Chapter I

Introduction

I- INTRODUCTION

Corrosion of metals is a major industrial problem that has attracted a lot of investigators in recent years. One of today's most important considerations in industry is the reduction of overall costs by protection and maintenance of materials used because steel is the backbone of industrial constructions. Nowadays the study of carbon steel corrosion phenomena has become an important industrial and academic topic. The carbon steel is widely used as constructional material in many industries due to its excellent mechanical properties and low cost. The highly corrosive nature of aqueous mineral acids on most metals requires degree of restraint to achieve economic maintenance and operation of equipment, minimum loss of product and maximum safety condition. The carbon steel pipelines have been widely used for transportation in the oil and gas industrials. Metals and alloys are exposed to corrosive fluids during service which are constantly in contact with the nascent hydrogen produced by the corrosion reaction and could be damaged by it [1-100].

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 destructive attack of metals and alloys by chemical or electrochemical reaction with their environment [101,102].The products of this process may be solid, liquid or gaseous. Both physical and chemical nature of the products is important, since they frequently influence the subsequent rate of reaction [103]. The reaction of metals represents a terrible waste of both natural resources and money.

1.1- Cost of Corrosion

In recently, corrosion by chemical and electrochemical reactions has assumed great economic importance throughout the world [104-107]. The estimated annual loss due to corrosion is

enormously large. Studies worldwide have shown that the overall cost of corrosion amounts to at least 2-3% of the Gross National Product and that 20-25% of the cost could be avoided by using appropriate corrosion control technology [108]. In USA the cost of corrosion per year has been estimated to be over 126 (billion) dollars in 1982. The problem of preventing of metallic corrosion is extremely complex but it is of great technological and economical importance. Corrosion of metals can be controlled by taking suitable preventive measures such as painting, plating, use of expensive alloys, use of inhibitors etc. Corrosion of engineering components many times leads to the loss of production and sometimes it may be hazardous [109].

1.2-Classification of Corrosion

Corrosion can be classified in many ways as low and high temperature corrosion, direct oxidation and electrochemical corrosion, etc., the preferred classification [101,110] is:
(i) Dry or chemical corrosion.
(ii) Wet or electrochemical corrosion.

Dry corrosion occurs in the absence of a liquid phase or above the dew point of the environment. Vapors and gases are usually coordinates; it is often associated with high temperature, for example the attack of steel by furnace gases

Wet corrosion occurs when a liquid is present. This usually involves aqueous solution or electrolytes and accounts for the greatest amount of corrosion by far. A common example is corrosion of steel by aqueous media.

The nature and extent of corrosion depend on the metal and the environment. The important factors, which may influence the corrosion process, are:
(i) Nature of the metal   (ii) Nature of the environment.
(iii) Electrode potential.   (iv) Temperature.

(v) Solution concentration   (vi) Aeration

(vii) pH of the solution.   (viii) Agitation

(x) Nature of the corrosion products.

1.3- Various forms of corrosion

Corrosion can manifest itself in the following main forms:

1.3.1- General corrosion or uniform attack [85,111-112]

This is the most common type in which the corrosion is uniform over the entire exposed surface [101]. The example of this type of corrosion is water tank exposed to the environmental conditions.

1.3.2- Pitting or localized attack

It is one of the most destructive and insidious forms of corrosion [1,113-116]. It is a highly localized corrosion; the attack is being limited to extremely small areas. The corrosion of stainless steels and its alloy in chloride solutions is an example of this type of corrosion.

1.3.3- Galvanic corrosion

It is an accelerated electrochemical action due to two different metals being in electrical contact and exposed to an electrolyte. Heat exchanger failure in which aluminum tubes are supported by a perforated steel sheet is an example of this type of corrosion [117-118].

1.3.4- Crevice corrosion

This type of corrosion takes place when only one metal is in contact with different concentrations of the environment. Rectangular metal containers and reverted lap joints offer the possibility for this type of corrosion [119-120].

1.3.5- Stress corrosion

It is the spontaneous cracking resulting from the combined effect of prolonged stress and corrosive attack. Caustic embitterment of boilers provides an example for this type of corrosion [121-122].

1.3.6- Erosion – corrosion

It is the acceleration in the rate of attack of a metal because of the relative movement between a corrosive fluid and the metal surface. Heat exchanger tubes with water movement undergo this type of corrosion [123].

1.3.7- Fretting corrosion

It is a case of deterioration resulting form repetitive rumbling at the interface between two surfaces in a corrosive environment. It is found in aircraft engine parts [124].

1.3.8- Filiform corrosion

This is a special type of crevice corrosion which results in irregularly developed fair-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 [125].

1.4- 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.' Outhers [14,104] 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 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 :

$$M \rightarrow M^{++} + 2e^- \qquad (1.1)$$

This represents oxidation of the metal.

The cathodic reaction is:

$$2H^+ + 2e^- \rightarrow H_2\uparrow \qquad (1.2)$$

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

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (1.3)$$

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

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \qquad (1.4)$$

1.5- Corrosion Problems in Oil Field

Corrosion problems requiring the application of inhibitors exist in the oil industry at every stage of production processing, refining and storage prior to use. The main reason of corrosion problems is attributed to the presence of formation water, which accompanies the oil production [98,126,186]. It has been shown

that corrosion is related to water content which contains a various corrosive agents including carbon dioxide, hydrogen sulfide, organic acids and salts such as chlorides and sulphates[19-20,57].

The ionic composition which coming from dissolved salts and gases has a considerable influence on performance of inhibitors. In near- neutral aqueous system, the presence of certain ions tends to oppose the action of inhibitors. Chlorides are the most common examples of these aggressive ions and thus the concentration of the inhibitor required for protection will depend on the concentration of these aggressive ions [60,100,127].

1-6- Corrosion Inhibitors

Corrosion inhibitor is one of the most practical methods for protecting the corrosion of metal. The protection of metals against corrosion can be achieved either with inhibitors or with passivating agents [1-127]. An inhibitor is any compound that suppresses corrosion, regardless of which electrochemical reaction affects passivators; on the other hand, they are defined as compounds that reduce the corrosion rate via a preferential retardation of the anodic reaction [2-13, 19,100,128-130]. In accordance with these definitions, an inhibitor may not be passivators, but every passivator is an inhibitor [131].

Inhibitors can be used to great advantage for the protection of metals in many environments [132-143]. However, it is important to note that inhibitors are generally specific to a given metal and often specific to that metal in a particular environment and under particular service conditions, this specificity derives from the inhibitors mode of action. Inhibitors most useful in closed systems where the corrosive environment is either retained for long periods or recycled.

1.6.1- Classifications of inhibitors

Inhibitors are classified as acid, neutral, alkaline and vapour phase inhibitors depending upon the environment and the mechanism of inhibition, they are classified as cathodic, anodic and mixed type of inhibitors. Acid inhibitors can be further classified as inorganic and organic inhibitors [144]. Corrosion of steel in acidic solutions has practical importance [21, 47, and 78]. For example, corrosion is of significant concern in the acid pickling of iron and steel, chemical cleaning of scale in metallurgy and other industries, and acidising in oil recovery and other petrochemical process [3, 60,100,127].

Usually corrosion of metals and alloys in acidic, neutral and alkaline solutions can be inhibited by a large number of organic substances. In general, nitrogen[145-172], oxygen [150,151,153,158,160,165,172-179], and sulphur[177,180-181] containing compounds with a hydrocarbon part attached to the polar group are used as inhibitors[182-191]. Triple bonded hydrocarbons, acetylenic alcohols, thioureas, sulfoxides, sulphides and mercaptans, aliphatic, aromatic or heterocyclic compounds and condensation products formed by the reaction between two different species such as aldehydes, amines and schiff bases are commonly used[192-196].

Schmitt [197] has reviewed the application of inhibitors in acid media. The performance of inhibitors depends on various factors such as size, solubility, chemical structure, substituent effect, steric effect, carbon chain length, Hammett constant[112,198], molecular weight, basicity (pk), dipole moment, magnetic susceptibility, NMR shift, temperature, acid concentration, velocity of liquid flow, nature of metal and pH of the solution. Synergistic behaviors were also reported [17] in

the case of inhibitors mixture. The study of various organic compounds in relation to their different aspects of inhibition in different environments has been reviewed by Sanyal[83].Some organic compounds as azoles[13,78,79,82], amines[3,6,59,65], thiourea[61,199] etc. ,are adsorbed or chemisorbed on the surface of the metal and form a protective layer.

