

CHAPTER (1)

INTRODUCTION

Corrosion may be defined as an unintentional attack on a material through reaction by the surrounding environment, the term refers to a process or to the damage caused by such a process, corrosion is also defined as the destruction or deterioration of materials under chemical action of the surrounding environment ⁽¹⁾. Shreir ⁽²⁾ describes corrosion as the reaction of solid with the environment.

1.1- Forms of corrosion:

Almost all corrosion problems and failures encountered in service can be associated with one or more of the following forms of corrosion:

1.1.1- General and local electrochemical corrosion ⁽³⁾

When separate corrosion cells can be distinguished by variation of the electrode potential over the metal surface, by the appearance of corrosion currents or of separate anodic and cathodic corrosion products, local electrochemical corrosion is said to occur. General electrochemical corrosion occurs when separate anodic surfaces do not appear or they are of small dimensions (sub micro cells) or fluctuate over the surfaces, the attack will be more uniform. Hence there are possibilities for corrosion products to form a continuous film and retard continuous attack. Therefore general electrochemical corrosion leads to uniform attack whereas local electrochemical corrosion results in localized attacks.

1.1.2- Galvanic corrosion or dissimilar metal corrosion

Galvanic corrosion occurs when two or more dissimilar metals in electrical contact are placed in an electrolyte. The tendency of a metal to corrode in a galvanic cell is determined by its position in the “galvanic series” of metals and alloys in seawater as listed in Table (1.1). Several

investigators ^(4,5) have shown that galvanic corrosion is directly proportional to the area ratio of the cathodic metal to the anodic metal.

Table (1.1)

Galvanic Series in Seawater at 25 °C

Corroded end (anodic, or least noble)

Magnesium

Magnesium alloys

Zinc

Galvanized steel or galvanized wrought iron

Aluminum alloys - 5052, 3004, 3003, 1100, 6053, in this order

Low-carbon steel

Wrought iron

Cast iron

Ni-Resist (high-nickel cast iron)

Type 410 stainless steel (active)

50-50 lead-tin solder

Type 450 stainless steel (active)

Type 304 stainless steel (active)

Type 316 stainless steel (active)

Lead

Tin

Copper alloy C28000 (Muntz metal, 60% Cu)

Copper alloy C67500 (manganese bronze)

Copper alloys C46400, C46500, C46600

Alloy 200 (active)

Alloy 6700 (active)

Alloy B

Chlorimet 2

Copper alloy C27000 (yellow brass, 65% Cu)

Copper alloys C44300, C44400, C44500 (admiralty brass)

Copper alloys C60800, C61400 (aluminum bronze)

Copper alloy C23000 (red brass, 85% Cu)

Copper C11000 (ETP copper)

Copper alloys C65100, C65500 (silicon bronze)

Copper alloy C71500 (copper nickel, 30% Ni)

Copper alloy C92300, cast (lead tin bronze G)

Copper alloy C92200, cast (lead tin bronze M)

Alloy 200 (passive)

Alloy 600 (passive)

Alloy 400

Type 410 stainless steel (passive)

Type 304 stainless steel (passive)

Type 3316 stainless steel (passive)

Alloy 825

Alloy 62

Alloy C

Chlorimet 3

Silver

Titanium

Graphite

Gold

Platinum

Protected end (cathodic, or most noble)

1.1.3- Crevice corrosion ^(6,7)

Only metals and alloys, which depend upon the oxide film for corrosion resistance, are susceptible to crevice corrosion. It is an intense

localized corrosive attack which occurs within the confined space or crevices created by certain mechanical configurations.

1.1.4- Filiform corrosion

This is a special type of crevice corrosion which results in irregularly developed hair- fine lines or filaments of corrosion products below coatings of paints, tin, silver, etc. It does not destroy the component but affects the surface appearance.

1.1.5- Intergranular corrosion ⁽⁸⁾

Grain boundaries are usually more reactive than the grain matrix. Hence localized attack occurs at adjacent to grain boundaries with relatively little corrosion of the matrix. This attack is usually rapid and penetrates deep into the metal resulting in loss of strength and causes catastrophic failures ^(9,10).

1.1.6- Pitting corrosion

This is also a form of intensive localized attack, the rate of attack being non-uniform. It is most destructive form of corrosion and results in sudden failure of the equipment due to the formation of pits or holes. It is reported to occur in the presence of chloride ions depending upon the concentration of chloride ions ⁽¹¹⁻¹⁴⁾.

1.1.7- Exfoliation ⁽¹⁵⁾

The loss of metals as layers or leaves from a solid metal or alloy is called exfoliation. This type is observed mostly in wrought products.

1.1.8- Stress corrosion cracking ^(16,17)

The Cracking of metal or alloy due to the simultaneous presence of tensile stress and a specific corrosive environment is known as stress corrosion cracking.

1.1.9- Corrosion fatigue cracking ^(18,19)

Reduction in the fatigue strength due to the presence of a corrosive environment is known as corrosion fatigue cracking. It occurs due to the combined action of cyclic stress and corrosive environment.

1.1.10- Fretting corrosion ⁽²⁰⁾

This type of corrosion occurs between two surfaces in contact with each other in dry or humid air when subjected to slight relative motion of small amplitude. Various alternate terms such as friction oxidation, wear oxidation, chafing, false brinelling are used to describe this phenomena.

1.1.11- Erosion Corrosion

Erosion corrosion is defined as increased corrosion rate to relative motion between metal surface and the environments usually liquid or gas. This type of corrosion is also known as impingement corrosion ⁽¹⁵⁾. Such corrosion occurs in agitators, copper pipes, centrifuge etc. Localized attack due to erosion corrosion usually has bright surface free from corrosion products. e.g. pits, grooves, rounded holes and valleys.

1.1.12- Cavitation corrosion ⁽²¹⁾

This is a special type of erosion corrosion caused due to the formation of vapor bubbles in a corrosive environment near a metal surface and when the bubbles collapse attack arises. e.g. Hydraulic turbulence, ship propellers etc.

1.2- Theories of corrosion

The corrosion of metals in aqueous solutions is an electrochemical process as established in the first half of the 19th century. Whitney ⁽²²⁾ gave the most acceptable electrochemical theory. The other theories such as acid theory ⁽²³⁾ chemical attack theory, colloidal theory ^(24,25) and biological theory ⁽²⁶⁾ were proved to form apart of electrochemical theory.

