CHAPTER (1)

1. Introduction

1.1. Surfactants

The term surfactant is a compression of "surface active agent" also known as wetting agents, lower the surface tension of a liquid, allowing easier spreading. Surfactants are usually organic compounds that contain both hydrophobic and hydrophilic groups, and are thus semi-soluble in both organic and aqueous solvents [1].

Certain molecules may be said to contain two distinct components, differing in their affinity for solutes. The part of the molecule which has an affinity for polar solutes, such as water, is said to be hydrophilic. The part of the molecule which has an affinity for non-polar solutes, such as hydrocarbons, is said to be hydrophobic. Molecules containing both types of components are said to be amphiphilic [1, 2].

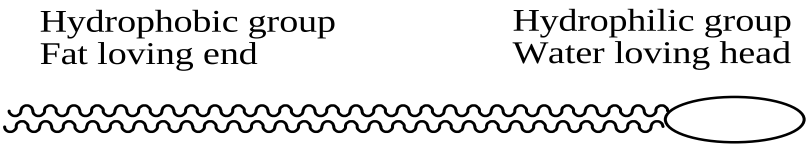

Fig. (1:1): Schematic sketch of surfactant molecule.

A particular type of molecular structure performs as a surfactant. This molecule is made up of a water soluble (hydrophilic) and a water insoluble (hydrophobic) component.

1.2. Classification of surfactants

A surfactant can be classified by the presence of formally charged groups in its head. A nonionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic [3].

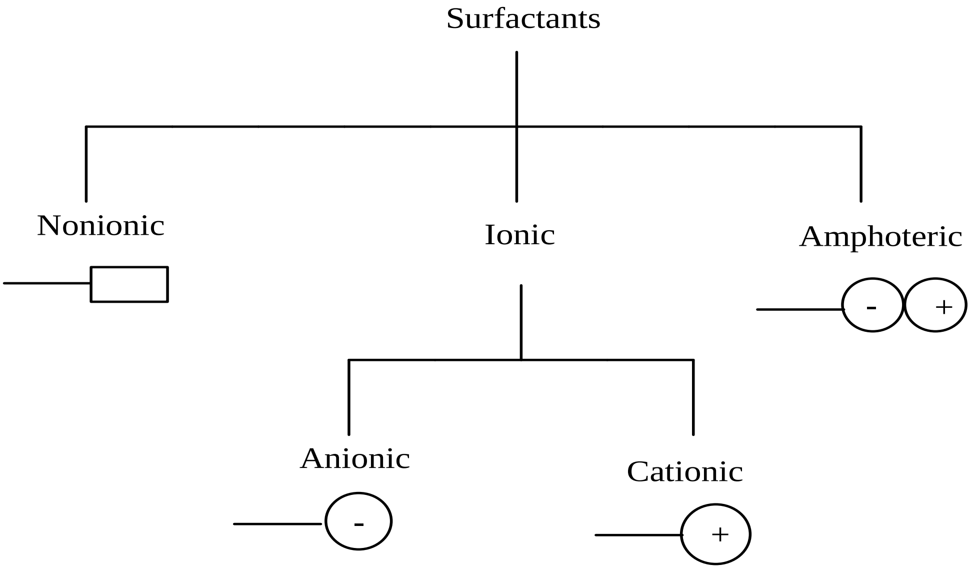

Fig. (1:2): Different types of surfactants.

1.2.1. Anionic surfactants

In solution, the head is negatively charged. This is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties. The surfactant is particularly good at keeping the dirt away from fabrics, and removing residues of fabric softener from fabrics [2]. An example: carboxylates

$$C_nH_{2n+1}COO^-X^+$$

where, n = 8–16 atoms and the counter ion X is usually Na^+.

1.2.2. Cationic surfactants

In solution, the head is positively charged. Cationic surfactants play an important role as antiseptic agents in cosmetic, as general fungicides and germicides, as fabric softeners and hair conditioners, corrosion inhibitors as well as solid particle dispersant. They are used as emulsifiers in asphaltic emulsions and coatings in general, in inks, wood pulp dispersions, and magnetic slurry. Many new applications for cationic surfactants have been developed since World War II [3, 4].

The economic importance of the cationic surfactants has increased significantly because of some of their unique properties. Most cationic are biologically active in that they kill or inhibit the growth of many microorganisms. They have also become extremely important to the textile industry as fabric softeners, waterproofing agents, and dye fixing agents. Because many important mineral ores and metals carry a net negative charge, the cationic surfactants are also useful in flotation processing, lubrication, and corrosion inhibition [3].

$$C_nH_{2n+1}\overset{+}{N}HR_2\overset{-}{X}$$

where, R = H or low molecular weight alkyl groups

1.2.3. Nonionic surfactants

These surfactants do not have an electrical charge, which makes them resistant to water hardness deactivation. They are excellent grease removers that are used in laundry products, household cleaners and hand dishwashing liquids. The main part of nonionics can be classified into alcohols, polyethers, esters, or their combinations [5].

$$RX\ (CH_2CH_2O)_nH$$

where, R is normally a typical surfactant hydrophobic group, but may also be a hydrophobic polyether such as polyoxypropylene (POE), and X is O, N, or another functionality capable of linking the POE chain to the hydrophobe. In most cases, n, the average number of OE units in the hydrophilic group, must be greater than 5 or 6 to impart sufficient water solubility to make the materials useful [3].

1.2.4. Amphoteric (zwitterionic) surfactants

These surfactants are very mild, making them particularly suited for use in personal care and household cleaning products. They can be anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in solution, depending on the acidity or pH of the water [3].

Most commercially important imidazoline-derived amphoteric surfactants can be described as fatty acid/aminoethylethanolamine condensates of the general structure

$$\mathbf{RONHCH_2CH_2NR^{\backslash}R^{\backslash\backslash}}$$

where, R is the fatty acid residue and $R^{\backslash}$ and $R^{\backslash\backslash}$ can be any of several functionalities [3].

1.3. Micelle and critical micelle concentration, (CMC).

A micelle (rarely micella, plural micellae) is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms a roughly spherical or globular aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic tail regions in the micelle center.

Critical micelle concentration (CMC) is the concentration of an amphiphilic component in solution at which the formation of aggregates (micelles, round rods, lamellar structures etc.) in the solution is initiated [6]. An amphiphilic molecule can arrange itself at the surface of the water such that the polar part interacts with the water and the non-polar part is held above the surface (either in the air or in a non-polar liquid). The presence of these molecules on the surface disrupts the cohesive energy at the surface and thus lowers the surface tension. Such molecules are called ‘surface active’ molecules or surfactants [7].

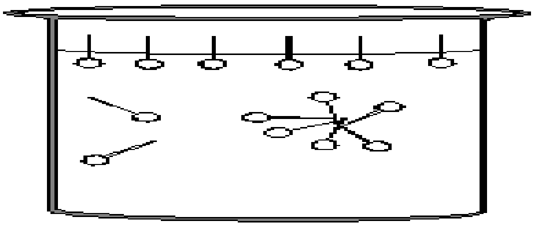

Fig. (1:3): Schematic Sketch of Surfactant Molecules in Water

Another arrangement of these molecules can allow each component to interact with its favored environment. Molecules can form aggregates in which the hydrophobic portions are oriented within the cluster and the hydrophilic portions are exposed to the solvent [8]. Such aggregates are called micelles. An example of a spherical micelle is diagrammed below.

