing the inhibitor concentration until the critical micelle concentration (cmc) is reached. It was found that, the adsorption ability of the surfactant molecules on carbon steel surface increased with the increase of the molecular size of the surfactant. Potentiostatic polarization curves indicate that the inhibitors under investigation act as mixed type. Finally, the mechanism of carbon steel dissolution in acidic medium was discussed both in absence and presence of the inhibitor molecules.

The anti-corrosive properties of 2-aminomethylbenzimidazole (AMB) and bis(benzimidazol-2-ylethyl)sulfide (BBES) were analyzed by electrochemical techniques such as polarization curves and electrochemical impedance spectroscopy (EIS)(53). The results show that AMB behaves as a cathodic inhibitor, while BBES functions as mixed inhibitor. Furthermore, BBES inhibits the corrosive process more strongly than AMB; because in the former benzimidazoles and thioether sulfur work as active sites for the adsorption process over the metal surfaces. This observation is supported by density functional theoretical (DFT) parameters such as frontier molecular orbitals (HOMO and LUMO), Mulliken charges and the electrostatic potential map.

The inhibiting action of some polyethylene glycols on the corrosion of carbon steel in 3N sulphuric acid as corroding solution, was evaluated by the weight loss method, polarization and impedance spectroscopy techniques(54). In order to study the effect of polyethylene glycol structure on the inhibition efficiency, different molar weights (200–10,000 g mol^{-1}) were selected. This work has demonstrated that the polyethylene glycols have an inhibition effect on the corrosion process and the inhibition efficiency is more than 90%. It was shown that polyethylene glycol is adsorbed physically on carbon steel in acid medium.

The aqueous extract of the leaves of henna (lawsonia) is tested as corrosion inhibitor of C-steel in acidic, neutral and alkaline solutions, using the polarization technique(55). It was found that the extract acts as a good corrosion inhibitor in all tested media. The inhibition efficiency increases as the added concentration of extract is increased. The degree of inhibition depends on the nature of metal and the type of the medium. The extract acts as a mixed inhibitor. The inhibitive action of the extract is discussed in view of adsorption of lawsonia molecules on the metal surface. It was found that this adsorption follows Langmuir adsorption isotherm in all tested systems. The formation of complex between metal cations and lawsone is also proposed as additional inhibition mechanism of C-steel corrosion.

The effect of some mercapto-triazole derivatives synthesized in the laboratory containing different hetero atoms and subsituents in the organic structure on the corrosion and hydrogen permeation of mild steel in 1.0M HCl was investigated by weight loss and various electrochemical techniques (56). Results obtained reveal that all the mercapto-triazole derivatives perform excellently as corrosion inhibitors for mild steel in 1.0M HCl. Potentiodynamic polarization studies have shown that all these compounds suppress both the anodic and cathodic process and they behave as mixed-type inhibitors. Double layer capacitance and charge transfer resistance values were derived from Nyquist plots obtained from AC impedance of these compounds on the metal surface. The inhibition efficiency mainly depends on the nature of the investigated compounds. The values of the inhibition efficiency calculated from these techniques are in reasonably good agreement. The extent or reduction of hydrogen permeation current through mild steel surface was studied by the hydrogen electropermeation technique. The adsorption of these compounds on mild steel surface is found to obey Langmuir adsorption isotherm. The free energy of adsorption for inhibiting process was determined on the basis of Langmuir adsorption isotherm.

The inhibitive capability of some organic dyes namely; safranine-o (SO), thymol blue (TB) and fluorescein-Na (F-NA) on the electrochemical corrosion of mild steel in sulphuric acid solution was rapidly assessed using the gasometric technique (57). The result indicate that all of the studied compounds act as inhibitor in the acidic corrodent. Inhibition efficiency increased with concentration for SO and TB but decrease with concentration for F-Na. The gasometric technique provides a means for rapid assessment of inhibitor effects on corrosion rates.