1.2.1- Electrochemical Theory of Corrosion

An atom has a massive positively charged central nucleus surrounded by a cloud of negatively charged electrons. This cloud of

electrons is accommodated in a series of shells. The outermost shell should have eight electrons in the most stable state of an element. If the electrons are insufficient to fill the outer most shell, the atom tends to obtain a cloud of complete shells by gaining or losing electrons to give rise to modified atoms called 'ions'. Evans ⁽²⁷⁾ has explained the role of these ions in the corrosion and dissolution of metals and alloys under the influence of the exchange of ionic charges. This has laid down the basis of the electrochemical theory of corrosion. When a metallic object is immersed in a corrosive medium the metallic surface gets divided into areas having different potentials under the influence of various metallic phases, grain boundaries stress and strain, impurities etc. In an electrolyte the metal undergoes disintegration due to the displacement of a hydrogen ions in the electrolyte by those of the anode metal, resulting in the formation of a galvanic cell.

The corrosion generally involves the formation of hydrogen gas at the cathode in an acidic medium.

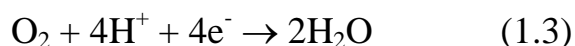
The anodic reaction is



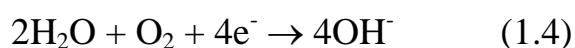
This represents oxidation of the metal. The cathodic reaction is



The other possible cathode reaction is the reduction of oxygen in acidic solutions



In neutral and alkaline solutions, however, the accumulation of electrons on the cathode is prevented (except for a very active metal) only by the intervention of oxygen which is reduced according to the equation



The essential concept of the electrochemical mechanism is that the corrosion of a metal is a redox reaction, occurring at a metal/solution interface with consequent transfer of electrons through the metal and ions through the solution. The tendency of a metal to corrode may be expressed by the amount of energy liberated in the changes from the metallic state to the oxidized state or in electrochemical terms by the standard electrode potential of the metal. The metals are arranged in order of their electrode potential, the noble metals appearing at the passive end and the more reactive metals appearing at the active end of the series. Although brass has fairly a good corrosion resistance, owing to the presence of zinc (electronegative) the corrosion behavior of brass is shifted towards higher electronegativity.

1.3- Mechanism of corrosion processes

All the corrosion processes involve the reduction reaction confined to hydrogen evolution or oxygen absorption and the oxidation reaction, i.e., anodic dissolution of the metal. Prediction of the rate of corrosion based on the hydrogen evolution is easier compared to oxygen absorption in which reaction takes place in many steps on the oxide-covered surface—a poor electron carrier. The anodic reaction which involves the movement of metal ions from the metal phase to the solution phase is also complicated which takes place through several steps like diffusion of ions on the surface, entry into solution phase as an intermediate step and solvation of ion as the final step. Five possible mechanisms for the corrosion of iron have been given ^(28, 29,30)

1.4- Expression for corrosion rate

Weight loss measurement is the commonly used technique to measure the corrosion rate. The rate of corrosion is calculated from:

$$R = \frac{534W}{DAT} \quad (1.12)$$

where R is the corrosion rate in mpy (mils penetration per year)

W is the weight loss in milligram

A is the area of the specimen in square inches

T is the time of exposure in hour

D is the density in g/cm^3

A variety of units have been used in the literature to express the corrosion rate. Corrosion rates are usually expressed in two basic units mpy and mdd. (milligram per square decimeter per day).

1.5-Corrosion Prevention

Methods of preventing corrosion have been conveniently summarized as follow:

1.5.1- Prevention Based on the Environment

- i- By addition of corrosion inhibitor.
- ii- By decreasing the electrical conductance, electrolytic corrosion can be reduced.
- iii- By purification of or de-humidifications of air.
- iv- By raising the pH value, the acidity of solution can be eliminated.
- v- By deaeration using an inert gas or use of an oxygen scavenger e.g. hydrazine and Na_2SO_3 , oxygen reduction of differential aeration can be stopped.

1.5.2- Prevention Based on the Metal

- i- By addition of alloying element that increases corrosion resistance e.g. steel-containing chromium is more resistant than normal steel.
- ii- By raising purity of metals, impure metals corrode at much faster rates than pure metals.
- iii- By heat treatment, these reduce the probabilities of stress corrosion cracking.
- iv- By plating with a less reactive metal like copper on normal steel that can. make surface coating.

1.5.3- Prevention Based on Protective Coating

Metal coating.

Organic coating (paints, resins, etc.).

Inorganic coating (cements).

Coating by reaction product (electrochemical or chemical treatment of metal surface).

Temporary protection.

1.5.4- Prevention Based on Electrochemistry

The corrosion in aqueous solution is electrochemical in nature, so the prevention is achieved by preventing the cathodic reaction, the anodic reaction or both:

1.5.4-(i) Anodic protection:

The prevention occurs by interfering with the anodic reaction which is based on changing the potential on the corroding metal in the positive direction to the extent of passing the domain of metal dissolution and bringing the metal into the region of passivity. This is achieved by oxidizing inhibitor e.g. chromate, nitrite and nitrate.

1.5.4-(ii) Cathodic protection:

The prevention occurs by interfering with the cathodic reaction, which is based on changing the potential of the corroding metal towards negative direction to an extent whereby the dissolution reaction

$M = M^{+n} + ne^-$ becomes no more feasible.

1.6-The Limitations and Uses of Inhibitors

Inhibitors have been used for many years to protect metals whose mechanical and physical properties must be considered before deciding their use⁽³¹⁾:-

- (i) Inhibitors, which contaminate the environment and are often toxic, these cannot be used in food industries or in any system, which could indirectly allow the consumption of inhibitors by humans.
- (ii) They are most useful in closed system where the corrosive environment is either retained for long period or recycled.
- (iii) Inhibitors generally lose their effectiveness as the concentration of the consumption corrosive material and temperature are increased. This can be remedied by keeping the concentration of the inhibitors at a level, which exceeds the optimum value, necessary for protection.
- (iv) Inhibitors can offer a cheap, easy to apply and highly effective methods for corrosion when certain consideration are taken.

1.7-Correlation Between Inhibition and Stability of Organic Compounds

The factors which are responsible for inhibition of corrosion by organic compounds depend on the nature of the corroding metal, the composition of the corrosive medium and the conditions under which the corrosion process occurs; added to this, the chemical properties and structure of organic compounds.

An organic substance can effectively protect a given metal under certain condition or with other metals. If different kinds of inhibitors are considered separately, the factor responsible for inhibitive action of the organic compound could be understood better.