1.6.2- Applications of inhibitors

The addition of inhibitors to minimize the corrosion rate is the other mainly used method, where the protection of the metal is achieved either by changing the characteristics of the electrolyte or by forming a protective passive film on the substance surface. This can be done by adding certain anions like chromate, nitrate and phosphate to form a protective oxide film and by retarding the cathodic current density or by increasing the flade potential to more negative values and subsequently promoting the anodic process[55,63].

1.6.3- Mechanism of inhibition

The following mechanisms are suggested to explain the phenomenon of corrosion inhibition.

1.6.3.1- Formation of a physical barrier and reduction in metal reactivity

The inhibitive action observed on the addition of organic compounds is due to the surface coverage (θ) by the compound owing to the adsorption or chemisorption. The inhibitor may be selectively adsorbed onto the cathodic or anodic sites on the surface of the metal. This results in the decrease of cathodic or anodic reaction rate and thus corrosion is retarded. The adsorption on cathodic sites increases cathodic polarization[64] and on anodic sites increases anodic polarization[35, 39, and 42].

1.6.3.2- Change in the electrical double layer structure

According to the mechanism, adsorbed organic molecules physically block the sites on the metal surface resulting in the change of double layer structure at the metal/solution interface [200-212]. Though the action of inhibitors has been explained on the basis of various considerations, it is now generally accepted that organic compounds inhibit corrosion by adsorbing at the metal solution interface [213-217].

1.7- Theories of Corrosion Inhibition

1.7.1- Adsorption theory

Organic inhibitors which presumably are not capable of oxidizing or precipitating the metal ion, must have the ability to adsorb and impede either cathodic or anodic or both the reactions [19, 49, 59,100, 128,130,246-252].

Organic inhibitors are inhibiting corrosion by adsorption at metal/solution interface. Most of the heterocyclic compounds containing nitrogen were believed to be cathodic inhibitors. But it has been shown by Hoar[102] that in some cases anodic inhibition is observed.

The mode of adsorption depends on the nature of the metal surface, the chemical structure of the molecule and the electrochemical potential at the metal/solution interface. The different types of adsorption associated with organic inhibitors are the electrostatic adsorption or electrosorption, chemisorption and π-orbital adsorption and physical or Van der Waals type of adsorption.

1.7.2- Electrosorption

In electrosorption the coulombic electrical forces which stretch out from the metal are much longer in range than the chemical forces which affect the molecules in chemisorptions.

1.7.3- π-Orbital adsorption

In this type, the adsorption may result from π-orbital interaction with the metal. Organic compounds with double and triple bonds, and those containing aromatic nucleus interact with metal by their π-bond orbital.

1.7.4- Van der Waals adsorption

The adsorbed molecules are held by weak Van der Waals forces and physically adsorbed molecules on solids forming multilayer, as the forces operating are weak Van der Waals type, the adsorbed molecules may easily be removed or desorbed from the surface by lowering the bulk concentration of the adsorbate.

1.7.5- Film theory

In order to explain the inhibitive action of inhibitors in neutral and alkaline media, Evans [84] attributed the inhibition to the formation of an insoluble film. In acid solutions according to Hausler[85] and Putilova et al.[219] appreciably effective protection of metals by inhibitors is due to the formation of a layer of insoluble or slightly soluble corrosion products on the metal surface. The formation of insoluble or slightly soluble complex compounds or metal sulphide with compounds like thio-ethers, thio-alcohols and the formation of a protective film on the metal surface have been quoted as examples in support of the film theory.

1.8- 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 (the amount adsorbed) and the concentration of the species in solution. Various adsorption isotherms have been formulated. A list of various isotherms and the corresponding equations are given in the Table (1) [86]. A common procedure is to convert isotherm to a linear form and plot the experimental data accordingly. The data can be fitted to any one of the adsorption isotherms from the suitable plot and the free energy of adsorption of the organic inhibitors can be obtained.

Most of the organic inhibitors obey Langmuir's or Temkin's adsorption isotherms. An inhibitor is found to obey Langmuir's isotherm if a plot of log $\theta/1-\theta$ vs log C is linear. Similarly for Temkin's plot of θ vs log C, for Bockris Devanathan and Muller (BDM) a plot of (log C – log $\theta/1-\theta$) vs $\theta^{3/2}$ and for the Frumkin's a plot of log $\theta/(1-\theta)C$ Vs θ will be linear.

Table 1: Adsorption Isotherms

No	Isotherm	Equations
1	Langmuir	$\beta C = \dfrac{\theta}{(1-\theta)}$
2	Freundlisch	$\beta C = \theta (\theta < n < 1)$
3	Frumkin	$\beta C = \dfrac{\theta}{(1-\theta)} \exp(-2a\theta)$
4	Temkin	$\beta C = \dfrac{\exp(a\theta) - 1}{1 - \exp[-a(1-\theta)]}$
5	Parsons	$\beta C = \dfrac{\theta}{(1-\theta)} \exp \dfrac{2-\theta}{(1-\theta)^2} \exp[-2a\theta]$
6	Bockris, Devanathan and Muller (BDM)	$\log C \pm \log \dfrac{\theta}{(1-\theta)} = C + \beta \theta^{3/2}$

Note: $\beta = e^{-\Delta G_{ads}/RT}$
a = interaction Parameter
a > o = attraction
a < o = repulsion

1.9- Techniques for Studying Corrosion

1.9.1- Chemical methods

1.9.1.1- Gravimetric analysis (weight loss method)

The gravimetric analysis is old test for evaluating the corrosion rate by measuring the change in the weight of coupon after exposing the metal specimen of known area to the particular environment for a specific period. This method yields the average rate and is inherently inaccurate for measuring very low corrosion rates. Methods of surface preparation and cleaning of corroded specimens are described by Champion [25]. This method is very. important to apply in petroleum, petrochemical and different industrials [19-20,100].

1.9.1.2- Solution analysis

In this method [220] chemical or physical techniques are used to identify and estimate the concentration of metal ions or metals under examination dissolving in the test environment.

1.9.1.3- Gas-volumetric method

In this method [27] a definite correlation between the cathodic reaction rate and the anodic dissolution rate can be established.

1.9.2- Electrochemical Methods

1.9.2.1- Electrical resistance method

The electrical resistances methods are depend on the area of working electrode [221]. A decrease in the cross section due to corrosion increases the electrical resistance. The resistance of the exposed element is measured by Kelvin's bridge along with another element which is protected against corrosion. Instruments have been developed to measure these resistance

ratios which are calibrated in mils per year (mpy). The major advantage of this method is its ability to measure corrosion rates in the liquid and vapour phases and in aqueous and non-aqueous media. This method is used for continuous corrosion monitoring in petroleum, petrochemical and chemical process industries.

1.9.2.2- Tafel extrapolation method

This method [89] is also described as Tafel plot method or Evan's diagram method or logarithmic polarization method [222-227]. Actually the measurement of corrosion rate of the system involves the measurement of potential of the electrode for various applied current densities. A plot of potential (E) vs. log current densities (I) gives a figure known as polarization diagram. The intercept of anodic and cathodic Tafel lines provides the corrosion current and Tafel slopes give β_a, and β_c. In actual practice, polarization curves are obtained from galvanostatic/potentiostatic or potentiodynamic methods [228-232].

1.9.2.3- Polarization resistance method

Stern and Geary [16] have shown that there is a linear relationship between current and potential when $\eta < 20$ mV and on measuring $(d\eta/di)$ $\eta \to o$ the corrosion current can be obtained from,

$$\frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)}$$

$$i_{corr} = \frac{b_a x b_c}{2.3(b_a + b_c)} x \left(\frac{di}{d\eta} \right) \qquad (1.5)$$

The above relationship is valid only for activation controlled reactions. The simultaneous determination of Tafel slopes and corrosion current at the corrosion potential have been suggested

by many authors. Barnartt[87], Reeve and Bech- Nielsen[232], Oldham and Mansfeld[11] , Periasamy and Krishnaswamy[233] have made some improvements in this method. Mansfeld[36,65] has developed a computer programme (CORFIT) for the quantitative determination of i_{corr} which requires simultaneous determination of both R_p and β. Various applications and the developments of this technique have been reviewed by Lorenz and Mansfeld[90].

1.9.2.4- Coulostatic method

This method [92,234] is suited especially for the measurement of corrosion rates of metals in high resistant media. The polarization resistance (R_p) is measured from the η-t transient of the electrode on discharging a charged capacitor (C) through the cell. The electrode potential decay is

$$\eta_t = \eta_0 \exp (-t/C_{dl} R_P) \qquad (1.6)$$

η_t = overpotential at any time "t",

η_0= overpotential immediately after charging the double layer of the electrode

C_{dl} = differential capacity of the double layer.