Experimental and theoretical study of 1-(2-ethylamio)-2 methylimida-zoline as an inhibitor for corrosion of carbon steel in acidic media(58). The electrochemical behaviour of 1-(2-ethylamio)-2 methylimida-zoline (imidazoline), its precursor N-[3-(2-amino–ethylaminoethyl)]-acetamide (amide) and its derivative 1-(2-ethylamion)2-methylimidazolidine (imidazolidine), was evaluated by using potentiodynamic polarization curves and electerochemical impedance spectroscopy, (EIS), techniques in deareated acid media to compare their corrosion inhibition efficiency. The experimental results suggest that imidazoline is a good corrosion inhibitor at different concentrations whereas amide shows low efficiency values; however, the properties of a corrosion inhibitor were not found in imidazolidine. The reactivity of these compounds was analyzed through theoretical calculations based on density functional theory (DFT) to explain the different efficiencies of these compounds as corrosion inhibitors both in the neutral and protonated form. The theoretical results indicate that active sites (two nitrogen atoms) and the plane geometry of the heterocyclic ring, thus promoting coordination with the metal surface.

The effect of some aminopyrimidine derivatives on the corrosion of 1018 carbon steel in 0.05M HNO_3 solution was studies using the weight loss and polarization techniques(59). The percentage inhibition efficiency was found to increase with increasing concentration of inhibitor and with decreasing temperature. The addition of KI to amino pyrimidine derivatives enhanced the inhibition efficiency due to synergistic effect. The inhibitors are adsorbed on the steel surface according to Temkin isotherm. It was found that the aminopyrimidine derivatives provide a good protection to steel against pitting corrosion in chloride containing solutions.

The inhibition effects of some new dithiophosphonic acid monoesters, namely, o-methyl-p-methoxyphenyl-dithiophosphonic acid (MTPA), o-ethyl-p-methoxy-phenyl dithioph-osphonic acid (ETPA) and o-isopropyl-pmethoxyphenyl dithiophosphonic acid (IPTPA) ammonium salts on the corrosion of the steel in 1M HCl medium was studied(60). Concentration of the inhibitors were in the rang 10^{-3} to $2x10^{-2}$ M, five different temperatures between 298 and 338K were tried; Tafel extrapolation and linear polarization technique were employed. Corrosion parameters and adsorption isotherm were determined from current-potential curves. At room temperature, the three compounds were found to decrease the corrosion rate by around 80% at $1x10^{-3}$ M, and 95% at $2x10^{-2}$M concentration. The inhibition efficiencies weaken slightly at higher concentration but in any case, more than 75% inhibition is observed at a temperature of 338K with an inhibitor concentration of $2x10^{-2}$M. Surface coverage degree indicate that the adsorption pattern is consistent with the Temkin isotherm.

A triazole-based cationic Gemini surfactant, 3,5-bis (methylene octadecyl dimethyalammonium chloride)-1,2,4- triazole (18- triazole-18) was synthesized, and its effect on corrosion of carbon steel in 1M HCl was studied using the weight loss method (61). The result showed that 18-triazole-18 acted as an excellent inhibitors in 1M HCl. It was found that the adsorption mechanism of 18-triazole-18 on the steel surface in acid medium was quite different from that of cationic Gemini surfactants containing dimethylene as a spacer, as well as that of conventional cationic single-chained surfactants, which is due to unique molecular structure of 18-triazole-18. 18-triazole-18 may be adsorbed on the steel surface in acid medium through a maximum of four atoms or groups, i.e., the two nitrogen atoms of triazole ring and two quaternary ammonium head groups. Four regions of surfactant concentration could be divided to illustrate the adsorption of 18-triazole-18 on the steel surface, and four different adsorption mechanism may take place in different regions of surfactant concentration.