1.7.1- Inhibition by Chemically Stable Surface Active Organic Compounds

In many cases the stability and the ability of organic compounds to be adsorbed depends on the nature of the corroding metal. It is very difficult indeed to find compounds, which do not undergo any chemical changes in solution during the course of corrosion process⁽³²⁾. For a given solution the adsorption of inhibitors depends⁽³³⁾, first of all on the charge on the metal and on the potential of the metal in solution, the

charge on the metal is relative to the zero charge potential. (Q) potential controls the electrostatic interaction of the metal with dipoles in adsorbed neutral molecules and hence the orientation of the dipole and the adsorbed molecule. Thus, as the Q potential becomes more positive, the adsorption of the anions is favored, and as the Q potential becomes more negative the adsorption of the cation is favored.

1.7.2-Inhibition by Surface Active Chemically Unstable Organic Compounds:

The inhibition efficiency-concentration relationship had been considered and the probability of maxima or minima had been noted. As a result of interaction with the cathodic hydrogen, the significance of the chemical change in the nature of additives was realized. The following three cases have been discussed⁽³⁴⁾:

- (i) Surface active additives reducible to surface inactive compounds.
- (ii) Surface inactive additives reducible to surface active compounds.
- (iii) Surface active reducible to new surface active compounds.

1.7.2.1-The types of chemical transformation

a) Protonation:

Antropov^(33,34), in discussing electro-organic reduction process considered the following points as being important with regard to protonation reaction.

- (i) It occurs usually on the surface of a metal and can under definite conditions be a rate-determining step of the overall reaction.
- (ii) Its rate depends on the surface concentration of the organic substance and therefore on the charge on the surface (its Q-potential).
- (iii) As a result of the opposite effect of electric field and the charge of a metal, the rate of reduction (protonation) can reach maximum value.

b) Reduction:

The reduction of organic compounds could take place only if the corrosion potential is sufficiently negative. If this condition is fulfilled, the main principles of the theory of electroreduction of organic compounds ^(33,35) could be applied to that particular case of organic electrochemistry. Thus, the selective reduction of inhibitors on various metals should be expected.

c) Polymerization:

Cathodic reduction under certain conditions may lead to the formation of dimer and polymers. If polymerization is a surface process, and the formation of copolymer between the inhibitors and corroding metal is possible, the degree of protection should be increased ⁽³⁶⁾.

1.7.3-Effect of molecular structure on corrosion inhibition.

The inhibition attributable to the initial compound is called “primary inhibition” and that brought about by the reduction products “secondary inhibition” ^(37,38). The inhibition efficiencies calculated for different homologous series of organic compounds have sometimes underlined the difficulty of attributing the variation in inhibition within a series mono functional substances to a single molecular property such as electron density. It is necessary to know the possible steric effect including molecular size and mode of interaction, which may provide, a screening action on the reaction center for the adsorption of the molecule at the metal surface ⁽³⁹⁾. Complexation between the organic molecule and the metal and the stability constants of the resulting complexes was taken in consideration. Kinetic and equilibrium processes in organic chemistry have been found to an empirical equation proposed by Hammett ⁽⁴⁰⁾ and discussed and extended by Jaffe ⁽⁴¹⁾ and Taft ⁽⁴²⁾. The family of relationships thus obtained is a form of linear free energy relationship (LFER) usually designated as the Hammett relation and is given by

$$\log k/k_o \text{ or } \log K/K_o = \rho\sigma \quad (1.13)$$

where k' s = rate constants, or K' s = equilibrium constants. The zero subscripts, o, refer to parent or reference compounds, ρ = reaction constant and σ = substitution constant. By setting the reaction constant equal unity, for the substituted benzoic acid, the reaction further simplified to yield:

$$\log k/k_o = (pk_o - pk) = \log K/K_o = \sigma \quad (1.14)$$

This equation is then taken as the definition of the substituent constant σ i.e. a substituent is given a numerical value, which is dependent on its effect on the pK of the substituted benzoic acid compared to benzoic acid. From this definition, hydrogen has a σ of zero. Substituents which increase ionization (i.e. weaken the O–H bond) have positive value of σ and those which decrease ionization (i.e. strengthen the O–H bond) have negative value. Therefore, σ is a measure of the electron density or distribution on an atom. This measure of the electron density or distribution at a specific atom in the molecule is justified on the basis of quantum-mechanical calculations of electron charge density of individual atom within a molecular orbital structure ⁽⁴³⁾. Steric effects have not been considered since Hammett correlated only meta and para substituent and aliphatic systems caused Tafel to develop σ scale. In general, this leads to rate or equilibrium equations, which are due to polar effects resulting from structural changes.

A comprehensive approach to corrosion inhibition was suggested by Fouda ⁽⁴⁴⁾. According to this approach, metallic corrosion inhibition depends not only on the polar effect or the electron charge density of functional groups or adsorption active centers in the molecule, but also on the molecular size of the inhibitor, its mode of adsorption on the metal surface, its heat of hydrogenation, and its ability to form insoluble

metallic complexes that can be incorporated in the oxide layer thus reinforcing it or soluble ones that enhance dissolution.

1.7.4 Adsorption isotherms

An adsorption isotherm is the mathematical expression, which relates the bulk concentration of an adsorbing species to its surface concentration at constant temperature. An adsorption isotherm gives the relationship between the coverage of an interface with an adsorbed species and the concentration of the species in solution. Various adsorption isotherms have been formulated. A list of some isotherms and the corresponding equations are given in Table (1.2).

Table (1.2)

Name	Isotherm equation
Langmuir	$\theta/(1-\theta) = K C$
Frumkin	$K C = \theta / 1 - \theta \exp (-2 a \theta)$
Temkin	$\ln K C = a \theta$
Freundlich	$\theta = K C^n$
Volmer	$K C = \theta / 1 - \theta \exp (\theta / 1 - \theta)$
Henry	$\theta = K C$
Parsons	$K C = \theta / 1 - \theta \exp ((2 - \theta / (1 - \theta))^2 - 2 a \theta)$

where θ = the degree of surface coverage which varies between

$$0.1 < \theta < 0.9 .$$

K is the adsorption equilibrium constant, which equals $\Delta G/2.303 RT$, ΔG is free energy of adsorption, R is gas constant and T is Temperature.

C = the concentration of the adsorbate in the bulk phase in moles per liter

n = number of water molecules replaced by inhibitor molecule, $0 < n < 1$.

a = inhibitor interaction parameter (0, no interaction, +, attraction, -, repulsion)

1.5- Literature Survey on Corrosion Inhibition of Carbon Steel in Aqueous Solutions.