The plot of log η_t vs t is a straight line and the slope gives $1/2.3$ C_{dl}/R_p and the intercept is η_0.

1.9.2.5-Alternative current (A.C.) Impedance measurements

Electrochemical impedance measurements is an appropriate method for corrosion studies, particularly for corrosion rate determinations[91-95,235-245], mechanistic studies[69,188], passivation and passivity process[246-247] and for investigation in inhibited systems[16,68,72,89,248-249]. The theoretical analysis of (A.C) impedance measurements has been analyzed by Warburg[247], to explain the frequency dispersion of the electrode-electrolyte interface and impedance in terms of

mass transport (diffusion controlled) process. Haruyama and Tsuru[88] and Mansfeld et al.[91] have reviewed impedance methods. A review of the application of these techniques in corrosion studies has been published by MacDonald et al.[67-68, 95]. The use of (A.C) impedance technique in various cases has been reviewed by Gabrielli[250]. Solution resistance is represented by R_S, charge transfer resistance is given by R_{Ct} or R_t and the double layer capacitance is represented by C_{dl}., Using Stern-Geary equation, i_{corr} is obtained from R_t since.

$$i_{corr} = \frac{\beta_a . \beta_c}{2.3 (\beta_a + \beta_c)} . \frac{1}{R_t} \qquad (1.7)$$

Thus, the cell impedance Z consists of real (Z`) and imaginary (-Z") parts. A plot of Z' vs – Z" for various frequencies is a semicircle. At high frequency, Z corresponds to R_s and at low frequency Z corresponds to $(R_s + R_t)$ and the difference between the two values gives R_t. The double layer capacitance (C_{dl}) can be calculated from the frequency ω at the top of the semicircle (Z" maximum).

$$f(Z"_{max}) = \frac{1}{2\pi C_{dl} R_t} \qquad (1.8)$$

The main disadvantage of this method is that only R_t can be determined directly while the Tafel parameters have to be obtained by other methods.

Literature survey

I.10.Corrosion Inhibition of Metal and its Alloy by Different Organic Compounds in Different Media

1- Carbonyl compounds

The carbonyl compounds were used as corrosion inhibitors for mild steel in HCl solution [128]. Galvanostatic polarization data indicated that selected carbonyl compounds act predominantly as cathodic inhibitors. In a subsequent work, the same authors examined schiff bases as corrosion inhibitors for mild steel in different concentrations of HCl solution [129]. The obtained results showed that, these compounds also behave as cathodic inhibitors.

The effect of 1, 10 phenanthroline has been examined as a corrosion inhibitor for mild steel in 1N solution of both HCl and H_2SO_4 [130]. The weight loss and galvanostatic methods were applied. Activation energy (Ea*) in absence and presence of inhibitor has been evaluated. Galvanostatic polarization data indicated that the compound was predominately cathodic inhibitor.

The inhibitor effect of benzoic acid and salicylic acid in sulfuric acid medium on the steel with known composition was investigated [77]. It was found that in all cases the corrosion rates decreased and the percentage inhibition efficiencies and surface coverage degrees increased with increasing acid concentration. However, benzoic acid acts as a better inhibitor compared to salicylic acid with the same concentration. It was determined that the adsorption for both organic acids on the steel complies with the Langmuir isotherm.

2-Hetero Compounds

Heterocyclic compounds are widely used in diverse industries for preventing corrosion of different metallic materials, for example carbon steel, in rather a wide variety of environments. An assortment of organic compounds having two or more heteroatoms such as O, N, S and multiple bonds in their molecular structure, are of particular interest because of their better inhibition efficiency as compared to those containing N or S alone[251, 258]

The effect of the concentration of four types of inhibiting heterocyclic molecules on the corrosion susceptibility of steel pipeline samples grade API 5L X52 in 1 M H_2SO_4 was studied by electrochemical testing and SEM analysis[254]. The compounds used were: 2-mercaptobenzo – imidazole (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. Furthermore, the MBI displayed the best inhibiting characteristics for this system, with a maximum IE of approximately 99%. It is also found that this compound can affect both the anodic and cathodic processes, thus it can be classified as a mixed-type inhibitor for API 5L X52 steel corrosion in sulphuric acid. Moreover, this compound follows an adsorption mechanism, which can be adequately described by the Langmuir isotherm.

The inhibiting properties of a number of N-heterocyclic amines in 0.1 M/L $HClO_4$ were studied [260]. The test series included piperidine (pip), 2-methylpiperidine (2mp), 3-methylpiperidine (3mp), cis-2, 6-Dimethyl piperidine (26dp), 3, 5-dimethylpiperidine (35dp), 3-hydroxy piperidine (3hp), 4-hydroxypiperidine (4hp), 4-aminopiperidine (4ap), piperazine(pz), 2-methylpiperazine (2mpz) and cis-2,6-

dimethylpiperazine (26dpz). The inhibiting effect was investigated in 0.1and thinsp; mol/L $HClO_4$ by Potentiodynamic polarization (DC) and electrochemical impedance spectroscopy (EIS). The results showed that these compounds suppressed both cathodic and anodic processes of iron corrosion in 0.1 M/L $HClO_4$ by adsorption on the surface, which followed a Langmuir adsorption isotherm. Experimental observations indicated that basic piperidine and piperazine were better corrosion inhibitors than their derivatives. The inhibition properties of N-heterocyclic amines were found to be related to the charge on the nitrogen atom and the sum of the net charge of the all six atoms from the cyclic ring.

Corrosion inhibitions of carbon steel in sulfuric acid by bicyclic isoxazo-lidines were studied [261]. The cycloaddition of cyclic nitrone1-pyrroline-1-oxide with1-dodecene and 1-hexadecene afford a bicyclic (isoxazolidines).These isoxazolidines were tested for corrosion inhibition of carbon steel in 1N H_2SO_4 in the temperature range 30-60°C by gravimetric and electrochemical methods. The isoxazolidines exhibited excellent inhibition efficiency in the acidic corrosion environment. The presence of heteroatoms such as N and O induce greater adsorption of the inhibitor molecules onto the surface of carbon steel and the long hydrocarbon chains ensure coverage of the metal surface. The values of activation energy and free energy of adsorption indicated the physical nature of the adsorption on the surface of the carbon steel. Thermodynamic parameters were determined for the adsorption process, and kinetic parameters for the metal dissolution (or hydrogen evolution) reaction in the presence of the isoxazolidines. The adsorption of inhibitors on the metal surface was found to obey the Langmuir adsorption isotherm. The isoxazolidines were found to be mixed-type inhibitors. It was found that the isoxazolidine which had a tetradecyl hydrophobe was a better inhibitor than the decyl analogue.

Inhibition by some newly synthesised pyridazine compounds to corrosion of pure iron in 1MHCl solution has been studied [262] using weight loss measurements, polarisation and impedance spectroscopy methods. The inhibiting action is more pronounced with stet-5-benzyl-6-methyl-pyridazin-3-yl thioethanoic (P1) and (5-benzyl-6-methylpyridazin-3-yl) ethyl thioethanoate (P3) and their inhibition efficiency increases with concentration to attain the maximum value of 85% and 81% at the 10^{-4} M, respectively. Good agreement between gravimetric and electrochemical methods (potentiodynamic polarization and impedance spectroscopy (EIS) is observed. Polarization measurements also show that the pyridazines act essentially as cathodic inhibitors and the cathodic curves indicate that the reduction of proton at the pure iron surface happens with an activating mechanism. The presence of the sulphur atom increases the inhibition efficiency changing the adsorption mechanism.

The inhibition of corrosion of steel in molar hydrochloric acid solution by two bipyrazolic compounds was studied [263] by weight loss and electrochemical polarisation measurements. The two methods give consistent results. The polarisation curves indicate that the bipyrazolic compounds act as mixed-type inhibitors. These compounds are efficient inhibitors. The inhibition efficiency increases with the increase of inhibitor concentration to reach 96 and 92% at 5×10^{-4} M for Bipyr **1** and Bipyr **2**, respectively. The temperature effect on the corrosion behaviour of steel in 1M HCl with and without the bipyrazolic compounds at 5×10^{-4} M is studied in the temperature range from 308 to 353 K. The adsorption of inhibitors on the steel surface was found to obey the Frumkin adsorption isotherm model. From the adsorption isotherm, some thermodynamic data for the adsorption process were calculated and discussed.