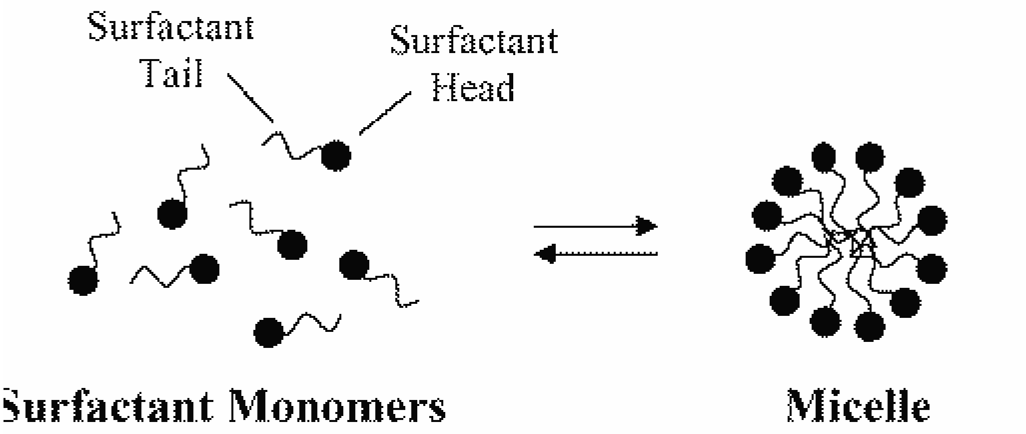

Fig. (1:4): Schematic formation of micelles.

The proportion of molecules present at the surface or as micelles in the bulk of the liquid depends on the concentration of the amphiphile. At low concentrations surfactants will favor arrangement on the surface. As the surface becomes crowded with surfactant more molecules will arrange into micelles. At some concentration the surface becomes completely loaded with surfactant and any further additions must arrange as micelles [9]. This concentration is called the critical micelle concentration (CMC)

[10]. It follows that measurement of surface tension may be used to find CMC Fig. (1:4).

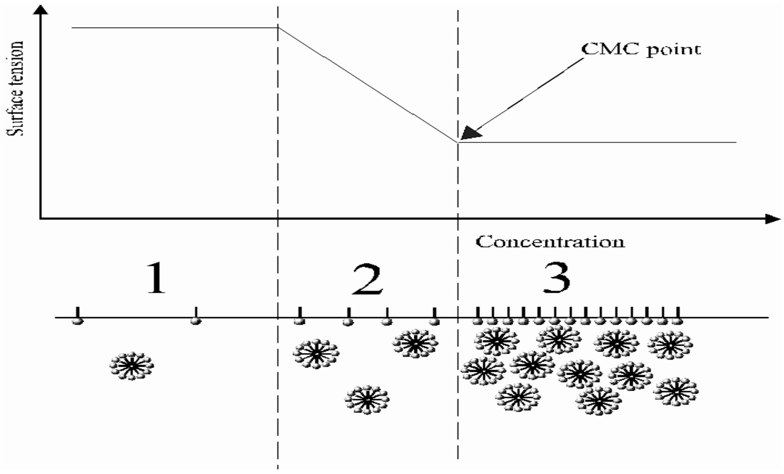

Fig. (1:5): Relationship between surface tension and surfactant concentration.

In this graph you can see three phases:

1) At very low concentrations of surfactant only slight change in surface tension is detected.

2) Additional surfactant decreases surface tension

3) Surface becomes fully loaded, no further change in surface tension.

1.4. Application of Surfactants

Surfactants play an important role in many practical applications and products, like as: Corrosion inhibitor, detergents, emulsifiers ,paints, adhesives, inks, wetting agents, foamers, defoamers and shampoos.

1.4.1. Corrosion inhibitor

It is well known in surface chemistry that surface reactions are strongly affected by the presence of foreign molecules. Corrosion processes, being surface reactions, can be controlled by compounds known as inhibitors which adsorb on the reacting metal surface. The term adsorption refers to molecules attached directly to the surface, normally only one thick molecular layer, and not penetrating into the bulk of the metal itself. The technique of adding inhibitors to the environment of a metal is a well known method of controlling corrosion in many branches of technology. A corrosion inhibitor may act in a number of ways: it may restrict the rate of the anodic process or the cathodic process by simply blocking active sites on the metal surface. Alternatively it may act by increasing the potential of the metal surface so that the metal enters the passivation region where a natural oxide film forms. The surfactant inhibitors have many advantages such as high inhibition efficiency, low price, low toxicity and easy production [11–14].

1.4.2. Detergents

A detergent is a material intended to assist cleaning. The term is sometimes used to differentiate between soap and other surfactant used for cleaning "detergency" indicates presence or degree of cleaning property [15]. The quaternary ammonium is used as a common fabric softener [16, 17].

1.4.3. Emulsifiers

An emulsion is a mixture of two or more immiscible (unblendable) liquids. One liquid (the dispersed phase) is dispersed in the other (the continuous phase) [18]. Emulsions include butter, milk and cream.

1.4.4. Paints

Paint is any liquid, liquifiable, or mastic composition which after application to a substrate in a thin layer is converted to an opaque solid film [5].

1.4.5. Adhesives

Adhesive or glue is a compound in a liquid or semi-liquid state that adheres or bonds items together. Adhesives may come from either natural or synthetic sources.

1.4.6. Inks

An ink is a liquid containing various pigments and/or dyes used for coloring a surface to produce an image, text, or design.

1.4.7. Wetting agents

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. Wetting is important in the bonding or adherence of two materials [1].

1.4.8. Foamers

A foaming agent is a surfactant, which when present in small amounts, facilitates the formation of a foam, or enhances its colloidal stability by inhibiting the coalescence of bubbles. Sodium laureth sulfate, or sodium lauryl ether sulfate (SLES), is a detergent and surfactant found in many personal care products [1, 19] (soaps, shampoos, toothpaste etc.).

1.4.9. Defoamers

A defoamer or an anti-foaming agent is a chemical additive that reduces and hinders the formation of foam in industrial process liquids. The terms anti-foam agent and defoamer are often used interchangeably [1]. A defoamer is normally used in industrial processes to increase speed and reduce other problems.

1.4.10. Shampoos

Shampoo is a hair care product used for the removal of oils, dirt, skin particles, dandruff, environmental pollutants and other contaminant particles that gradually build up in hair [1].

1.5. The Chemistry of Corrosion

As in all chemical reactions, corrosion reactions occur through an exchange of electrons. In electrochemical reactions, the electrons are produced by a chemical reaction in one area, the anode, travel through a metallic path and are consumed through a different chemical reaction in another area, the cathode. In some cases, such as the common dry cell battery, electrochemical reactions can be used to supply useful amounts of electrical current.

Components

In order for electrochemical reactions to occur, four components must be present and active. These components are the anode, cathode, electron path, and electrolyte.

1. Anode

In an electrochemical cell, the anode is the site where electrons are produced through the chemical activity of the metal. The anode is the area where metal loss occurs, the reaction is called oxidation. The metal loses electrons and migrates from the metal surface through the environment. The electrons remain in the metal but are free to move about in response to voltage gradients.

2. Cathode

The cathode in an electrochemical cell is the site where electrons are consumed. For each electron that is produced at an anodic site, an electron must be consumed at a cathodic site. No metal loss occurs at sites that are totally cathodic.

3. Electrolyte

Electrolytes are solutions that can conduct electrical currents through the movement of charged chemical constituents called ions. Positive and negative ions are present in equal amounts. Positive ions tend to migrate away from anodic areas and toward cathodic areas. Negative ions tend to migrate away from cathodic areas and towards anodic areas.

4. Anodic reactions

Metal loss at anodic sites in an electrochemical cell occurs when the metal atoms give up one or more electrons and move into the electrolyte as positively charged ions.

Typical reactions

The generic chemical formula for this metal loss at anodic sites is:

$$M \text{ ---> } M^{+} + e^{-} \qquad (1:1)$$

where, M = uncharged metal atom at the metal surface

M^{+} = positively charged metal ion in the electrolyte

e^{-} = electron that remains in the metal

This type of chemical reaction is called oxidation even though it does not directly involve oxygen but only results in an increase in positive charge on the atom undergoing oxidation.