Amines are well known as corrosion inhibitors for iron and its alloys^(45,46). The relatively high water solubility of low molecular weight amines is an advantage for using it as corrosion inhibitors. Four n-alkylamines (6,8,10 and 12 carbon atoms) were investigated as corrosion inhibitors for dissolution of mild steel in 2M hydrochloric acid solution using gravimetric and polarization techniques⁽⁴⁷⁾. The influence of temperatures (278-308 K) and inhibitor concentrations (10^{-1} - 10^{-6} M) were studied. Protection efficiency improved when the inhibitor concentration and length of the alkyl chain were increased. The four amines tested were adsorbed on mild steel surface according to Frumkin isotherm.

The inhibition efficiency of n-decylamine on the corrosion of low carbon steel in 1N sulphuric acid at different temperatures has been investigated potentiokinetically⁽⁴⁸⁾. 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 have been calculated. It has been found that n-decylamine is adsorbed 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 molybdate ion acts as a corrosion inhibitor for mild steel at pH 6 and above. Below pH 6 molybdate accelerates corrosion⁽⁴⁹⁾. The result from the polymerization of molybdate to the hepta or octa molybdate species as the formation of soluble complex with iron ions. Nitrite can act as a corrosion inhibitor at pH 4.5 and above when a hydrous oxide layer can exist on the surface, but accelerates corrosion at pH 3. The acceleration of corrosion at the lower pH value is caused by the absence

of oxide on the surface, which led to the passage of the produced ferric ions directly into the solution.

Synergism is defined as the reinforcement of inhibitive action of a compound, usually employed at higher concentrations, by the addition of small amount of a second compound, even though the second compound is less effective when used alone, Gonzalez et al.⁽⁵⁰⁾ studied the inhibition of the corrosion of carbon steel (0.35% C) in 0.5 M NaCl by zinc salt/phosphonic acid association. Steady state current voltage curves and electrochemical impedance measurements carried out in the presence of each compound and for the mixture showed a synergistic effect between the two molecules. The concentrations of the compound in the mixture were lower than the concentration used for each compound separately. Phosphonic acid was observed to act as an anodic inhibitor whereas cathodic action was shown for the zinc chloride. Electrochemical measurements and surface analysis [X-ray photoelectron spectroscopy (XPS)] at grazing incidence showed that the synergistic effect afforded by mixture was attributable to the reaction of the phosphonic acid with the zinc salt. The inhibitor film acts as a protective layer impermeable to ionic or molecular diffusion. The film is very thin and homogenous in composition.

Electrochemical measurements (steady state current-voltage curves and AC impedance) were coupled with analytical techniques (reflection-adsorption spectroscopy at grazing incidence and XPS) to investigate the inhibition of corrosion of carbon steel by a mixture of a zinc salt and phosphonic acid ⁽⁵¹⁾. From the polarization curves and impedance measurements, it was shown that the electrochemical reactions at the metal interface were not controlled by mass transport. The inhibitor film acts as a protective layer impermeable to ionic or molecular diffusion. Corrosion proceeds only through small defects in the inhibitor film. XPS

analysis showed that the film is very thin and homogenous in composition. It is essentially composed of Zn, P and O. The formation of an iron oxide under the inhibitor layer was observed. The Fourier Transform Infrared (FTIR) spectroscopy of the film formed on steel indicates a reaction of the phosphonic acid with the zinc hydroxide and the iron oxide to produce metal salts.

Synergistic effect of Zn^{2+} and sodium salt of aminotrimethylene phosphonic acid (ATMP) in corrosion inhibition of carbon steel (0.2% C) in water containing low concentration (60 ppm) of Cl^- has been evaluated by weight loss method ⁽⁵²⁾. The results showed that 98% inhibition efficiency is achieved with the binary system consisting of 200 ppm ATMP and 50 ppm Zn^{2+} . Potentiostatic polarization studies showed that while ATMP alone acts as anodic inhibitor, ATMP- Zn^{2+} combination acts as mixed inhibitor. The mechanistic aspects of corrosion inhibition and the nature of the film formed on the metal surface have been analyzed with the help of UV-visible reflectance spectra, FTIR spectra, luminescence spectra and XRD patterns. The protective film appears to be consisting of Fe^{2+} -ATMP complex and $\text{Zn}(\text{OH})_2$ which is also found to be luminescent.

The corrosion behavior of mild steel in 1M H_2SO_4 solution containing some selected thiols viz. 2-mercaptobenzothiazol; 2-mercaptobenzimidazol and 2-mercaptobenzoxazol together with halide ions was studied by galvanostatic polarization technique, at different temperatures ranging from 30 to 60 °C ⁽⁵³⁾. The inhibition efficiency increases as the concentration of thiol is increased and the temperature is decreased. 2-mercaptobenzimidazol gave the highest inhibition efficiency compared to the other thiols. The structure of the investigated thiols is the responsible factor for this behavior. The polarization studies indicated that the investigated thiols are mixed type inhibitors, affecting

both anodic and cathodic processes by simple blocking of the active sites of the metal. The corrosion process is controlled by a charge transfer process. The addition of halide ions to the corrosive medium containing the investigated thiols increases the inhibition efficiency at all the examined concentration and temperatures. The presence of halide ions together with thiols caused a shift in the corrosion potential as well as the linear part of the cathodic Tafel line to the anodic direction. The corrosion process was found to be under activation control. Moreover, the inhibitors do not change the mechanism of the corrosion process.

The influence of phosphonic acid with Ca^{2+} cation on the mild steel surface in neutral aerated media ($0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$) was studied by electrochemical and surface analytical methods.⁽⁵⁴⁾ X-ray induced photoelectron (XPS) and Auger electron spectroscopy (AES) provided the possibility for identification of different chemical states of the constituents of corrosion protective layers. The presence of certain cations led to a synergistic effect. It was found that, calcium ions were incorporated into film that developed on mild steel surface containing a mixed oxide and hydroxide complex.

Anodic and cathodic polarization measurements for corrosion of carbon steel in aqueous solution containing various concentrations of boric acid and sodium borate was studied by potentiodynamic polarization⁽⁵⁵⁾. The values of open circuit potentials for corrosion of steel electrode at 303K become more negative with increasing pH in the anodic region. The presence of borate ions in the solution leads to the formation of Fe-borate complex during anodic polarization which is sparingly soluble at low pH value and causes passivity.

The effect of amino trimethylenephosphonic acid (ATMP), molybdate and Zn^{2+} ions on the inhibition of corrosion of mild steel in neutral aqueous environment containing 60 ppm Cl^- ions has been

evaluated by the weight loss method ⁽⁵⁶⁾. It was found that; the formulation consisting of 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} has 96 percent inhibition efficiency. The nature of the protective film has been analyzed by X-ray diffraction technique, FTIR and luminescence spectra. It seems that protective film consisting of $\text{Fe}_2(\text{MoO}_4)_3$, ZnMoO_4 , Fe^{2+} -ATMP complex and $\text{Zn}(\text{OH})_2$. This film is found to be luminescent.