New synthesized pyridazine derivatives as effective inhibitors for the corrosion of pure iron in HCl medium were

investigated [24]. The inhibition of pure iron in 1M HCl by new synthesized pyridazine compounds had been studied by weight loss, electrochemical polarization and electrochemical impedance spectroscopy (EIS) measurements. The results obtained reveal that these compounds were efficient inhibitors. The inhibition efficiency increased with the increasing of inhibitor concentration and reached 98 % at 10 $^{-4}$ M for 5 – benzyl – 6- methyl pyridazine – thion. Potentiodynamic polarization studies clearly reveal that the presence of pyridazines does not change the mechanism of hydrogen evaluation and that they act essentially as cathodic inhibitors. The temperature effect on the corrosion behavior of pure iron in 1 M HCl without and with the pyridazines at 10^{-4} M was studied in temperature range from 238 to 253 K. EIS measurements showed that the transfer resistance increases with increasing the inhibitor concentration.

Dithiazolidines- a new class of heterocyclic inhibitors for prevention of mild steel corrosion in hydrochloric acid solution was investigated [81]. Heterocyclic compounds, namely 3,5 – diphenyl – imino-1,2,4- dithiazolidine (DPID) ; 3 – phenyl – imino-5- chlorophenyl- imino- 1,2,4-dithiazolidine (PTID) ; and 3 – phenyl – imino-5- anisidylimino-1,2,4-dithiazolidine (PAID) , were synthesized and applied as corrosion inhibitors. Their influence on the inhibition of corrosion of mild steel in 1N HCl was investigated by weight loss and potentiodynamic polarization techniques. The inhibition efficiency of these compounds was found to vary with concentration, temperature, and immersion time. Good inhibition efficiency (> 90%) was evidenced even at a concentration of 25ppm. Potentiodynamic polarization results revealed that three compounds (DPID, PCID, and PAID) act as cathodic inhibitors while PTID was a mixed – type inhibitor. Adsorptions on the metal surface were obeyed Timken's adsorption isotherm.

3- Triazol Compounds

Triazole and triazole-type compounds used as corrosive inhibition of metals in acids have been studied in considerable detail [264-270]. Some new triazole derivatives have been still continuously synthesized and investigated as inhibitors for corrosion of metals in acidic solutions [275-280]

Corrosion inhibition of mild steel in neutral aqueous solution by new triazole derivatives were studied [277]. Selected triazole derivatives had 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 (IE). The effect of changing functional groups of some triazole derivatives on their inhibition efficiency was also reported using weight loss and potentiodynamic technique. 3-Salicylalidene amino-1, 2, 4-triazole phosphonate (SATP) was found to be the best corrosion inhibitor compared to the other compounds.

Triazoles and thiazole derivatives were studied as corrosion inhibitors for AA2024 aluminium alloy [278]. The 1, 2, 4-triazole, 3-amino-1, 2, 4-triazole, benzotriazole and 2-mercaptobenzothiazole were evaluated as corrosion inhibitors for protection of the 2024 aluminium alloy in neutral chloride solutions. The corrosion protection performance was investigated by means of DC polarization and electrochemical impedance spectroscopy (EIS). Scanning Kelvin probe force microscopy (SKPFM) and atomic force microscopy (AFM) were used to study the evolution of the Volta potential distribution and the surface topography during corrosion tests. The results show that all inhibitors under study confer corrosion protection to the AA2024 alloy forming a thin organic layer on the substrate surface. Benzotriazole and 2-mercaptobenzothiazole offer better corrosion protection in

comparison with the other two. The inhibitors decreased the rate of both the anodic and cathodic processes. In the latter case the de-alloying of the copper-reach particles was hindered, slowing down the oxygen reduction.

Effect of benzotriazole derivatives on the corrosion of brass in NaCl solutions were studied [279]. The corrosion behaviour of brass in the presence of two organic inhibitors that belong to the benzotriazole derivatives namely N-[1-(benzotriazol-1-yl)methyl]aniline (BTMA) and 1-hydroxy methyl benzotriazole (HBTA) has been investigated in neutral aqueous NaCl solution.Weight-loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were applied to analyze the effect of the organic compounds on the corrosion inhibition of brass. Polarization studies showed that these inhibitors were found to act as mixed type for brass in chloride solution. It suppresses the cathodic and anodic reactions rates and it renders the open circuit potential to more noble directions.

The inhibitive action of triazoles and surfactants on the corrosion of carbon steel were studied [280] using the weight loss method and electrochemical studies. Results obtained showed that these organic compounds were very good inhibitors. Potentiodynamic polarisation studied clearly reveals the type of inhibitor. The corrosion parameters such as corrosion current (icorr), corrosion potential (Ecorr), inhibition efficiency (IE), corrosion rate, and activation energy (Ea) were calculated at different temperatures ranging from 303 to 333 K. The adsorption of triazole compounds on carbon steel surface obeyed Langmuir's adsorption isotherm.

Electrochemical and analytical study of corrosion inhibition on carbon steel in HCl medium by 1,12-bis(1,2,4-triazolyl)dodecane were illustrated[281]. 1,12-bis(1,2,4-triazolyl)dodecane (dTC12) is an excellent corrosion inhibitor

for carbon steel in deaerated 1 M HCl solution. In this work 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 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 showed that the inhibition efficiency increases in early stage and decreases for a long immersion time.

4- Imidazolines and Amide Compounds

Surface analysis of inhibitor films formed by imidazolines and amides on mild steel in an acidic environment were studied [282]. Imidazolines and amidic precursors were synthesized with good yields through an optimized process. These compounds were evaluated as corrosion inhibitors in an aqueous solution of 1.0 M HCl by gravimetric and polarization techniques. AISI 1018 carbon steel displayed a corrosion rate dependent on the molecular structure and concentration of inhibitor in the testing environment. Adsorption of inhibitors was found to follow the Langmuir's isotherm; this concept together with Gibbs' free energy provided the basis to arrange corrosion inhibitors according to efficiency and stability. The surface analysis by AFM was displayed that the damage on the metallic surface was considerably reduced in the presence of certain inhibitors. XPS determined the presence of a layer of inhibitor on the metal surface with protective properties.

The inhibition of benzimidazole derivatives on corrosion of iron in1 M HCl solutions were investigated [283]. The inhibitive action of some benzimidazole derivatives namely 2-amino-benzimidazole (AB), 2-(2-pyridyl)benzimidazole (PB), 2-Aminomethyl-benzimidazole (MB), 2-hydroxybenzimidazole

(HB) and benzimidazole (B), against the corrosion of iron (99.9999%) in solutions of hydrochloric acid has been studied using potentiodynamic polarization and electro-chemical impedance spectroscopy (EIS). At inhibitor concentration range (10^{-3}-10^{-2} M) in 1 M acid, the results showed that these compounds suppressed both cathodic and anodic processes of iron corrosion by adsorption on the iron surface according to Langmuir adsorption isotherm. The efficiency of these inhibitors increases in the order B> PB> MB> HB>B. Both potentiodynamic and EIS measurements reveal that these compounds inhibit the iron corrosion in 1 M HCl and that the efficiency increases with increasing of the inhibitor concentration. Data obtained from EIS were analyzed to model the corrosion inhibition process through equivalent circuit. A correlation between the highest occupied molecular orbital E HOMO and inhibition efficiencies was sought.

The effect of some phenoxy acetamide derivatives as corrosion inhibition of iron in 3N nitric acid was studied by thermometric and weight loss techniques [255]. It was found that the maximum reaction number (RN) decreases by increasing the additive concentration. The authors were attributed the inhibition efficiency of these compounds to the adsorption through the carbonyl group on iron surface, while the aromatic nucleus lies flat on iron surface. The inhibitory character of the compounds depends upon the concentration of the inhibitor as well as its chemical composition.

Experimental and theoretical study of 1-(2-ethyl amino) – 2-methyllimidazoline as an inhibitor of carbon steel corrosion in acid media were illustrated [79]. The electrochemical behaviour of 1-(2-ethyl amino) – 2- methyllimidazoline (imidazoline), its precursor n-[3-(2- amino – ethylamino- ethyl) - acetamide (amide) and its derivative 1-(2-ethyl amino – 2-methylimidazolidine (imidazolidine), were evaluated by using potentiodynamic polarization curves and electrochemical

impedance spectroscopy (EIS), techniques in deaeratation acid media and compared their corrosion inhibition efficiency. The experimental results suggest that imidazoline was a good corrosion inhibitor at different concentrations as amide shows low efficiency values; however, the properties of a corrosion inhibitor were not found in imidazolidine. The reactivity of these compounds were analyzed through theoretical calculation 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 indicated that imidazoline was 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.