More than one electron can be lost in the reaction as in the case for iron where the most common anodic reaction is:

$$Fe \text{ ---> } Fe^{2+} + 2e^{-} \qquad (1:2)$$

where, Fe = metallic iron

Fe^{2+} = ferrous ion that carries a double positive charge

5. Cathodic reactions

The electrons that are produced at anodic sites are consumed at cathodic sites. The types of chemical reactions that consume electrons are called reduction and have the generic chemical formula:

$$M^{z+} + ze^{-} \text{ --> } M^{o} \qquad (1:3)$$

where, M^{+} = a positive ion in solution

e^{-} = an electron in the metal

M^{o} = the reduced chemical

During corrosion of steel in contact with water the cathodic reactions usually is:

$$O_2 + 2H_2O + 4e^{-} \text{ -----> } 4OH^{-} \qquad (1:4)$$

The final reaction in the chemistry of corrosion is the formation of iron oxides:

$$Fe^{2+} + 2\,OH^{-} \text{ ------> } Fe(OH)_2 \qquad (1:5)$$

$Fe(OH)_2$ will then react to give Fe_2O_3 and Fe_3O_4 (rust)[20].

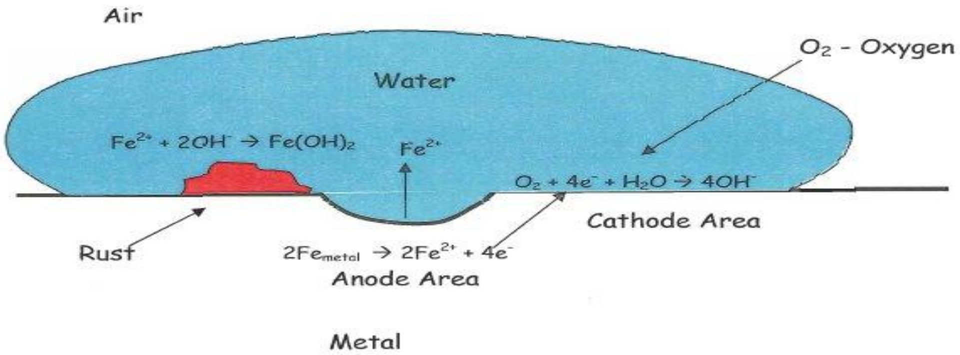

Fig. (1:6): Sschematic of iron corrosion.

1.6. Corrosion definition

The word “corrosion” stands for material or metal deterioration or surface damage in an aggressive environment. Corrosion is a chemical or electrochemical oxidation process, in which the metal transfers electrons to the environment and undergoes a valence change from zero to a positive value. The environment may be a liquid, gas or hybrid soil-liquid. These environments are called electrolytes since they have their own conductivity for electron transfer [21].

Millions of dollars are lost each year because of corrosion. Much of this loss is due to the corrosion of iron and steel, although many other metals may corrode as well. The problem with iron as well as many other metals is that the oxide formed by oxidation does not firmly adhere to the surface of the metal and flakes off easily causing "pitting" [22, 23].

Corrosion products (rust) may act as a barrier between the metal and its surroundings, slowing down the corrosion rate. In some cases this barrier very effectively retards corrosion. This is called passivation [21]. Passivation can increase the corrosion resistance of metal remarkably.

1.7. Corrosion types

Corrosion can be divided into different groups according to their form of occurrence [20].

1. Dry corrosion

The dry corrosion is the corrosion of the metal that takes place in the absence of conducting (aqueous) medium. The reaction between metal and oxygen (atmosphere) at elevated temperatures in perfectly dry conditions is an example of dry corrosion [22].

At room temperature, most metals carry a thin oxide layer as a result of the reaction of metals with oxygen in the atmosphere. Increase of temperature may cause formation of a heavier layer, or the layer may detach [24]. Some corrosion takes place even under completely dry conditions.

2. Wet corrosion

Wet corrosion takes place in environments where the relative humidity exceeds 60 %. The corrosion may be uniform destruction of the metal surface or localized destruction (pitting, stress corrosion cracking). The corrosion can be concentrated adjacent to a more noble metal or at points where the oxygen supply is limited [24].

Wet corrosion is an electrochemical phenomenon. When two metals are in contact with water solution containing salts, an electric potential is formed between two different metals or the surfaces of the same metal with different surface conditions. This causes the dissolution of the less noble metal. The more noble metal remains protected but the less noble metal corrodes [26].

Wet corrosion is most efficient in water containing salts, such as NaCl (e.g. marine conditions), due to the high conductivity of the solution. Chlorides also may increase the corrosion rate of metals.

1.8. Corrosion control

Corrosion protection refers to a situation in which all the inherent factors to prevent corrosion have been optimized and external intervention is deemed necessary to minimize the corrosion There are a number of means of controlling corrosion. The choice of a means of corrosion control depends on economics, safety requirements, and a number of technical considerations. Corrosion protection can be achieved by: (i) use of protective coatings, (ii) Cathodic protection, (iii) Anodic protection and (iv) addition of inhibitors.

1.8.1. Protective Coatings

Protective coatings are the most commonly used method of corrosion control. Coating is an effective method to control corrosion. Coatings must have the following characteristics for good corrosion resistance:

a) A high degree of adhesion to the substrate

b) Minimum discontinuity in coating (porosity)

c) A high resistance to the flow of electrons

d) A sufficient thickness (the greater the thickness, the more the resistance)

e) A low diffusion rate for ions such as Cl^- and for H_2O.

There are three general classes of coatings: organic, inorganic, and metallic coatings. However, protective coatings often refer to integrated multifunctional systems that may combine more than one type of coatings.

a) Organic coatings

Organic coatings protect more metal on a weight basis than any other means of corrosion protection. Besides providing protection by creating a physical barrier between the metal and the environment, these coatings may also contain corrosion inhibitors or other additives to stifle corrosion processes. Organic coatings include paints, resins, lacquers, and varnishes.

b) Inorganic coatings

Inorganic coatings include enamels, glass linings, and conversion coatings. Porcelain enamel coatings are inert in water and resistant to most weathers.

c) Metallic coatings

Metallic coatings also create a barrier between the metal substrate and the environment. In addition, metallic coatings can sometimes provide cathodic protection when the coating is compromised [25]. The use of organic or metallic barrier coatings between a possibly aggressive environment and a material surely has become the most widely used method of protecting most engineered materials.

1.8.2. Cathodic Protection

Cathodic protection is an electrical means of corrosion control. Cathodic protection can be applied using sacrificial (galvanic) anodes or by means of more complicated impressed current systems.

Cathodic protection is probably the most important of all approaches to corrosion control. Using an externally applied electric current, corrosion is reduced essentially to zero. A metal surface that is cathodically protected can be maintained in a corrosive environment without deterioration for an indefinite time. There are two types of cathodic protection: impressed current cathodic protection (ICCP) and sacrificial anode cathodic protection (SACP), also known as galvanic cathodic protection [26].

1.8.3. Anodic Protection

Reduction in corrosion, achieved by making a metal structure anode (positive electrode) with a low voltage direct current so that it attains and retains an electrochemically passive state in a particular environment. Developed anodic protection is more suitable than cathodic protection for certain metals such as stainless steels specially in extremely corrosive environments, as in the handling and storage of concentrated sulfuric (sulphuric) acid.

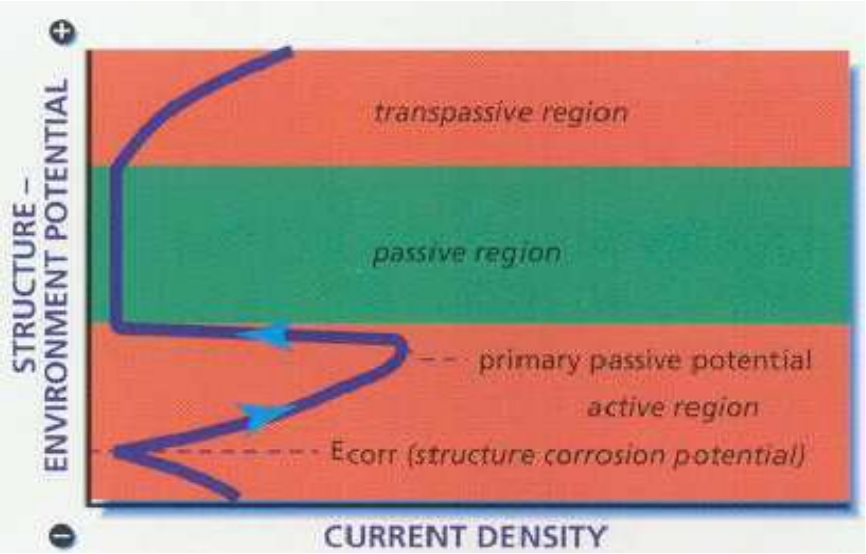

Fig. (1:7): Relation between potential and current density.