The synergistic influence caused by iodide ions on the inhibition of corrosion of mild steel in 0.5 M H_2SO_4 in the presence of n-hexylamine (n-HA) was studied using potentiodynamic polarization, linear polarization and a.c. impedance techniques ⁽⁵⁷⁾. It was found that n-hexylamine accelerates the corrosion of mild steel at lower concentrations but inhibits the corrosion at higher concentrations. The addition of iodide ions enhances the inhibition efficiency to 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 ion indicates that iodide ions enhance the adsorption of n-HA on the metal surface. Synergism parameter (S) was defined and evaluated. The synergism parameter values were found to be more than unity indicating 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 then adsorbed by coulombic interaction on the metal surface, where iodide ions are already adsorbed and thus reduce the corrosion rate.

The inhibitive effect of some amino phosphonic acid derivatives towards the corrosion of carbon steel in HCl solution was studied by gravimetric and electrochemical methods ⁽⁵⁸⁾. The inhibitive effect depends on the structure of molecule, the number of N-atoms and the number of phosphonic groups. Probably the inhibition effect of

diethylenetriaminepentamethylene phosphonic acid depends mainly upon the protective inhibitor film formed on the surface of steel.

Abd El-Nabey et. al.,⁽⁵⁹⁾ studied the corrosion inhibition of carbon steel (0.34% C) in sulfuric acid by four selected S-alkylisothiuronium 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 inhibitory character of the additives depends upon the length of the hydrocarbon chain in the alkyl moiety of the S-alkylisothiuronium compound and on the type of the halide ions. Results from potentiodynamic polarization measurements indicated that all compounds studied were mixed type inhibitors affecting both the anodic and cathodic processes by simple blocking of active sites of the metal.

Arab and Noor⁽⁶⁰⁾ studied the effect of five selected S-alkylisothiuronium iodides as acid corrosion inhibitors at 30°C for dissolution of carbon steel in 0.5 M H₂SO₄ using gasometry, mass loss and direct current (DC) polarization techniques. All of the data revealed that the compounds act as inhibitors in the acid environments. Furthermore, polarization curve showed that the compounds act as mixed type inhibitors. It was found that the inhibition efficiency increases with the increase of the length of the additive alkyl chain. Langmuir's adsorption isotherms fit the experimental data for the studied compounds. Thermodynamic parameters were obtained from experimental data of temperature ranging from 30-70°C. It was observed that the activation energy is slightly increased with the increase of the additive alkyl chain. On the other hand the sudden large increase of the inhibition behaviour of S-hexylisothiuronium iodide was attributed to different adsorption process.

The influence of azathiones as corrosion inhibitors for the corrosion of carbon steel (0.14% C) in 1N H₂SO₄ and 1N HCl was investigated by weight loss and potentiostatic polarization techniques ⁽⁶¹⁾. Potentiostatic polarization data showed that these inhibitors are of mixed type. Azathiones can exist as cationic species like other amino compounds ⁽⁶⁷⁾. These cationic species adsorb 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 in 1N H₂SO₄. This explained on the basis of synergistic mechanism, according to which Cl⁻ ions and azathiones molecules can jointly adsorb on the steel surface giving higher efficiency.

The inhibition effect of dihydroxy pyridine on the corrosion of steel (0.15% C) in 1N sulfuric acid was studied at different temperatures by galvanostatic and X-ray photon spectroscopy (XPS) measurements ⁽⁶²⁾. Tafel slopes, corrosion potential and corrosion current have been calculated in the absence and in presence of inhibitors. XPS measurements indicated the presence of N peak at 400.2 eV for the additive. It was concluded that, the adsorption of additives takes place through the lone pair of electron on nitrogen atom as well as through the dn / pn interaction between the additives and the metal.

Gomma and Wahdan ⁽⁶³⁾ studied the inhibition of the dissolution of mild steel in 0.5 M sulfuric acid by adenine at different temperatures. Adsorption of adenine on metal surfaces was shown to follow the Langmuir adsorption isotherm over a wide concentration 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 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.

The effect of methyl red as inhibitor for corrosion of low carbon steel in 1M sulfuric and perchloric acid solutions was studied ⁽⁶⁴⁾. The inhibition efficiency increases with increase of concentration of the inhibitor and decreases with increase of temperature. Methyl red is physically adsorbed on the surface of steel and acts as a mixed inhibitor. Langmuir adsorption isotherm is followed by the inhibitor and adsorption is physically in nature. Activation energy values for inhibited system are higher than those of uninhibited system.

Moretti et. al., ⁽⁶⁵⁾ studied the ability of certain sulphones [methyl-phenyl-sulphone (MPS), phenyl-1,2- bismethylsulphone (P-1,2-MS), phenyl -1,4- bismethylsulphone (P- 1,4-MS), 1,4- methoxy methyl phenyl sulphone (1,4-MMPS)] to inhibit the corrosion of carbon steel in 1N sulfuric acid at temperatures of 25 and 50°C. Results from electrochemical and weight loss tests conducted on saturated solutions (because of the low solubility $< 10^{-5}$ M) revealed that these molecules are quite efficient inhibitors at 25°C. Decrease of inhibition efficiency at 50°C indicates that the adsorption mechanism is probably due to electrostatic forces. The presence of substituents increases the inhibition efficiency because the barrier effect due to the increase of the number of extension of the metal surface covered.

Makhlouf et. al., ⁽⁶⁶⁾ studied the effect of uracil compound on the electrochemical corrosion behavior of mild steel in 1M sulfuric and hydrochloric acid solutions as corrosive media , using weight loss measurements and potentiostatic polarization techniques. The anodic and

cathodic parameters (e.g. Tafel slopes, charge transfer coefficient, corrosion current and corrosion potential) were calculated. Values of activation energies and the cathodic protective current in the absence and in presence of different uracil concentrations revealed that this compound has an anticorrosive character. The $E_{\text{corr.}}$ of steel was affected by increasing uracil concentration. The slight shift in $E_{\text{corr.}}$ and the increase in the activation energies due to addition of the investigated compound, together with the shift of the potentiostatic anodic polarization curves to slightly higher potential regions denoted a mixed type inhibitors. The polarization studies indicated that inhibition occurs by simple blocking of both the adsorption process.