Comparison of inhibition efficiency of some azoles on corrosion was studied [78]. Inhibition efficiencies were investigated for two types of azole, namely 2- mercaptobenzoazole (CBA) and 2- methyl benzoazole (MBA), containing nitrogen, sulphur, oxygen, or selenium atoms, on the corrosion of type 304 stainless steel in 2M H_2SO_4 and 3M HCl. The study was conducted using weight loss, geometry, and polarization methods. It was showed that some of the compounds tested provide 90% inhibition efficiency at a concentration of 5×10^{-4} .The efficiency depends on the heteroatom and decreases in the order Se >S> N>O. These inhibitors were more efficient in H_2SO_4 than HCl whereas the opposite was true for inhibitors with nitrogen alone. Adsorption isotherms were fitted to the experimental findings and some thermodynamics functions were obtained.

3- Thio Compounds

The inhibition of the corrosion of the steel in 0.5M H_2SO_4 by thiophene compounds was studied [284] .The weight loss and electrochemical polarization were applied. The results obtained

reveal that these compounds are very efficient inhibitors. The inhibition efficiency increases with the increase of inhibitor concentration to reach 98% at 5×10^{-3}M for the 2-ethylamine thiophene. Potentiodynamic polarization studies clearly reveal that the presence of thiophene does not change the mechanism of the hydrogen evolution reaction and they act essentially as cathodic inhibitors. The temperature effect on the corrosion behaviour of steel is studied in the range from 298° to 353°K without and with thiophene at 10^{-3}M. The inhibitors 2-ethylamine thiophene and 3-ethylamine thiophene adsorb on steel according to Frumkin isotherm model.

The variation in the inhibition efficiency of thiosemicarbazide and thiosemicarbazone derivatives was explained in terms of molecular Parameters [285]. The effect of concentration was taken into account by assuming that the adsorption of the corrosion inhibitors follows the Langmuir isotherm. The model used differs from that proposed earlier, because instead of the adsorption constant K, ln$K$ was considered the dependent variable in the quantitative structure–efficiency relationships. This modification allowed treating the variation in terms of linear free-energy relationships. The numerical procedure used to obtain the regression coefficients was based on a non-linear regression technique. The results indicated that variation can be explained in terms of the energy of the highest occupied molecular orbital and the dipole moment, or alternatively, by the difference in the energy of the highest occupied and lowest unoccupied molecular orbital.

Inhibitions of mild steel corrosion in the presence of fatty acid thiosemicarbazides were studied [99]. The thiosemi-carbazides of fatty acids with $C_{11} - C_{18}$ carbon atoms were synthesized and evaluated as corrosion inhibitors of mild steel (MS) in 1N HCl and 1N H_2SO_4 by weight loss and potentiodynamic polarization methods . The values of activation energy and free energy of adsorption of all the

thiosemicarbazides were calculated to investigate the mechanism of corrosion inhibition. The potentiodynamic polarization studies were carried out at room temperature revealed that all the compounds blocked the corrosion reaction. The adsorption of all the thiosemicarbazides on the MS surface in both acid solutions was found to obey Timken's adsorption isotherm. All of these compounds showed good inhibition efficiency in both acids. The inhibition efficiency of these 4 compounds was found to vary with the nature and concentration of the compounds, solution temperature, immersion time, and nature of the acids. Electrochemical impedance spectroscopy was used to investigate the mechanism of corrosion inhibition.

6- Schiff base Compounds

Corrosion inhibitions of mild steel by some schiff base compounds in hydrochloric acid were investigated [286]. The corrosion inhibition of mild steel in 1 M HCl by benzylidene-pyridine-2-yl-amine (A), (4-benzylidene)-pyridine-2-ylamine (B) and (4-chloro-benzylidene)-pyridine-2-yl-amine (C) has been studied at 258°C using electrochemical and weight loss measurements. Polarization curves reveal that the used compounds are mixed type inhibitors. Results show that inhibition efficiency increases when the inhibitor concentration increases. The inhibition efficiency changes with the type of functional groups substituted on benzene ring. The experimentally obtained adsorption isotherms follow the Langmuir equation. The effect of temperature on the corrosion behaviour in the presence of 10^{-2} M of inhibitors was studied in the temperature range of 25°- 438°C. The associated activation energy of corrosion and other thermodynamic parameters have been determined. It has been found that all those schiff base compounds are excellent inhibitors.

Effects of some pyrimidinic Shciff bases on the corrosion of mild steel in hydrochloric acid solution were studied [287]. The

efficiency of benzylidene-pyrimidin-2-yl-amine(A),(4-methyl-benzylidene)-pyrimidine-2-yl-amine (B) and (4-chloro-benzylidene)- pyrimidine-2-yl-amine, as corrosion inhibitors for mild steel in 1M HCl have been determined by weight loss measurements and electrochemical polarization method. 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's 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 quantitative structure–activity relationship (QSAR) method.

Corrosion inhibition of iron in 1 M HCl solution with schiff base and its derivatives were studied [80]. The efficiency of N-(2- hydroxy phenyl) salicyaldimine (1) , N,N - bis – (salicyaldehyde)- 1,3- diamino propane(2) and N, N - bis – (2- hydroxy – benzyl)- 1,3- diamino propane (3) ,derived from the reduction of N,N - bis – (salicyaldehyde)- 1,3- diamino propane(2), as corrosion inhibitors were studied. Weight loss, polarization and electrochemical impedance spectroscopy experiments showed that inhibition efficiency of compound 3 is the best amongst the compounds studied.

5- Amine Compounds

Influences of flow on the corrosion inhibition of carbon steel by fatty amines in association with phosphonocarboxylic acid salts were studied [288]. This work was carried out to study the inhibition mechanism of carbon steel in a 200mg 1M NaCl solution by a non-toxic multi-component inhibitor used for water treatment in cooling circuits. The inhibitive formulation was composed of 50 mg fatty amines associated with 200 mg phosphonocarboxylic acid salts. Steady-state current–voltage curves, obtained with a rotating disc electrode, revealed that the properties of the protective layer were dependent on the electrode rotation rate and on the immersion time. The cathodic process of oxygen reduction was not modified in the presence of the inhibitive mixture. As expected, the current densities increased when the rotation rate was increased. In the anodic range, original behaviour was observed: the current densities decreased when the electrode rotation rate increased.

The morphology and the chemical composition of the inhibitive layers allowed the electrochemical results to be explained. Two distinct surface areas were visualized on the metal surface and the ratio between the two zones was dependent on the flow conditions. This behaviour was attributed to a mechanical effect linked to centrifugal force. XPS analysis.

Corrosion inhibition of mild steel in HCl by different concentrations of hexylamine and dodecylamine were investigated [2]. For a given inhibitor concentration, dodecyl amine showed higher effectiveness than hexylamine. The inhibition mechanism was treated as a substitution adsorption

process according to Flory-Hugging (FH), Dhar- Flory-Hugging (DFH) and Bochris - Swinkels isotherm. The best approach was obtained using FH and DFH isotherms with one molecule of inhibitor replacing three molecules of water.

Influence of poly (aminoquinone) on corrosion inhibition of iron in acid media was reported [289]. The inhibitor performance of chemically synthesized water soluble poly (aminoquinone) (PAQ) on iron corrosion in 0.5 M sulphuric acid was studied in relation to inhibitor concentration using potentiodynamic polarization and electrochemical impedance spectroscopy measurements. On comparing the inhibition performance of PAQ with that of the monomer o-phenylenediamine (OPD), the OPD gave an efficiency of 80% for 1000 ppm while it was 90% for 100 ppm of PAQ. PAQ was found to be a mixed inhibitor and was able to improve the passivation tendency of iron in 0.5 M H_2SO_4 markedly.

The effect of addition of diamine derivatives on the corrosion of steel in 0.5M H_2SO_4 solution were studied [290] using weight loss measurements, electrochemical polarization and impedance spectroscopy (EIS) methods. This study permits to follow the evolution of the inhibitive effect of diamine derivatives on steel in 0.5M H_2SO_4. Polarization measurements show that the diamine act as mixed inhibitors. The cathodic curves indicate that the reduction of proton at the steel surface happens within a pure activating mechanism. The inhibitors are adsorbed on the steel surface according to the Frumkin adsorption isotherm model. There is a good agreement between gravimetric, electrochemical polarization and impedance spectroscopy methods.