The efficiency of benzylidiene-pyrimidin-2-yl-amine (A), (4-methyl-benzylidene)-pyrimidine-2yl- amine and (4-chloro-benzylidine)-pyrimidine-2-yl-amine, as corrosion inhibitors for mild steel in 1M HCl was studied by weight loss measurements and electrochemical polarization method (62). The results showed that these inhibitors revealed a good corrosion inhibitors even at very low concentration. Polarization curves indicate that all compounds are mixed type inhibitors. The effect of various parameters such as temperature and inhibitor concentration on the efficiency of the inhibitors was studied. Activation energies of corrosion reaction in the presence and absence of inhibitors were calculated. The adsorption of used compounds on the steel surface obeys Langmuir's isotherm. It appears that an efficient inhibition is characterized by a relatively greater decrease in free energy of adsorption. Significant correlation are obtained between inhibition efficiency and quantum chemical parameters using quantitative structure activity relationship (QSAR) method.

A new class of thiadiazole derivatives, namely 3,5-bis(2-thienyl)-1,3,4-thiadizole (2-TTH) and 3,5-bis (3-thienyl)-1,3,4-thiadiazole (3-TTH), have been studied as possible corrosion inhibitors for mild steel hydrochloric acid solution (63). Weight loss measurement, polarization curve and AC impedance methods have been used. These studies have shown that the thiadiazole derivatives were very good inhibitors for mild steel in 1M HCl. Comparison of results showed that 3-TTH was the best inhibitor. The potential of zero charge (PZC) of mild steel was studied by AC impedance method, and the mechanism of adsorption has been predicted. X-ray photoelectron spectroscopy surface analysis with thiadiazole derivatives shows that it chemisorbed at the mild steel /HCl interface. The electronic properties of 2-TTH and 3- TTH, obtained using the AMI semi-empirical quantum chemical approach, were correlated with their experimental efficiencies using the linear resistance model. These inhibitors are considered as non- cytotoxic substances.

The inhibition action of some polyethylene glycols on corrosion of carbon steel in 3N H_2SO_4 solution was evaluated by the weight loss, polarization and impedance spectroscopy techniques(64). It was found that the inhibition efficiency IE increases with the increasing mean molecular weight of polymer and its concentration and decreases with rising of temperature. These polymer predominately inhibit the anodic reaction of the corrosion process. The activation energy is also increased with increasing mean molecular weight of the polymer. The adsorption of the polymers on carbon steel is found also as physical adsorption. The difference in adsorption of inhibitors results are related to the shape and size of the polyethylene glycols.

The effect of N-prpylaminolaurylamido and three of it ethoxylated derivatives as corrosion inhibitors of carbon steel in 1M HCl solution was studied by weight loss and galvanostatic polarization techniques(65). A significance decrease in the corrosion rate of carbon steel was observed in the presence of the investigated inhibitors. The inhibition efficiency increases with increasing the inhibitors concentration. The inhibition process was explained in terms of adsorption on the metal surface. The adsorption process obeyed Langmuir adsorption isotherm. The galvanostatic polarization data indicated that, the inhibitors were of mixed type, but the cathodic effect is more pronounced. The slopes of the cathodic and anodic Tafel lines are approximately constant and independent on the inhibitor concentration. The relation between the surface tension (γ) and logarithm of their concentrations was investigated to obtain the adsorption ability of the inhibitor on the steel surface.

A nonionic surfactant namely, octylphenol polyethylene oxide (OPPEO)was evaluated as an inhibitor for corrosion of low-carbon steel in 0.5M H_2SO_4(66). Potentiodynamic and potentiostatic methods with the aid of scanning electron microscopy were used to study the inhibiting effect of the surfactant compound. The inhibition efficiency was found to increase with the inhibitor concentration and decrease with temperature. OPPED showed higher constant inhibiting efficiency near its critical micelle concentration which decrease with increasing temperature. The activation energy of corrosion reaction was found to be higher in presence than the absence of the inhibitor. The adsorption process obeys Flory-Huggins isotherm. The Gibbs free energy of adsorption decreases with temperature. The inhibitors have relatively lower inhibition efficiencies at ambient and higher temperatures. This was attributed to the molecular structure of the inhibitor.