Schultze et. al.,⁽⁶⁷⁾ investigated the action of polyacrylic acid (PA) and polyacrylamide (PAA) on the corrosion of iron and steel in both H_2SO_4 and HCl solutions using both polarization and double layer capacity measurements. They found that, these two compounds show a fairly good protection efficiency (up to 80%). On the other hand, the polarization measurements indicated that PA and PAA are slightly increased while the capacity measurements showed a decrease of double layer capacitance in the presence of polymer indicating that adsorption of the polymer occurs at the metal surface.

Hanguo et. al.,⁽⁶⁸⁾ studied the effect of both polyvinylpyrrolidone and polyethylenimine 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 retard the anodic and cathodic corrosion reaction with emphasis on the former.

The effect of propargyl alcohol on the corrosion of carbon steel in a various concentrations of hydrochloric acid solutions at 313 and 333 K

was studied ⁽⁶⁹⁾. The rate of corrosion was measured electrochemically using a polarization technique. The results obtained showed that the rate of dissolution of carbon steel is considerably decreased by propagyl alcohol in aqueous hydrochloric acid solutions at 313K and 333K. Capacitance measurements indicated that the inhibitor species are adsorbed on the steel solution interface to a greater extent in the range of negative polarization. On the basis of impedance spectroscopy measurements the characteristics of the adsorption were separated from those of the electron transfer process.

Fouda et. al., ⁽⁷⁰⁾ studied the inhibitive effect of some substituted phenyl N-phenylcarbamates on the corrosion of iron in 2N HCl using galvanostatic polarization measurements. Studies were carried out with different concentrations of the inhibitor indicate that the compounds act as mixed type inhibitors. The results indicate that the additives reduce the corrosion rate by a way of adsorption through the oxygen atom of phenoxy group and nitrogen atom of NH group. The inhibitory character of the compounds depends upon the concentration of the inhibitor as well as its chemical composition. The results of electrocapillary measurements are consistent with the electrochemical measurements.

The effect of sodium N,N-diethyldithiocarbamate (SDEDTC) on the corrosion of C-steel in 0.5M hydrochloric acid solution was studied using weight loss, potentiodynamic polarization curves and impedance measurement methods ⁽⁷¹⁾. Experimental results revealed that SDEDTC acted as an inhibitor in acid environments. Moreover, the compound was a mixed type inhibitor, Inhibition efficiency increased with increasing SDEDTC concentration at different temperatures.

The beneficial effect of halide ions on the inhibition of corrosion of C-steel in 20 percent HCl solution in the presence of some nitrogen-bromide, and hexamine was investigated using potentiodynamic

polarization measurements ⁽⁷²⁾. Potentiodynamic polarization studies revealed that all the tested compounds were of anodic type inhibitors. All of the compounds were able to reduce the corrosion of C-steel and their performance was enhanced by the addition of iodide ions. The increase in surface coverage in the presence of the iodide ions indicated that iodide ions enhanced the absorption of inhibitor compounds on the metal surface. Auger electron spectroscopic analysis confirmed the joint absorption of the compounds with KI.

The effect of N-propylaminolaurylamide (I) and three of its ethoxylated derivatives (II, III and IV) as corrosion inhibitors of C-steel in 1M hydrochloric acid solution was studied by weight loss and galvanostatic polarization techniques ⁽⁷³⁾. A significant decrease in the corrosion rate of C-steel was observed in the presence of the investigated inhibitors. The study revealed that, the inhibition efficiency (IE) increases with increasing the inhibitor concentration. All these inhibitors seem to have obeyed the Langmuir's 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 of the inhibitor (γ) and the logarithm of their concentrations was investigated to obtain the adsorption ability of the inhibitors on the C-steel surface. Scanning electron microscopy was used to examine the surface morphology of the C-steel specimens after immersion in 1M HCl for 6 days in absence and presence of 500 ppm of the inhibitor IV. The mechanism of inhibition was discussed in the light of the chemical structure of the undertaken inhibitors.

A new corrosion inhibitor, namely, 3,5-bis (2-thienyl)-4-amino-1,2,4-triazoles (2-TAT) has been synthesized and its inhibiting action on the corrosion of mild steel in acid baths (1 M HCl and 0.5 M H₂SO₄) has been investigated by various corrosion monitoring techniques⁽⁷⁴⁾, such as weight loss tests and electrochemical impedance spectroscopy. The electrochemical study reveals that this compound is an anodic inhibitor. Changes in impedance parameters (R_t and C_{dl}) are indicative of the adsorption of 2-TAT on the metal surface, leading to the formation of a protective film which grows with increasing exposure time. 2-TAT is able to reduce the steel corrosion more effectively in 1 M HCl than in 0.5 M H₂SO₄. The adsorption of this inhibitor is also found to obey the Langmuir adsorption isotherm in both acids. 2-TAT is considered as a non-cytotoxic substance.

The effect of a new class of corrosion inhibitors, namely, arylazobenzoyl acetonitrile derivatives, on the corrosion of carbon steel in 2 M HCl and 1 M H₂SO₄ solutions has been studied by electrochemical polarization methods (potentiodynamic, Tafel extrapolation and the determination of polarization resistance)⁽⁷⁵⁾. Generally, inhibition efficiency of the investigated compounds was found to increase 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 H₂SO₄. The adsorption of the compounds on the carbon steel in both acidic media follows a Langmuir adsorption isotherm.

The inhibitory effects of progargyl alcohol and ethynylcyclohexanol on the corrosion behavior of carbon steel were studied in aerated and de-aerated solutions of 5% hydrochloric acid at 30°C by the planned-interval test and electrochemical polarization methods⁽⁷⁶⁾. The time dependence of the corrosion data was practically the same for the

investigated inhibitors, but ethynylcyclohexanol displayed some specific features. The established relations and the FTIR results for ethynylcyclohexanol confirm the film formation mechanism involving chemical change of the inhibitor. It is suggested that species with carbonyl groups in conjunction with C=C bonds take part in an oligomerization reaction.

The electrochemical behavior of 1-(2-ethylamino)-2-methylimidazoline (imidazoline), its precursor N-[3-(2-amino-ethylamino-ethyl)]-acetamide (amide) and its derivative 1-(2-ethylamino)-2-methylimidazolidine (imidazolidine), is evaluated by using potentiodynamic polarization curves and electrochemical impedance spectroscopy, EIS, techniques in deaerated acid media to compare their corrosion inhibition efficiency⁽⁷⁷⁾. 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 imidazoline is the more efficient corrosion inhibitor because of its two very active sites (two nitrogen atoms) and the plane geometry of the heterocyclic ring, thus promoting coordination with the metal surface.