Inhibition of corrosion of iron in citric acid media by amino acids were studied [291] .The effect of some amino acid compounds: glycine, leucine, d–l aspartic, arginine and methionine on the corrosion behaviour of pure iron in citric

acid solution at pH = 5 is investigated by weight-loss, polarization and EIS measurements. Results obtained show that methionine was the best inhibitor and its efficiency reaches 96% at 2 x 10^{-2} M. Polarization measurements show that the compounds tested were cathodic inhibitors. Methionine adsorbs on the iron surface according to the Temkin isotherm model. Effect of pH and temperature were also studied.

The inhibition effect of amino acids against steel corrosion in HCl solution was investigated by potentiodynamic polarization method [38]. Corrosion data such as corrosion rate, corrosion potential (Ecorr) and corrosion resistance (Rp) were determined by extrapolation of the cathodic and anodic Tafel region. Adsorption isotherm was investigated by weight – loss measurement. The amino acids as alanine, glycine and leucine were used. The effect of inhibitor concentration and amino acid concentration against inhibitor action was investigated. The inhibition efficiency depends 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 followed Langmuir isotherm.

The influence of amino benzoic acid derivatives on the corrosion and hydrogen permeation through mild steel in 1M HCl and 0.5 M H_2SO_4 were studied [292]. The weight loss, gasometric measurements and various electrochemical techniques were applied. The isomers of amino benzoic acid were inhibited the corrosion rate of mild steel in both HCl and H_2SO_4 in the order $-$ O $> -$ m $> -$ p. The inhibition efficiency was greater in HCl than in H_2SO_4. The predominant behaviour was in the cathodic inhibitor mode. These compounds were reduced the permeation current in 1M HCl and enhance it in 0.5 M H_2SO_4. The adsorption of these compounds on mild steel in 1M HCl and 0.5 M H_2SO_4 were studied through Langmuir adsorption isotherm.

Two new organic inhibitors, namely dibenzylidene acetone (DBA)and Di-N-dimethylaminobenzylidene acetone (DDABA), has been evaluated on corrosion of N-80 steel and mild steel (MS) in HCI by weight loss technique [293]. These compounds exhibited the inhibition efficiency (IE) of 94.4 per cent and 56.5 per cent for mild steel, whereas for N-80 steel these compounds showed inhibition efficiency (IE) of 99.7 per cent and 73.8 per cent. The potendiodynamic polarization studies revealed that both compounds were mixed type inhibitors. The noteworthy feature of the investigation was that inhibition efficiency (IE) of both compounds increased on addition of potassium iodide (KI) due to synergism, and they inhibit corrosion by an adsorption mechanism.

Corrosion behaviour of reinforcing steel exposed to an amino alcohol based corrosion inhibitor was studied [294]. Electrochemical impedance measurements were performed in order to obtain information on the corrosion behaviour of reinforcing steel in the presence of a penetrating amino alcohol corrosion inhibitor. The investigation was performed in solutions contaminated with chlorides, in the presence of inhibitor. The electrochemical results indicate that the inhibitor was able to penetrate through mortar, minimizing steel corrosion.

The behaviour of amino alcohol based mixed corrosion inhibitors were studied [58]. These organic and mixed (organic / inorganic) inhibitors were used as concrete admixtures or in reappear products to delay the onset of corrosion or to reduce the rate of corrosion of reinforcing steel in concrete structure. The inhibiting properties were documented in solution and in concrete. The interaction mechanism of the inhibitors with steels surface were studied using sophisticated surface analytical methods. The penetration of the surface – applied type could be shown. The inhibitors reduced the rate of corrosion.

Inhibition of pure iron in sulphuric acid by N, N – dipropynoxy methylamine acetate and its synergism with chloride were studied [4] .The potentiodynamic polarization and electrochemical impedance techniques were applied. The results showed that the inhibition mechanism was mixed type .The inhibitor molecules blocked the active sites on the iron surface and had a distinct inhibition synergism with chloride on the surface of the pure iron. Inhibition efficiencies and synergism were related to the concentration and molecular structure of the inhibitor.

Adsorption and inhibitive properties of four primary aliphatic amines on mild steel in 2M HCl were studied [20] . Four n - alkyl amines (6, 8, 10 and 12 carbon atoms) were investigated as corrosion inhibitors for mild steel in 2M HCl solution using gravimetric and polarization techniques. The influences of temperature (278°– 308° k) and different concentrations of inhibitor were studied. Protection efficiency was improved when the inhibitor concentration and the length of the alkyl chain were increased. The four amines were adsorbed on the mild steel surface according to a Frumkin isotherm.

Hexadecyl trimethyl ammonium bromide (HTABr) was studied as an effective inhibitor for the corrosion of steel in sulphuric acid solution [47]. The studies were carried out over the temperature range 30°– 60°C at different inhibitor concentrations by the mass loss method and Langmuir adsorption isotherm. The experimental data of thermodynamic parameters for dissolution and adsorption were calculated. It was observed that HTABr could be used as an effective inhibitor.

New and effective corrosion inhibitors for oil – well steel (N – 80) and mild steel in boiling hydrochloric acid were examined[100]. The aromatic aldehydes and p- phenylene-

diamine were synthesized and evaluated as corrosion inhibitors for mild steel (MS) and oil – well steel (N-80) in 15 % hydrochloric acid (HCl) at105°C ± 2°C by the weight loss method. All the condensation products showed excellent performance. 2,4 – dicinnamyledene aminophenylene (DCAP) was found to be the best corrosion inhibitor. It exhibited 99.75% inhibition efficiency (IE) for MS and 99.12 for N – 80 steel at 5,000 ppm of inhibitor concentration. The potentiodynamic polarization studies carried out at room temperature on MS in 15 % HCl containing 500 ppm of condensation product. The compounds act as a mixed type inhibitors, where as 500 ppm DCAP on N – 80 steel behaved predominatly as anodic inhibitors. The adsorption of all the condensation products was found to obey Temkins adsorption isotherm.

Synthesis of N- benzeylidine phenylamine – N- oxide (nitrone) and eight of its derivatives with constituents in the Para position of the α – phenyl group were synthesized and their inhibition of the corrosion of mild steel in 1 M HCl was investigated[49]. The weight loss, Potentiodynamic polarization studies, hydrogen permeation measurements, and impedance measurements were applied. Determination of inhibition efficiency in the presence of these compounds at different temperatures clearly indicated that the dimethyl derivative showed the best performance even at temperatures 70°C. Potentiodynamic polarization studies clearly revealed the fact that nitrone and derivatives act as mixed type inhibitors. All of these compounds were found to reduce the permeation of hydrogen through mild steel in HCl solution. Values of double layer capacitance and charge transfer resistance were derived from Nyquist plots obtained from Ac impedance studied. The adsorption of these compounds on the mild steel surface obeyed Timken adsorption isotherm.

8- Surfactant Compounds

A new corrosion inhibition model for surfactants that more closely accounts for actual adsorption than traditional models that assume physical coverage was proportional to inhibition were studied[128]. Many corrosion inhibition researchers utilize the assumption that inhibitor coverage was proportional to corrosion inhibition as a tool to evaluate their inhibition data. Although this assumption is very useful, it was inconsistent with observed surfactant adsorption data. Corrosion and adsorption data indicate that corrosion inhibition by surfactants was not directly proportional to surfactant coverage. This paper discusses the discrepancy between physical and effective coverage and provides an alternative relationship between coverage and inhibition that was more consistent with observed surfactant adsorption than the traditional relationship, which for most researchers means that physical coverage was proportional to corrosion inhibition.
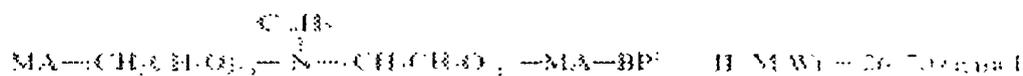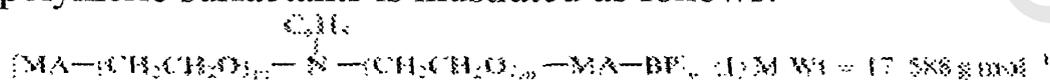
Effectiveness of some non ionic surfactants as corrosion inhibitors for carbon steel pipelines in oil fields were studied [295]. The ability of new synthesized non ionic surfactants to protect carbon steel in acid chloride solution was investigated using potentiostatic polarization, open circuit potential, weight loss and surface tension measurements. The experimental results showed that these inhibitors revealed a very good corrosion inhibition even at low concentrations. The percentage inhibition efficiency (IE %) 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.