1.8.4. Corrosion inhibitor

An inhibitor is a chemical substance which, when added in small concentrations to corrosive environment effectively decreases or prevents the reaction of the metal with the environment [1]. Inhibitors often work by adsorption on the metallic surface and protect it by forming an isolating film. One important corrosion inhibition tool is the use of surfactant as inhibitor [27]. Some organic compounds such as amines [28, 29], aminothiols [30, 31], acetylenic compounds [32, 33], and a number of ionic surfactants such as alkyl pyridinium [34], and alkyl dimethyl-ammonium bromide [35, 36] have been studied.

Electrochemically inhibitors slow the corrosion processes by increasing the anodic or cathodic polarization behavior, reducing the movement or diffusion of aggressive ions to the metallic surface or by increasing the electrical resistance of the metallic surface. In oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion.

1.9. Classification of inhibitors

Inhibitors are chemicals that react with a metallic surface, or the environment this surface is exposed to, giving the surface a certain level of protection. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [37]. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation [38]. Inhibitors slow corrosion processes by either: Increasing the anodic or cathodic polarization behavior (Tafel slopes); Reducing the movement or diffusion of ions to the metallic surface; Increasing the electrical resistance of the metallic surface [39].

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

i. Passivating inhibitors
ii. Cathodic inhibitors

iii. Organic inhibitors
iv. Precipitation inhibitors
v. Volatile corrosion Inhibitor

1.9.1. Passivating (Anodic) Inhibitors

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

Oxidizing anions, such as chromate, nitrite and nitrate that can passivate steel in the absence of oxygen. Non oxidizing ions such as phosphate, tungstate and molybdate that are require the presence of oxygen to passivate steel. These inhibitors are the most effective and consequently the most widely used [40]. Chromate based inhibitors are the least expensive inhibitors and were used until recently in a variety of applications, e.g. recirculation-cooling systems of internal combustion engines, rectifiers, refrigeration units, and cooling towers.

In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason it is essential that monitoring of the inhibitor concentration be performed [40].

1.9.2. Cathodic inhibitors

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

i. Cathodic poisons
ii. Cathodic precipitates
iii. Oxygen scavenger

Some cathodic inhibitors, such as compounds of arsenic and antimony, work by making the recombination and discharge of hydrogen more difficult. Other cathodic inhibitors, ions such as calcium, zinc or magnesium, may be precipitated as oxides to form a protective layer on the metal. Oxygen scavengers help to inhibit corrosion by preventing the cathodic depolarization caused by oxygen. The most commonly used oxygen scavenger at ambient temperature is probably sodium sulfite (Na_2SO_3) [40, 41].

1.9.3. Organic Inhibitors

Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors but, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors usually designated as 'film-forming', protect the metal by forming a hydrophobic film on the metal surface. The effectiveness of these inhibitors depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors. Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines, or anionic inhibitors, such as sulfonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The adsorption behavior of surfactants at the solid/solution interface is described by many references [42, 43]. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors.

1.9.4. Precipitation Inhibitors

Precipitation inducing inhibitors are film forming compounds that have a general action over the metal surface, blocking both anodic and cathodic sites indirectly. Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film [40].

The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water.

1.9.5. Volatile Corrosion Inhibitors

Volatile Corrosion Inhibitors (VCI), also called Vapor Phase Inhibitors (VPI), is compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH towards less acidic and corrosive values. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine are used. On contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods [40].

1.10. Gemini surfactants as corrosion inhibitors

Gemini (also called dimeric) surfactants represent a new class of surfactants made up of two identical or different amphiphilic moieties having the structure of conventional (monomeric) surfactants connected by a spacer group [44]. The first report on gemini surfactants in the scientific literature is that of Bunton et al [45]. These authors synthesized bisquaternary ammonium bromide gemini surfactants and studied how the micelles of these surfactants affect the rate of chemical reactions. The variety of gemini surfactants that have been synthesized to this day is already enormous. It includes anionic, cationic, zwitterionic, and non-ionic surfactants with all kinds of spacer group. Gemini surfactants with alkylaryl or perfluorinated chains [46] are now available. Raw materials are starting to be used for the synthesis of gemini surfactants. The first studies of gemini surfactants [47, 48] and other ones emphasized the low critical micelle concentration (CMC), high efficiency by reducing the surface tension of water, and micelle structural characteristics of gemini surfactants. Devinsky et al. [49] reported on the relationship between the structure and surface activity of four series of cationic dimeric surfactants and on their high antimicrobial activity [50]. Gemini surfactants as corrosion inhibitors for pipelines carbon steel in acidic media have been studied [51-57].

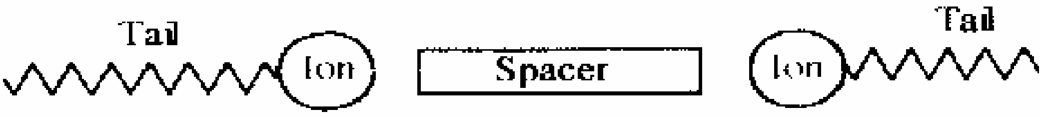

Fig. (1:8): Schematic sketch of gemini surfactant molecule.

There are several reasons for the current interest in gemini surfactants in both the academic and the industrial circles working on surfactants.

1. Gemini surfactants are characterized by CMC's that are one to two orders of magnitude lower than for the corresponding conventional (monomeric) surfactants.
2. Gemini surfactants are much more efficient than the corresponding monomeric surfactants in decreasing the surface tension of water.

3. Aqueous solutions of some gemini surfactants with a short spacer can have a very high viscosity at a relatively low surfactant concentration, whereas the solution of the corresponding monomeric surfactant remains low viscous.

4. Gemini surfactants show other favorable features or properties. Thus, they increase wetting, promote emulsification of oil in water, enhance dispersion of solids, and possess a high foaming stability. They can also show better solubilizing properties, stronger tolerance to multivalent metal ions, stronger antimicrobial ability, a good mildness to skin owing to their low cmc values, safe ecology, and environmental control. Finally, some gemini surfactants can be manufactured at a reasonable cost.

5. Several recent articles emphasize the importance of Gemini surfactants in biological sciences.

Gemini surfactants bis-quaternary ammonium compounds m-2-m has been investigated as potential inhibitors of corrosion of iron in 1M HCl by different techniques [58–61]. The results showed that the gemini surfactants act mainly as cathodic inhibitors by adsorbing on the electrode surface and forming a protective layer [62]. The efficiency plateau at high concentration is attributed to the formation of a full bimolecular surfactant layer on the iron surface.

1.11. Adsorption isotherms

As far as inhibition process is concerned, it is generally assumed that the adsorption of inhibitor at metal/solution interface is the first step in the action mechanism of inhibitors in aggressive acid media. Four types of adsorption may take place in the inhibiting phenomena involving organic molecules at metal/solution interface, namely:

i. Electrostatic attraction between charged molecules and the charged metal.
ii. Interaction of electron pairs in the molecule with the metal.

iii. Interaction of electrons with the metal.

iv. A combination of all above [63].

Chemisorption involves charge sharing or charge transfer from coordinate bond. In fact, electron transfer is typical for transition metals having vacant, low energy electron orbital. Concerning inhibitors, electron transfer can be expected with compounds having relatively loose bound electrons [64]. This situation may arise because of the presence in the adsorbed inhibitor of multiple bonds or aromatic rings, having a π-bound character [65-70]. The inhibition efficiency of homologous series of organic substances, differing only in the hetero atom, is usually in the following sequence: P > Se > S > N > O. Interpretation may be found in the easier polarizability and lower electronegativity of the elements on the left in the above sequence [71].