1,12-bis(1,2,4-triazolyl)dodecane (dTC12) is an excellent corrosion inhibitor for carbon steel in deaerated 1 M HCl solution. Electrochemical and analytical techniques were used to study the inhibition of corrosion of carbon steel in acidic medium⁽⁷⁸⁾. 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 inhibited by dTC1₂.

The effect of some pyridine derivatives on the corrosion of carbon steel in 2 M HCl solutions has been studied⁽⁷⁹⁾ by electrochemical polarization method (potentiodynamic, Tafel extrapolation) as well as weight loss method. 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 reveal 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 influence of some new bipyrazole derivatives synthesized in the laboratory on the corrosion inhibition of mild steel in 1 M HCl solution was studied using weight loss and electrochemical polarization techniques⁽⁸⁰⁾. The inhibition efficiency of all compounds tested increases with increase of concentration. The polarization measurements indicate that the inhibition efficiency of bipyrazolic compounds depends upon electrode potential without changing the mechanism of the cathodic hydrogen evolution reaction. It is found that ethyl 4-[bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl] amino benzoate (bipyrazol-4) is the best inhibitor. The effect of temperature indicates that the inhibition efficiency of bipyrazol-4 decreases with increasing temperature in the range 308–353 K.

Bereket et al⁽⁸¹⁾ carried out potentiodynamic polarization studies on the inhibition of low C-steel in 0.1M hydrochloric acid solution over the temperature range 293-363K at different inhibitor concentrations by various quaternary ammonium salts and cationic surfactants. The

inhibitors examined were tetraethyl ammonium chloride, tetrabutyl ammonium chloride, benzyltrimethyl ammonium chloride, benzyltriethylammonium chloride, benzyltributyl ammonium chloride, phenyltrimethyl ammonium chloride, alkylbenzyltrimethyl ammonium chloride, tetradecyltrimethyl ammonium bromide and cetyltrimethyl ammonium bromide. Maximum inhibition efficiencies of cationic surfactants were observed around and above critical micelle concentration (cmc), while the inhibition efficiencies of the quaternary ammonium salts were found to increase with the increase in their concentrations. The degree of shift in E_{corr} value, together with change in anodic and cathodic Tafel slopes (β_a and β_c), revealed that cationic surfactants behave as an anodic inhibitor, while quaternary ammonium salts behave as mixed type inhibitors. Inhibition efficiencies of studied inhibitors seem to be closely related with the chain length of the alkyl group as well as the presence of benzene ring in quaternary ammonium compounds. Thermodynamic and kinetic parameters for dissolution and adsorption were also calculated.

Soror et al ⁽⁸²⁾ studied the influence of cetyltrimethyl ammonium bromide (CTAB) on the corrosion of C-steel in HCl and H₂SO₄ solutions using several techniques such as weight loss, Tafel polarization, linear polarization and open circuit potential. Inhibition efficiencies have been obtained from weight loss measurement, the effect of temperature on corrosion inhibition and the effectiveness of the inhibitor at higher acid strength have been examined. Polarization studies revealed that the inhibitor behaves as an effective inhibitor in H₂SO₄ as well as in HCl solutions. Measurements of values of polarization resistance (R_p) have also been carried out. The open circuit potential curves was shifted to less negative potential contrary to the blank.

Potentiodynamic polarization and ac impedance studies were carried out on the inhibition of carbon steel in 0.1 M hydrochloric acid

solution by various Schiff bases containing heteroaromatic substituents⁽⁸³⁾. The examined Schiff bases were 2-((1E)-2-aza-2-pyrimidine-2-ylvinyl)thiophene, 2-((1Z)-1-aza-2-(2-pyridyl)vinyl)pyrimidine, 2-((1E)-2-aza-2-(1,3-thiazol-2-yl)vinyl)thiophene, 2-((1Z)-1-aza-2-(2-thienyl)vinyl)benzothiazole. Polarization curves indicate that studied Schiff bases act essentially as anodic inhibitor. The variation in inhibitive efficiency mainly depends on the type and nature of the substituents present in the inhibitor molecule. Potentiodynamic polarization and ac impedance measurements carried out at different concentration of studied Schiff bases reveal that these compounds are adsorbed on steel surface and the adsorption obeys Temkin's adsorption isotherm. From the adsorption isotherms values of equilibrium constant, K_{ads} , values of free energies of adsorption, ΔG_{ads} , were calculated. Activation parameters of the corrosion process such as activation energies, E_a , activation enthalpies, ΔH^* , and activation entropies, ΔS^* , were calculated from the obtained corrosion rates at different temperatures.

The inhibitor effect of N,N'-bis(salicylidene)-2-hydroxy-1,3-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 impedance methods (EIS) that the corrosion rates decrease and 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 between the two compounds studied⁽⁸⁴⁾.

The effect of succinic acid (SA) on the corrosion inhibition of a low carbon steel (LCS) electrode has been investigated in aerated non-stirred 1.0M HCl solutions in the pH range (2–8) at 25°C. Weight loss,

potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques were applied to study the metal corrosion behaviour in the absence and presence of different concentrations of SA under the influence of various experimental conditions. Measurements of open circuit potential (OCP) as a function of time till steady-state potentials (E_{st}) were also established. Surface analysis using energy dispersive X-ray (EDX) and scanning electron microscope (SEM) allowed us to clarify the mechanistic aspects and evaluate the relative inhibition efficiency. Results obtained showed that SA is a good “green” inhibitor for LCS in HCl solutions. The polarization curves showed that SA behaves mainly as an anodic-type inhibitor. EDX and SEM observations of the electrode surface confirmed existence of a protective adsorbed film of the inhibitor on the electrode surface. The inhibition efficiency increases with increase in SA concentration, pH of solution and time of immersion. Maximum inhibition efficiency (97.5%) is obtained at SA concentrations $>0.01\text{M}$ at pH 8. The effect of SA concentration and pH on the potential of zero charge (PZC) of the LCS electrode in 1.0M HCl solutions has been studied and the mechanism of adsorption is discussed. Results obtained from weight loss, polarization and impedance measurements are in good agreements ⁽⁸⁵⁾.