Effect of octylphenol polyethylene oxide (OPPEO) on the corrosion inhibition of steel in 0.5M H_2SO_4 was studied [296].
A non-ionic surfactant, octylphenol polyethylene oxide, was evaluated as an inhibitor for corrosion of low-carbon steel in 0.5M H_2SO_4. Potentiodynamic and potentiostatic methods and scanning electron microscopy were used to study the inhibition effectiveness of the surfactant. The inhibition efficiency was found to increase with the inhibitor concentration increase and decrease with temperature decrease. Octylphenyl polyethylene oxide (OPPEO) showed higher constant protection efficiency near its critical micelle concentration. The activation energy of corrosion was found to be higher in presence than in absence of the inhibitor. The experimental data fitted with the Flory–Huggins isotherm at a molecular ratio of 5:1. The Gibbs energy of adsorption decreases with the temperature. The inhibitor has relatively lower inhibition efficiencies at ambient and higher temperature. This was attributed to the molecular structure of the inhibitor.

Impact of gamma-ray-pre-irradiation on the efficiency of corrosion inhibition of some novel polymeric surfactants was reported [297]. The effect of gamma-ray-pre-irradiation on the efficiency of two types of polymeric surfactants, as corrosion inhibitors for 304 stainless steel in 2M hydrochloric acid solution was examined. The inhibition efficiency of the undertaken additives was evaluated using both chemical and electrochemical techniques. The chemical structure of the two polymeric surfactants is illustrated as follows:

$$C_9H_4$$
$$[MA—(CH_2CH_2O)_n— N —(CH_2CH_2O)_m—MA—BP, (I) M Wt = 17 588 g mol^{-1}$$

$$C_{12}H_5$$
$$MA—(CH_2 H O)_n,— N —(CH CH O)_2 —MA—BP \quad II \; M Wt = 20 \; 7 \; g mol^{-1}$$

Where MA¼maleic anhydride; BP¼block polymer of polyoxy ethylene–polyoxy propylene (M.Wt =5000 g mol^{-1}). The obtained corrosion data, indicated that the corrosion inhibition efficiency of the inhibitor (II) was obviously not affected by

gamma-ray-irradiation, meanwhile the efficiency of the inhibitor (I) demonstrated a remarkable decrease. Scanning electron microscope (SEM) was used to examine the surface morphology of stainless steel samples after immersion in 2M HCl solution in absence and presence of the inhibitors at concentration of 400 ppm before and after exposure to gamma-ray-radiation up to a total of 100 kGy.

I.11. Corrosion Inhibition by Organosilicon Compounds in Different Media:-

The bonding of organosilanes to different substrate surfaces has considerable interest both for adhesion promotion and for corrosion protection [298-318]. Organosilanes are well known for their very good adhesion properties and are currently used as adhesion promoters for coating [298-302], mastic and joint [303]. However, recent works propose the use of organosilanes as corrosion inhibitors for different substrates such as aluminium [304], copper [305-308], iron [309-312], steel [313-314] and carbon steel alloy [315-318].

The barrier properties of silanes on cold rolled steel were investigated [303]. Goal of the study is to determine the effect of the molecular structure of silane monomers on the corrosion protection properties of the formed silane layers. During the curing process, the silane monomers crosslink to form a molecular network, which acts as a barrier and retards the ingress of corrosive species. Non-cured and "fully" cured silane films with a comparable thickness were applied on cold rolled steel surfaces. The layer thickness and the chemical state of the films were measured with Spectroscopic Ellipsometry (SE). Electrochemical impedance spectroscopy (EIS) measurements and linear voltammetry clearly show that the number of silanol groups of the fully hydrolyzed silanes and the presence of an organo-functional group have a big influence on the barrier

properties of silane layers and hence on their corrosion protection properties.

The inhibition action of different pretreatment aluminum with metacryloxy propylmethoxysilane (MAOS) on its corrosion in 3.5% NaCl aqueous solution has been examined [304]. Free corrosion and electrochemical tests (potentiodynamic polarization and electrochemical impedance spectroscopy) were performed to characterize the resistance to general and localized corrosion for pretreated specimens. The surfaces of uncorroded pretreated samples were characterized by SEM and AFM. Their surfaces were also examined with X-ray photoelectron spectroscopy (XPS) technique before and after corrosion attack. It was found that the inhibitory action of MAOS against general and localized corrosion depends on the nature of the solvent in which it is dispersed. The siloxane polymeric film formed by MAOS aqueous dispersion acts a good corrosion inhibitor in the whole exposure time range, whereas the inhibitory power of the polymeric film formed by MAOS methanol solution decreases with increasing immersion time.

Self- assembled monolayer of alkane thiol $C_n H_{2n+1}SH$ (n = 6 ~ 18) adsorbed on the surface of poly- crystalline bulk were constructed and characterized by X- ray photoelectron spectroscopy (XPS) and surface – enhanced Raman scattering (SERS) spectroscopy and contact angle impedance measurements [305]. The protection ability of the alkanethiol monolayers against copper corrosion in an aerated 0.5 M Na_2SO_4 solution was examined by impedance and polarization techniques. Results of XPS, SERS, and contact angle measurements showed that alkanethiols were chemisorbed on the copper surface by the formation of strong bonds between copper and sulphur atoms following cleavage of S-H bond and formed densely packed water – repellem monolayers on the surface. The advancing contact angle of these monolayer films was comparable to that of alkanethiolate monolayers adsorbed

at a vapor deposited copper on a silicon wafer. However, sufficiently high protection abilities of the films against Cu corrosion were not obtained in 0.5 M Na_2SO_4. A preliminary experiment demonstrated the formation of a promising protective film which was prepared on the Cu surface by modification of self – assembled 11 – mercapto – 1 undecanol monolayers with octyl trichlorosilane to form cross- linkages between the thiol molecules with siloxane bonds.

Protection of copper corrosion by ultra thin two – dimensional polymer film of alkanethiol monolayer was studied [306]. An ultra thin (Ca. 5.6 nm thick) , closely packed (self – assembly) , tightly interconnected (two – dimensional polymer) water – repellent (> $130°$ of the contact angle with water) film was prepared by modification of 11- mercapto-1-undecanol self – assembled monolayer adsorbed on copper surface with 1,2- bis (trichlorosilyl)ethane and subsequently with octadecyltrichloro-silane at $5×10^{-4}$ M for 24 h.This film prevented copper corrosion in aerated 0.5 M Na_2SO_4 with the primitive efficiency (p) of the film being maintained at over 95% in the solution for 15 h. the film provided excellent promotion against indoor atmospheric corrosion of copper for 300 days. The effect of the surface roughness on the water repel of the surface covered with the film and on the P value of an unmodified or modified alkanethiol monolayer was studied by using atomic force microscopy to examine mechanically abraded and electro polished copper surfaces.

Corrosion protection and adhesion promotion for polyimide/copper system using silane-modified polymeric materials were studied [307, 308]. The copolymers of vinyl imidazole (VI) and vinyl trimethoxy silane (VTS) were applied as corrosion inhibitors and as adhesion promoters for polyimide/copper system at elevated temperatures. The mole ratios of VI to VTS were 100:0, 70:30, 30:70 and 0: 100. Peel test was performed to evaluate the adhesion strength of polyimide/primer/copper system after heat treatment at $400°C$ in nitrogen atmosphere. The effect of the copolymer

composition on corrosion protection and adhesion promotion was investigated by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The adhesion strength of polyimide/primer/copper system depends on the thermal stability of the primer and the chemical interaction between polyimide and the primer. It showed the highest value when the mole ratio of VI to VTS is 30:70. The primer reduced or suppressed copper oxide formation in the polyimide layer. The degree of corrosion protection by the primer was affected by its thermal stability and its reactivity with copper.

Electrochemical impedance spectroscopy (EIS) on iron was carried out in alkaline and silica media by Amaral and Muller [309]. Polarization at 300 mV was used to determine the effect of silicate on passive films anodically formed on iron in alkaline solution. EIS proved that silicate increased film resistance (R_f), decreased its capacitance (C), and affected the kinetics of interfacial electrochemical reaction, leading to an increase in the charge – transfer resistance (R_t), which depend upon silicate concentration and polarization time.