As substitutional adsorption process occurs between the inhibitor molecule, I, in the aqueous phase, and the water molecules adsorbed on the electrode surface, $H_2O_{(s)}$ [72].

$$I_{(aq)} + x\, H_2O_{(s)} \rightarrow I_{(s)} + x\, H_2O_{(aq)} \qquad (1:6)$$

where, x is the size ratio which represents the number of adsorbed water molecules replaced by a single inhibitor molecule. The above process reaches equilibrium in which the chemical potential μ on the left side equal to that of the right side.

Now, depending on the expression of (i), as related to the physical model adopted to describe adsorption, one may obtain different expressions of adsorption isotherm.

For instance, the most used expressions are:

- **Frumkin [73].** $(\Theta/1-\Theta)\, e^{(-2a\,\Theta)} = K.C.$ (1:7)

where, (Θ) is the degree of coverage, (a), is a molecular interaction parameter depending on the molecular interaction in the adsorption layer and the degree of heterogeneity of the surface. It can have both positive and negative values and in a measure of the steeples of the adsorption isotherm. The more positive value of (a), the steeper is the adsorption isotherm. This has been interpreted [74] to imply those interactions between molecules with values and a measure of the steeples of the adsorption isotherm. The more positive value of (a), the steeper is the adsorption isotherm. This has been interpreted [75] to imply those interactions between molecules with positive (a) value cause an increasing in the adsorption energy with the increasing of (Θ), (K) is the equilibrium constant of the adsorption reaction, and (C) is the inhibitor concentration in the bulk of the solution.

- **Hill de Boer [75].** $(\Theta/1\text{-}\Theta)\ e^{(\Theta/1-\Theta)\ (-2a\ \Theta)} = K.C.$ (1:8)
- **Parson [76]** $(\Theta/1\text{-}\Theta)\ e^{(2-\Theta/1-\Theta)\ (-2a\ \Theta)} = K.C.$ (1:9)
- **Temkim [75]** $a\Theta = \ln K.C$ (1:10)
- **Flory-Huggins [77]** $\Theta/X(1-\Theta)^{x} = K.C$ (1:11)
- **Dahr et al [78]** $\Theta/[e^{(x-1)}(1-\Theta)^{x} = K.C$ (1:12)
- **Freundlich [79]** $\Theta = K.C^{n}$ (1:13)

where, x is the number ofwater molecules replaced by one molecule of organic adsorbate.

Basically, all above isotherm are of the form [80]:

$$F\ (\Theta,\ X)\ e^{(-a\ \Theta)} = K.C \qquad (1:14)$$

where, F(Θ,X) is the configurationally factor which depends essentially on the physical model and assumption underlying derivation of the isotherm[81].

Moreover, all above expressions include the equilibrium constant of the adsorption process (K) which is related to stander free energy of the adsorption ΔG°_{ads} by [73]:

$$K = 1/55.5e^{(-\Delta G^{\circ}ads\ /RT)} \qquad (1:15)$$

Equation (1:14) and (1:15) have been used to evaluate the most suitable isotherm describing the adsorption inhibitors on the electrode surface.

- **Langmuir.** $C/\Theta = 1/K+C$ (1:16)

K is the equilibrium constant of the adsorption process [82].

1.12. Literature survey on corrosion inhibition of C-steel in aqueous solution.

The corrosion behavior of carbon steel in 1MHCl solution in the absence and presence of three compounds of ethoxylated fatty amide (non ionic surfactant) was studied using weight loss and galvanostatic polarization techniques [83]. The percentage inhibition efficiency was found to increase with increasing of inhibitor concentrations, number of ethylene oxide unit and with decreasing temperature. The inhibitive action of these compounds was discussed in term of adsorption on the steel surface through ethylene oxide unit while the hydrocarbon parts protrude brush-like into the solution. The adsorption process follows Langmuir adsorption isotherm. The effect of temperature on the rate of corrosion in the absence and presence of these compounds was also studied. Some activated thermodynamic parameters were calculated.

The effect of chain length compatibility on corrosion inhibition effect of mixed inhibitor systems of cationic gemini surfactant (l,3-butan-bis(dodecyl dimethyl ammonium bromide) (designated as 12-4-12)), nonionic co-surfactants (C_7OH (1-heptanol), $C_{12}OH$ (1-dodecanol) and $C_{15}OH$ (1-pentadecanol)) on low carbon steel in acidic medium was studied using weight loss, open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) measurements [84]. Data represented that the corrosion rate decreased by increasing surfactant concentration. In addition, less chain length difference causes more compatibility and inhibition efficiency on behavior of surfactant and co-surfactant mixture. Increasing of inhibition efficiency for $C_{12}OH$ + gemini surfactant was more than other mixtures.

The inhibition effect of novel nonionic surfactants on the corrosion of carbon steel (CS) in 1M HCl was studied at different temperatures (20–60°C) by weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods [85]. The CS surface morphology was investigated by SEM. The obtained results showed that the prepared nonionic surfactants are excellent inhibitor in 1 M HCl, and the inhibition efficiency (η) increases with the inhibitor concentration and temperature increasing. The adsorption of inhibitors on the CS surface obeys the Langmuir adsorption isotherm equation. Thermodynamic parameters have been obtained by adsorption theory. Polarization curves show that the synthesized inhibitors are mixed-type inhibitors in hydrochloric acid.

The corrosion inhibition of cationic gemini surfactant, in the absence and presence of halide salts (NaCl, NaBr and NaI) on steel in HCl was investigated at 20 ±1°C [86]. The effects of pH, immersion time and salt concentration on the corrosion inhibition of steel were studied using weight loss, open circuit potential and electrochemical impedance spectroscopy. Inhibition efficiency increases by increasing surfactant concentration. Synergistic effect between surfactant and salts was studied. The inhibition efficiency increases by increasing salt concentration. This composite inhibitor containing gemini surfactant and halide was efficient and low-cost for steel corrosion inhibition in HCl.

The cationic gemini-surfactant, namely 1,4-bis (1-chlorobenzyl-benzimidazolyl)-butane (CBB) was synthesized and its inhibition effect on the corrosion of mild steel in 0.5M HCl solution was studied by weight loss and electrochemical techniques [87]. The results showed that

CBB acts as an excellent corrosion inhibitor in 0.5M HCl solution by suppressing simultaneously the cathodic and anodic processes via chemical adsorption on the surface of steel, which followed the Langmuir adsorption isotherm. The inhibition efficiency increased with the increase of CBB concentration and temperature. The adsorption mechanism of the compound was discussed in terms of thermodynamic and kinetic parameters deduced from the experimental data.

The corrosion inhibition characteristics of non-ionic surfactants of the TRITON-X series, known as TRITON-X-100 (TX-100), TRITON-X-165 (TX-165) and TRITON-X-305 (TX-305), on the corrosion of iron in 1M HCl solution were studied [88]. Measurements were conducted in 1M HCl solutions without and with various concentrations of the three selected surfactants using chemical (inductively coupled plasma atomic emission spectroscopy (ICP-AES) method of analysis of dissolved cations) and electrochemical (Tafel polarization and EFM) techniques at 25°C. These measurements were complemented with SEM and EDX examinations of the electrode surface. Polarization data showed that the non-ionic surfactants used in this study acted as mixed-type inhibitors with cathodic predominance. The protection efficiency increased with increase in surfactant concentration. Maximum protection efficiency of the surfactant was observed at concentrations around its CMC. From their molecular structure, these surfactants may adsorb on the metal surface through two lone pairs of electrons on the oxygen atoms of the hydrophilic head group.