The corrosion inhibition characteristics of non-ionic surfactants of the TRITON-X series, known as TRITON-X-100 and TRITON-X-405 toward the corrosion of ferrite stainless steel(SS) in sulphuric acid was investigated by potentiodynamic polarization measurements. It was found that these surfactants act as good inhibitors of the corrosion of stainless steel in $2\text{ mol L}^{-1}\text{ H}_2\text{SO}_4$ solution, but the inhibition efficiency strongly depends on the electrode potential. The polarization data showed that the non-ionic surfactants used in this study acted as mixed type inhibitors and adsorb on the stainless steel surface, in agreement with the Flory-Huggins

adsorption isotherm. The calculated values of free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) are $-57.79 \text{ kJ mol}^{-1}$ for TRITONX-100, and $-87.5 \text{ kJ mol}^{-1}$ for TRITON-X-405. From the molecular structure it can be supposed that these surfactants adsorb on the metal surface through two lone pairs of electrons on the oxygen atoms of the hydrophilic head group, suggesting a chemisorption mechanism⁽⁸⁶⁾.

The electrochemical behavior and corrosion of carbon steel in various types of naphthenic acid solutions was studied using cyclic voltammetry technique. The data reveal that the anodic excursion spans of carbon steel in naphthenic acid solution are characterized by the occurrence of a well-defined anodic peak (peak A), followed by a passive region. The passivation may be related to the formation and precipitation of oxide film on the electrode surface. The data reveal that increasing naphthenic acid concentration enhances the anodic peak current density and shifts its peak potential towards more positive values. The corrosion rate of carbon steel depended critically on the naphthenic acid types. The rate of the corrosion process increased with increasing in molar mass of naphthenic acid, reaching a maximum value in the presence of CHPA acid (C9), and then decreased. Potentiodynamic polarization measurements indicated that ethoxylated fatty acid derivatives have a strong effect on the corrosion behavior of the carbon steel in naphthenic acid solutions. The inhibition efficiency of these compounds was found to vary with their nature and concentration. The order of effectiveness of the inhibitors was $\text{OL(EO)80} > \text{OL(EO)40} > \text{OL(EO)20}$. The adsorption of ethoxylated fatty acid on the carbon steel surface in naphthenic acid solutions was found to obey Frumkin isotherm and kinetic-thermodynamic model.⁽⁸⁷⁾

Poly(3-octyl thiophene) (P3OT) and poly(3-hexylthiophene) (P3HT) dissolved in toluene were deposited onto 1018 carbon steel and corroded in 0.5M H_2SO_4 . P3OT and P3HT films were chemically deposited by drop casting onto 1018-type carbon steel with two surface finishing, i.e. abraded with 600-emery paper and with alumina (Al_2O_3) particles of 1.0 μm in diameter (mirror finish)⁽⁸⁸⁾. Their corrosion resistance was estimated by using potentiodynamic polarization curves, linear polarization resistance (LPR), and electrochemical impedance spectroscopy, (EIS), techniques. In all cases, polymeric films protected the substrate against corrosion, but the protection was improved if the surface was polished with Al_2O_3 particles of 1.0 μm in diameter. The polymer which gave the best protection was P3HT because the amount of defects was much lower than that for the P3OT films. The polymers did not act only as a barrier layer against aggressive environment, but they improved the passive film properties by decreasing the critical current necessary to passivate the substrate, increasing the pitting potential and broadening the passive interval.

Quaternized polyethyleneimine (QPEI) was prepared via two procedures of macromolecular reactions, tertiary amination reaction and quaterisation, and its chemical structure was characterized with infrared and UV spectra. In this paper, the corrosion inhibition property of QPEI for low carbon steel (A_3 steel) in H_2SO_4 solution was mainly investigated by using weight loss method, electrochemical technique (potentiodynamic polarization curves) and scanning electron microscopy (SEM) investigation. Meanwhile, the corrosion inhibition mechanism of QPEI was also fully explored. The experiment results show that as a polymeric quaternary ammonium salt, QPEI is quite an excellent corrosive inhibitor, it possesses outstanding inhibition action for low carbon steel, and only with 5mg L^{-1} of QPEI concentration, the inhibition efficiency of A_3 steel

can reach to 92% in 0.5M H₂SO₄ solution for 72 h of immersing time. The inhibition efficiency increases with the increase of QPEI concentration, and the inhibition efficiency also increases with the enhancement of the cationic degree (quaternized degree) of QPEI. QPEI acted as a mixed type inhibitor with anodic predominance. QPEI possesses functions of double filming, adsorption filming and polymer filming, so with the cooperation of the two filming effects, QPEI can form a compact barrier film on A₃ steel surface, and prevent metal dissolution and retard H⁺ discharging. The adsorption of QPEI on the steel surface was found to follow the Langmuir isotherm equation⁽⁸⁹⁾.

New compounds of alkylamides derived from α -amino acids were tested as corrosion inhibitors for carbon steel in an aqueous solution of hydrochloric acid. The chemical synthesis of these amides performed by aminolysis of α -amino acid methyl esters resulted in good yields. Electrochemical testing was carried out using polarization scans and weight loss measurements. Polarization scans indicated that compounds act as mixed corrosion inhibitors with an efficiency of 80–90% when dissolved in the testing solution at .50 ppm, whereas gravimetric results displayed a similar tendency. Microtox testing indicated a correlation with the molecular structure of inhibitors. Apparently, a long aliphatic chain (C > 12) promoted not only higher corrosion efficiency, but also a higher toxicity. The higher efficiency of dodecyl amine of tyrosine was apparently derived from its longer aliphatic chain, with some contribution from its phenyl ring, which reinforces the molecular interactions of π type bonding to the d orbital metal favouring film formation⁽⁹⁰⁾.

AIM AND SCOPE OF THE PRESENT WORK

THE PRESENT WORK WAS DESIGNED TO:

1-Study the corrosion and corrosion inhibition of C-steel in sulfuric acid solutions.

2-Investigate the inhibiting effect of some N-3-Hydroxyle -2-Naphthoyl Hydrazone derivatives for the corrosion of C-steel and determining the corrosion rate in absence and presence of these compounds by the chemical technique (weight loss method) and the electrochemical technique (galvanostatic polarization method) at 303K.

3-Investigate the effect of addition of potassium iodide, bromide, and thiocyanate on the corrosion inhibition of the N-3-Hydroxyle -2-Naphthoyl Hydrazone derivatives used.

4-Study the effect of temperature on the corrosion rate by one of these two methods to:

a. Calculate the thermodynamic parameters related to the corrosion process, and

b.Determine the type of adsorption isotherm and the type of adsorption (physical or chemical).

5-Determine the mechanism and percentage inhibition of these N-3-Hydroxyle -2- Naphthoyl Hydrazone derivatives.

6-Finally, ordered these N-3-Hydroxyle -2- Naphthoyl Hydrazone derivatives according to their percentage inhibition.