Prevention of iron at scratched surfaces in NaCl solution by thin organosiloxane polymer films containing octylthioprop-ionate were investigated [310].The films of 1,2-bis (tri-ethoxysilyl)ethane $(C_2H_5O)_3Si(CH_2)_2Si(OC_2H_5)_3$ polymer containing a nonchromate corrosion inhibitor, sodium octylthiopropionate $C_8H_{17}S(CH_2)_2COONa$ (NaOTP) prevented corrosion of iron at a scratched surface in aerated NaCl solutions. The healing ability of the film at the scratch was evaluated by polarization measurement. The protective efficincies of the films for iron corrosion at the scratched electrodes in 0.1 M NaCl were significantly high (more than 97%) in many cases, indicating that the scratches healed with NaOTP diffusing from the scratched films.X- ray photoelectron spectroscopy and electron – probe microanalysis of the surface

after immersion of the electrode in 0.1 M NaCl revealed that iron corrosion at the scratch was suppressed by the formation of an iron oxide layer containing a small amount of a compound derived from NaOTP, probably complex with octyl thiopropionate ion.

Chemical modification of alkanethiol monolayers for protecting iron against corrosion were studied [311]. Monolayer of alkanethiols adsorbed on an iron surface were prepared and characterized by polarization and impedance measurements in an aerated 0.5 M NaCl solution. Furthermore, contact angle measurement with a drop of water, and X- ray photoelectron spectroscopy were studied. The protective efficiency P_k of a C_{18} T monolayer against iron corrosion in 0.5 M NaCl was 76.3%. Chemical modification of 11- mercapto-1- undecanol HO $(CH_2)_{11}SH$ (MUO) monolayer adsorbed on iron with octyl triethoxy silane (C_8TES) was carried out to form a linear polymer film. The Pk value of C_8TES – modified MUO monolayer was 88.0% because the cathodic process of iron corrosion in the NaCl solution was suppressed by blocking diffusion of molecular oxygen.

One – and two – dimensional polymer films of modified alkanethiol monolayers for preventing iron from corrosion were studied [312]. A monlayer of 11- mercapto- 1- undecanol HO $(CH_2)_{11}SH$ (MUO) adsorbed on the electrolytically reduced iron surface was modified with tetraethoxy silane $(C_2H_5O)_4$ Si(TES), octyltriethoxysilane $C_8H_{17}Si(OC_2H_5)_3$ and/or octadecyltriethoxy silane $C_{18}H_{37}Si(OC_2H_5)_3$ ($C_{18}TES$) for preparing one and two- dimensional polymer films. The films thus were prepared and characterized by polarization, impedance and contact angle measurements as well as X- ray photoelectron and fourier transform infrared reflection spectroscopies. Two – dimensional polymer film of the MUO monolayer modified twice with TES and subsequently with $C_{18}TES$ on the iron surface protected

iron from corrosion in aerated 0.5 M NaCl and on exposure to room air.

The effects of unsaturated ethers of chloromethyl dimethylsilanol on sulphuric acid corrosion of steel were examined [313]. The effect was studied of some unsaturated organosilicon compounds of the general formula $ClCH_2SiMe_2OR$ (where R is CH_2O $CH_2C \equiv CH$, $CMe_2C\equiv CH$, $CMe_2C\equiv CH_2NEt_2$, $CHEtHC\equiv CHSiEt_3$, and $CHEtHC \equiv CHSiEt_3$, and CHEt $HC=CHGeEt_3$ on the sulphuric acid corrosion of carbon steel.

Silicate esters with additives as temporary protective on steel surfaces were examined [314]. A series of tetra–alkoxysilanes and dimethyldialkoxy -silanes (silicate ester) was prepared by reacting $SiCl_4$ and $(CH_3)_2SiCl_2$, respectively with different alcohols. The performance of the prepared silicate esters as temporary protective for mild steel surfaces has been studied by assessing the time of appearance of the first rust spot on the specimen surface, electrochemical potential changes, and the percentage protection given by these esters to steel plates under different conditions using natural sea water containing 1% Na_2SO_4 with various additives including thiourea and nicotinic acid. The corrosion resistance imparted by dimethyl dialkoxysilanes is greater than that imparted by tetra-alkoxy silanes. However, for both series of silicate esters, those which have high molecular weight and branching in the alkyl portion confer better corrosion resistance than those with low branching and a linear structure. Similar measurements were made for steel coated with silicon fluid and liquid paraffin and for uncoated steel for the purpose of comparison.

Trimethyl (aminoethoxy)silane (TMAEOS)was prepared [315] by the reaction of hexamethyldislazne with ethanolamine at 100°C. The prepared compound was purified and characterized by FTIR. It was tested as corrosion inhibitor for carbon steel

alloys provided from petroleum pipelines in distilled water, sea water and tap water media through weight loss determination. The rate of corrosion and the efficiency of TMAEOS as corrosion inhibitor were investigated.

Effects of addition of corrosion inhibitors to silane films on the performance of AA2024-T3 in a 0.5M NaCl solution were studied [316]. Water-based organofunctional silanes have been successfully used as an alternative to toxic chromate coatings for surface pretreatment of metals and alloys. To further improvement of the performance of these silane films, corrosion inhibitors were added to the silane films and their corrosion properties investigated in 0.5M NaCl solution. The inhibitors used were environmentally acceptable organic (tolyltriazole, benzotriazole) molecules and inorganic cerium salts. The inhibition efficiency of the individual inhibitor on the corrosion of AA2024-T3 alloy was discussed to understand the mechanisms of inhibition offered by these inhibitors. All of the above mentioned inhibitors effectively protected AA2024-T3 alloy against corrosion in a 0.5M NaCl solution.. The results indicated that these inhibitors were slowly leached out and thus further improved the corrosion protection by silane films and the inorganic inhibitors showed promise of self-healing of defects.

The inhibition effect of tri- ethoxysilyl- diethylphosphate (TEOSDEOP) on the corrosion resistance of carbon steel alloy A36 in distilled water, tap water and 1M hydrochloric acid were investigated by weight loss and electrochemical methods [317]. The results suggest that (TEOSDEOP) inhibition efficiencies provides 99.19% for 10ppm , 98.35% for 20 ppm in distilled ,tap and sea water, respectively, while 97.65% for 30 and 40 ppm in acid media . The corrosion potential in open circuit and electrochemical at low inhibitor concentrations were shifted toward positive direction (i.e cathodic protection). On the other hand at high inhibitor concentrations, the potentials were

shifted towards negative direction (i.e. anodic protection). Also, the electrochemical impedance results indicated that the inhibition efficiency increased with increasing the inhibitor concentrations. The graphical SEM images of coupon immersed 3hs in 1M HCl were investigated.

Novel preparation of benzyl- tri (ethyl-ethylamino – dimethylsiloxane) ammonium chloride (BTASOC) compound was prepared, purified and confirmed by FTIR. The inhibition effect of the BTASOC against carbon steel corrosion in 1M HCl solution has been investigated by weight losses, potentiodynamic polarization and electrochemical impedance spectroscopy methods [318]. The morphology of the formed films was studied by scanning electron microscope. Corrosion data such as corrosion rate, corrosion potential (Ecorr), corrosion resistance (Rp), coverage surface (θ) and efficiency (IE %) were determined by extrapolation of the cathodic and anodic Tafel region. The influence of temperature 25, 35, 45 and $55^{\circ}C$ at inhibitive concentration were studied protection and it was found that the efficiency improved when the inhibitor concentration was increased.

Aim of Work

Aim of the work

Although the corrosion and corrosion inhibition of carbon steel in particular have been received a great attention in different media without and with various types of inhibitors, the corrosion inhibition of such metal becomes and will be long time of much interest to do.

Carbon steel has wide applications in industry (especially in petroleum industry, eg. pipelines, pressure vessels, nozzles etc...) and domestic life and the acid chloride media are the most important one owing to its dangerous effect on carbon steel and its alloys.

The aim of the present study

1- Preparation of organoamide and novel organoamide silicon compounds and confirmation of the structure of the synthesized compounds by I.R and ^{1}HNMR.

2- Study of the corrosion and corrosion inhibition of carbon steel in acid chloride media in absence and presence of different concentrations of the synthesized compounds by chemical and electrochemical techniques and then the results obtained from both techniques were compared.

3- Study of the effect of inhibitors concentration and chemical structure on the inhibition efficiency to propose the inhibition mechanism.

4- Investigation of the effect of temperature on the inhibition process in order to:
   i) Determine the type of adsorption (chemical or physical).
   ii) Calculate some thermodynamic parameters for the activation process.

5- Study of the surface morphology of the formed films on the carbon steel alloy in 1M HCl in absence and presence of the inhibitors.