The corrosion inhibition of carbon steel in HCl and H_2SO_4 solutions in the presence of some benzimidazole derivatives such as benzimidazole (BI), 2-methylbenzimidazole (2-CH_3-BI) and 2-mercapto-benzimidazole (2-SH-BI) was studied using potentiodynamic polarization technique [89]. Results obtained showed that the benzimidazole derivatives retard both the cathodic and anodic reactions in both acidic media, by virtue of adsorption on the carbon steel surface. This adsorption obeyed Langmuir's adsorption isotherm. In the both media, 2-SH-BI showed the highest efficiency while the lowest efficiency was observed for BI. The comparative analysis of the inhibitor adsorption in both the media, as well as, the synergistic effect of bromide ions (Br^-) in H_2SO_4 solution suggests that the physical adsorption of the cationic form of BI and 2-CH_3-BI occurs, while 2-SH-BI is adsorbed chemically.

The corrosion inhibition of mild steel in 1M HCl solution by four Schiff bases was investigated using weight loss, electrochemical measurements and quantum chemical calculations [90]. All compounds showed >90% inhibition efficiency at their optimum concentrations. The activation energy (E_a) of corrosion and other thermodynamic parameters were calculated to elaborate the mechanism of corrosion inhibition. The adsorption of the inhibitors on the mild steel surface follows Langmuir isotherm model. Polarization studies indicated that all studied inhibitors are mixed type. The computed quantum chemical properties viz., electron affinity (EA) and molecular band gap (ΔE_{MBG}) show good correlation with experimental inhibition efficiencies.

Heterocyclic Schiff base furoin thiosemicarbazone as corrosion inhibitor towards mild steel in 1M HCl solution was studied using weight loss, Tafel polarization and electrochemical impedance spectroscopy techniques [91]. Furoin thiosemicarbazone revealed good corrosion inhibition efficiency even at low concentrations towards mild steel in HCl medium. Comparison of corrosion inhibition efficiency of Schiff base and its parent amine and effect of temperature on inhibition efficiency were also investigated. The adsorption of furoin thiosemicarbazone on mild steel surface obeys Langmuir isotherm.

The adsorption and inhibition effect of cefazolin on mild steel in 1M HCl at 308–338K was studied by weight loss, EIS, potentiodynamic polarization and atomic force microscopy techniques [92]. The results showed that inhibition efficiency increased with inhibitor concentration. The adsorption of cefazolin on mild steel surface obeys the Langmuir adsorption isotherm equation. Both thermodynamic (enthalpy of adsorption ΔH_{ads}, entropy of adsorption ΔS_{ads} and free energy of adsorption ΔG_{ads}) and kinetic parameters (activation energy ΔE_a and pre-exponential factor A) were calculated and discussed. Polarization curves showed that cefazolin acted as mixed-type inhibitor controls predominantly cathodic reaction.

Hegazy [93] studied the corrosion inhibition characteristics of the synthesized cationic gemini surfactants, namely bis(p-(N,N,N-decyldimethyl- ammonium bromide)benzylidenethiourea (10-S-10), bis(p-(N,N,N-dodecyldi- methylammonium bromide)benzylidene thiourea (12-S-12) and bis(p-(N,N,N-tetradecyldimethylammonium bromide)benzylidene thiourea (14-S-14) on the carbon steel corrosion in 1M HCl have been investigated at 25°C by weight loss, potentiodynamic polarization and (EIS) techniques. The inhibition efficiencies obtained from all methods employed are in good agreement with each other. The obtained results show that compound 14-S-14 is the best inhibitor with an efficiency of 97.75% at $5x10^{-3}$M additive concentration. The inhibition efficiency increased with increase of the inhibitor concentration. Changes in impedance parameters (charge transfer resistance, R_{ct}, and double-layer capacitance, C_{dl}) were indicative of adsorption of 14-S-14 on the metal surface, leading to the formation of a protective film. The potentiodynamic polarization measurements indicated that the inhibitors are of mixed type. The adsorption of the inhibitors on the carbon steel surface in the acid solution was found to obey Langmuir’s adsorption isotherm. The free energy of adsorption processes were calculated and discussed. The surface parameters of each synthesized surfactant were calculated from its surface tension including the critical micelle concentration (CMC), maximum surface excess (Γ_{max}) and the minimum surface area (A_{min}). The free energies of micellization (ΔG^{o}_{mic}) were calculated. The surface morphology of carbon steel sample was investigated by scanning electron microscopy (SEM).

Deyab et al [94] studied the conductivity, weight loss and A.C. impedance to establish the influence the presence of neutral copolymer (vinylpyrrodlidone /vinyl acetate copolymer) with anionic surfactant (AS) (Disodium laurethsulfosuccinate) in cyclohexane propionic acid (CHPA) on the corrosion behaviour of carbon steel. The protection efficiency (P%) of AS in the absence and presence of polymer increases with increase in AS concentration until it reaches a maximum constant value near the CMC of AS and decreases with increase in solution temperature. The protective efficiency of AS can be enhanced and its critical micelle concentration shifts to low value by adding of 0.05g/l of polymer. The critical micelle concentration of AS in the absence and presence of polymer increases with increase in temperature. The calculated thermodynamic parameters of micellization (ΔG_{mic}), (ΔH_{mic}) and (ΔS_{mic}) in the presence of neutral copolymer molecules with AS show that these processes are spontaneous and exothermic in nature and indicate the association between AS and neutral copolymer molecules.

The inhibiting effect of 12-aminododecanoic acid (AA) on the corrosion of carbon steel (CS) in CO_2-saturated hydrochloric acid was investigated [95]. It was found that AA acts as a mixed-type inhibitor, yielding a maximum inhibition efficiency of $98.1 \pm 0.1\%$. The mechanism of its corrosion inhibition is by formation of a self-assembled monolayer (SAM), which presents a tight hydrophobic barrier imposed by the $(-CH_2)_{11}$ chain. In-situ PM-IRRAS measurements revealed that the SAM is amorphous. The SAM formation process was found to be spontaneous and reversible. The corresponding standard Gibbs energy of AA adsorption on CS was calculated to be −28 kJ mol^{-1}.

Migahed et al [96] synthesized the dodecyl cysteine hydrochloride surfactant. The surface properties of this surfactant were studied using surface tension technique. The nanostructure of this surfactant with the prepared gold nanoparticles was investigated using TEM technique. The synthesized surfactant and its nanostructure with the prepared gold nanoparticles were examined as non-toxic corrosion inhibitors for carbon steel dissolution in 2M HCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results show that the percentage inhibition efficiency for each inhibitor increases with increasing concentration until critical micelle concentration (CMC) is reached. The maximum inhibition efficiency approached 76.6 % in the presence of 175 ppm of dodecyl cysteine and 90.8% in the presence of the same concentration of dodecyl cysteine hydrochloride self-assembled on gold nanoparticles. Polarization data indicate that the selected additives act as mixed type inhibitors. The slopes of the cathodic and anodic Tafel lines (β_c and β_a) are approximately constant and independent of the inhibitor concentration. Analysis of the impedance spectra indicates that the charge transfer process mainly controls the corrosion process of carbon steel in 2M HCl solution both in the absence and presence of the inhibitors. Adsorption of these inhibitors on carbon steel surface is found to obey the Langmuir adsorption isotherm. The relatively high value of (K_{ads}) in case of dodecyl cysteine hydrochloride self-assembled on gold nanoparticles reveals a strong interaction between the inhibitor molecules and the metal surface

The inhibition ability of benzimidazole and its derivatives against the corrosion of mild steel in 1M HCl solution was studied [97]. The change of impedance parameters observed by variation of inhibitors concentration within the range of 50–250 ppm was an indication of their adsorption. The thermodynamic adsorption parameters proposed that these inhibitors retard both cathodic and anodic processes through physical adsorption and blocking the active corrosion sites. The adsorption of these compounds obeyed the Langmuir's adsorption isotherm. The inhibition efficiency was increased with inhibitor concentration in the order of 2-mercaptobenzimidazole > 2-methylbenzimidazole > benzimidazole, which is in accordance with the variation of apparent activation energy of corrosion.

The corrosion inhibition effect of cationic surfactants, DTAB (dodecyl trimethyl ammonium bromide) and TTAB (tetradecyl trimethyl ammonium bromide), on low carbon steel was studied by weight loss, open circuit potential (OCP) and (EIS) measurements [98]. The effect of chain length compatibility on corrosion inhibition of surfactant and co-surfactant was investigated by C_7OH (1-heptanol), $C_{12}OH$ (1-dodecanol) and $C_{15}OH$ (1-pentadecanol) as nonionic co-surfactants in acidic media at different concentrations of DTAB and TTAB. Data represented that the corrosion rate decreased by increasing concentration of DTAB and TTAB, independently. The effect of chain length compatibility on surfactant behavior was discussed. Decreasing of corrosion rate for DTAB + $C_{12}OH$ was more pronounced than other mixtures.

The inhibition of C-steel in 2M HCl in the absence and presence of different concentrations of some thiosemicarbazide derivatives namely, 1-ethyl-4(2,4-dinitrophenyl)thiosemicarbazide (I), 1, 4-diphenylthiosemicarbazide (II), 1-ethyl-4-phenylthiosemicarbazide (III) was studied by weight loss, potentiodynamic polarization and (EIS) techniques [99].

Impedance measurements showed that the double-layer capacitance decreased and charge-transfer resistance increased with increase in the inhibitors concentration and hence increasing in inhibition efficiency. Potentiodynamic polarization study showed that all the inhibitors act as mixed-type inhibitors. Results obtained reveal that the inhibition efficiency (%IE) follows the sequence: I > II > III. The adsorption of these compounds on C-steel surface obeys Temkin's adsorption isotherm and has a chemisorptions mechanism.

Abdallah et al [100] studied the inhibition effect of Ni^{2+} cation, 3-methyl pyrazolone (3-MP) and mixture of them on the corrosion of carbon steel in 0.5M H_2SO_4 solution using weight loss, galvanostatic and potentiodynamic anodic polarization techniques. The inhibition efficiency increases with increasing concentration of Ni^{2+} and 3-MP. The mixtures of Ni^{2+} and 3-MP improved the inhibition efficiency. The formation of complex compound was discussed depending on the results derived from UV–visible spectrophotometric measurements as well as conductometric titration.

The change of open circuit potential (OCP) with immersion time, Tafel polarization, and electrochemical impedance spectroscopy (EIS) was studied to investigate the corrosion inhibitor layer forming on mild steel surface. 4-Amino-5-phenyl-4H-1, 2, 4-trizole-3-thiol (APTT) was used through out the experiments as the corrosion inhibitor in this study [101]. The investigation was conducted under hydrodynamic conditions with different pickling solutions of 0.5M HCl and 2.5M H_2SO_4 solution at 30°C.The hydrodynamic conditions experiments were simulated using the rotating cylinder electrode (RCE). In both solutions, the values of OCP were shifted to more positive direction, the corrosion current densities were decreased, and charge transfer resistances were increased with flow velocity, respectively. The fitted data recoded from EIS were in line with those of polarization measurements. Experimental results obtained from change of OCP with immersion time, Tafel polarization, and EIS measurements showed indicated that the formation and the development of the inhibitor layer in both pickling solutions were flow velocity dependence.

Polyethylene terephthalate waste (PET) was depolymerized by triethanolamine into glycolyzed product (GT), followed by esterification with bromacetic acid in the presence of manganese acetate as a catalyst to give (GT-Br) [102]. The obtained ester was reacted with thiourea to give thiol derivative (GT-SH). The effectiveness of the synthesized compound as corrosion inhibitor for API XL65 carbon steel, in 2 M hydrochloric acid solution was investigated by various electrochemical techniques such as open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results of these investigations showed enhancement in inhibition efficiencies with the increasing of inhibitor concentration. The protective film formed on carbon steel surface was analyzed using an energy dispersive X-ray analysis (EDX) technique. Also, scanning electron microscope (SEM) was used to study the surface morphology of steel surface in the absence and presence of 400 ppm of the additive.

The inhibitive effect of N,N-ortho-phenylen acetyle acetone imine (S1) and 4-[(3-{[1-(2-hydroxyphenyl)methylidene]amino}propyl]ethanemidol]-1,3-benzenediol (S2) in the concentration range of 50–400ppm for mild steel with two different microstructures resulted from two different heat treatments (annealed (A) and quenched and tempered (Q&T)) in 1M HCl solution was studied by ac impedance spectroscopy [103]. The tests were conducted in acid solutions in the absence and presence of different concentrations of S1 and S2 Schiff bases for both microstructures. A sole time constant was observed from Bode-phase angle plots in the presence of inhibitors which reveals that the action of inhibitors is through adsorption on the surface. The charge transfer resistance and inhibition efficiency increases with the increase in Schiff bases concentration for both microstructures. The perlite samples in the absence of inhibitors in 1M HCl indicated slightly less corrosion than martensite ones, which was because of more protective oxide layers. Furthermore in the presence of S1 and S2, these samples showed better adsorption than martensite one. Schiff base S1 showed a better inhibition against corrosion in comparison with S2. Both S1 and S2 adsorbed on steel surface according to a Langmuir adsorption isotherm model. The associated Gibbs free energies for S1 on both microstructures are more than S2.

The inhibition efficiency of acid extract of leaves of Citrus aurantiifolia [CAL] plant on the corrosion of mild steel in 1M HCl solution was studied by weight loss measurements and electrochemical studies [104]. The corrosion rate of mild steel and the inhibition efficiencies of the extract were calculated. The results obtained show that the extract could serve as an effective inhibitor for the corrosion of mild steel in HCl media. Inhibition was found to increase with increasing concentration of the plant extract. The inhibitive action of plant extract is discussed on the basis of adsorption of stable complex at the mild steel surface. Theoretical fitting of different isotherms, Langmuir, Temkin, Freundlich, Frumkin, Flory-Huggins and the kinetic thermodynamic model, were tested to clarify the nature of adsorption. Polarization curves revealed that this inhibitor act as a mixed type inhibitor and the inhibition efficiency of up to 97.51% can be obtained. The surface analysis study confirms the corrosion of mild steel and its inhibition by the inhibitor CAL.

The behavior of the Schiff base N,N′-bis(salicylidene)-1,2-ethylenediamine (Salen), its reduced form (N,N′-bis(2-hydroxybenzyl)-1,2-ethylenediamine) and a mixture of its preceding molecules, ethylenediamine and salicylaldehyde, as carbon steel corrosion inhibitors in $1\ \mathrm{mol\ L^{-1}}$ HCl solution was studied by corrosion potential measurements, potentiodynamic polarization curves, electrochemical impedance spectroscopy and spectrophotometry measurements [105]. The experimental results showed that the reduced Salen presented the highest efficiency among the inhibitors studied. The results obtained in the presence of Salen were similar to those obtained in the presence of the salicylaldehyde and ethylenediamine mixture, showing that in acid medium the Salen molecule undergoes hydrolysis, regenerating its precursor molecules.

Zaafarany [106] studied the effect of some phenyl phthalimide derivatives on the corrosion of carbon steel in 0.5M H_2SO_4 solution using weight loss and galvanostatic polarization techniques. The percentage inhibition efficiency was found to increase with increasing concentration of inhibitor and with decreasing temperature. Inhibition was explained by adsorption of these compounds on the metal surface. The adsorption follows Freundlich adsorption isotherms. Some thermodynamic functions were computed and discussed.

The inhibiting effect toward the corrosion of mild steel in nizoral (NZR), an antifungal drug, as mild steel corrosion inhibitor in 0.1M H_2SO_4 was studied by the weight loss method in the temperature range from 30–50°C [107]. Results obtained revealed that NZR acts as an inhibitor for mild steel in H_2SO_4 acid solution. Inhibition efficiency increased with increase in concentration of the inhibitor but decreased with increase in temperature. The addition of KI increased the inhibition of NZR to a considerable extent. The experimental results suggest that the presence of iodide ions in the solution stabilized the adsorption of Nizoral molecules on the mild steel surface thereby improving the inhibition efficiency of Nizoral. The adsorption characteristics of the inhibitor were approximated by Langmuir adsorption isotherm and kinetic/thermo-dynamic adsorption model of El-Awady et al. Mechanism of physical adsorption is proposed from the activation and thermodynamic parameters calculated.

The corrosion inhibition effect of cationic surfactants, Dodecyl Trimethyl Ammonium Bromide (DTAB) and Tetradecyl Trimethyl Ammonium Bromide (TTAB), on low carbon steel in 0.5M HCl solution was studied using weight loss, open circuit potential (OCP) and (EIS) measurements [108]. The effect of chain length compatibility on corrosion inhabitancy of surfactant and co-surfactant was investigated by C_7OH (1-heptanol), $C_{12}OH$ (1-dodecanol) and $C_{15}OH$ (1-pentadecanol) as nonionic co-surfactants in acidic media at different concentrations of DTAB and TTAB. Data represented that the corrosion rate decreased by increasing concentration of DTAB and TTAB, independently. The effect of chain length compatibility on surfactant behavior was discussed. Decreasing of corrosion rate for DTAB + $C_{12}OH$ was more pronounced than other mixtures.

The effect of synthesized tris-hydroxymethyl-(2-hydroxybenzyl-idenamino)-methane (THHM) as corrosion inhibitor of cold rolled steel (CRS) in 0.1M HCl solution was studied by Tafel polarization curve and electrochemical impedance spectroscopy (EIS). Polarization curve reveals the fact that THHM is a good cathodic type inhibitor [109]. EIS results confirm its corrosion inhibition ability. The inhibition efficiency increases with increasing THHM concentration but decreases with immersion time. Atomic force microscopy (AFM) reveals that a protective film forms on the surface of the inhibited sample. The adsorption of this inhibitor is found to follow the Langmuir adsorption isotherm.THHM adsorbs on the sample probably by chemisorption.

The corrosion behavior of carbon steel in 2M HCl solution with the addition of some cyanoacetohydrazide derivatives by weight loss, galvanostatic polarization, and potentiodynamic anodic polarization techniques [110]. The explored methods gave almost similar results. Results obtained reveal that inhibitor (I) is the best inhibitor and the inhibition efficiency (IE%) follows the sequence $I > II > III > IV$. The percentage inhibition efficiency was found to increase with increasing concentration of inhibitors and decreases with increasing temperature of the medium. The addition of KI, KSCN, and KBr to cyanoacetohydrazide derivatives enhanced the inhibition efficiency due to synergistic effect. The effect of temperature on C-steel corrosion in 2 M HCl and with the addition of 11×10^{-6} M of investigated compounds in the temperature range 30°-50°C was studied. Some thermodynamic functions were computed and discussed. The inhibitors are adsorbed on the carbon steel surface according to Temkin's adsorption isotherm. Polarization data suggested that the additives used act as mixed-type inhibitors. It was found that the cyanoacetohydrazide derivatives provide good protection to carbon steel against pitting corrosion in chloride-containing solutions.

The effect of 1-methyl-3-pyridin-2-yl-thiourea on the corrosion resistance of mild steel in H_2SO_4 solution was studied by different techniques [111]. The results show that the inhibition efficiency increases with the increase of inhibitor concentration. This compound affects both the anodic dissolution of steel and the hydrogen evolution reaction in 0.5 M H_2SO_4. The adsorption of this inhibitor is also found to obey the Langmuir adsorption isotherm. From the adsorption isotherm, value of the ΔG_{ads} for the adsorption process was calculated. From the corrosion rate obtained at 25–45±1°C, E_a, ΔH_a and possible mechanism have been proposed.

The effect of synthesized tris-hydroxymethyl-(2-hydroxybenzylidenamino)methane (THHM) on the corrosion of cold rolled steel (CRS) in 0.1M HCl solution was studied by Tafel polarization curve and electrochemical impedance spectroscopy (EIS) [112]. Polarization curves reveal the fact that THHM is a good cathodic type inhibitor. EIS results confirm its corrosion inhibition ability. The inhibition efficiency increases with increasing THHM concentration but decreases with immersion time. Atomic force microscopy (AFM) reveals that a protective film forms on the surface of the inhibited sample. The adsorption of this inhibitor is found to follow the Langmuir adsorption isotherm. THHM adsorbs on the sample probably by chemisorption.

Abdallah et al [113] studied the effect of some mono azo dye compounds on the dissolution of carbon steel (type L-52) in 2M HCl solution was studied using weight loss and galvanostatic polarization techniques. The inhibition efficiency was found to increase with increasing inhibitor concentration and decreasing temperatures. Inhibition was explained by formation of insoluble complex adsorbed on the metal surface. The adsorption follows Langmuir adsorption isotherm. The formation of stable complex was studied by conductometric titration. The stiochiometric ratio was found to be 1:1; 1:2 for Fe^{2+}/dye compounds and the mechanism of inhibition was explained in terms of these values. The thermodynamic functions of adsorption process was calculated and discussed.

The inhibiting effect of 3-[(E)-(phenylimino)methyl]quinoline-2-thione (PMQT), 3{(E)-[(4-chlorophenyl)imino]methyl}quinoline-2-thione (CPMQT) and 3{(E)-[(4-fluorophe-nyl)imino] methyl}quinoline-2-thione (FPMQT) toward the corrosion of mild steel in 1 mol dm^{-3} HCl was studied by mass loss, polarization and impedance (EIS) methods at 300K [114]. The investigated results showed that the corrosion rate decreased significantly with increase in the concentration of inhibitors. The shape of polarization profiles of all the three compounds indicated their mixed-type nature of inhibition. The inhibition efficiencies decreased in the order FPMQT>CPMQT>PMQT. The adsorption of the compounds on the mild steel surface obeys Langmuir's adsorption isotherm. The surface morphology of the tested mild steel specimens in the presence and absence of inhibitors was studied by using the respective images of SEM. FTIR studies were undertaken to confirm the interaction of molecules with surface atoms of the mild steel and established the adsorption process.

The corrosion inhibition effect of 3H-phenothiazin-3-one, 7-dimethylamin as a new inhibitor was studied by different electrochemical and weight loss methods [115]. It was found that this compound acts as a strong inhibitor for mild steel in 1M HCl even at very low concentration (1 ppm). Results showed that this compound acts as a mixed type inhibitor. As the inhibitor concentration increased, the charge transfer resistance of mild steel increased and double layer capacitance decreased. It was found that this inhibitor acts through adsorption on the metal surface. Also, adsorption obeys the Langmuir isotherm.

The corrosion inhibition effect of 4-{[(1Z)-(2-chloroquinolin-3-yl)methylene]amino}phenol(CAP),N-[(1Z)-(2-chloroquinolinyl)methylene]-N-(4-methoxyphenyl)amine (CMPA) and N-[(1E) -(2-chloroquinolin-3-yl)methylene]-N-(4-nitrophenyl)amine (CNPA) on mild steel in 1M HCl was studied using mass loss, polarization and electrochemical impedance techniques at 300 K [116]. The inhibition efficiencies increased with increase in inhibitors concentration. Polarization studies showed that the inhibitors are of predominantly cathodic character.

Among the three compounds studied, CAP exhibited the best performance giving more than 97 % IE. Some samples of mild steel were examined by SEM. All the inhibitors were found to adsorb on the mild steel surface according to the Langmuir adsorption isotherm.

The corrosion inhibition characteristics of N0-[(1E)-(4-hydroxy -phenyl)methylene]isonicotinohydrazide(HIH)& N0-[(1E)-(4-hydroxyl-3-methoxy phenyl) methylene]isonicotinohydrazide (HMIH) on mild steel corrosion in 1M HCl was studied by weight loss, potentiodynamic polarization and impedance techniques [117]. The inhibition efficiency increased with increase in inhibitor concentration but decreased with increase in temperature. The thermodynamic functions of dissolution and adsorption processes were evaluated. The polarization measurements indicated that the inhibitors are of mixed type. The adsorption of the compounds was found to obey Langmuir’s adsorption isotherm. Passive film characterization was done by Fourier transform infrared (FTIR) spectra and scanning electron microscopy (SEM).

The effectiveness and adsorption behaviour of aminobiphenyl (Aph) and 2-(3-hydroxybenzylideneamino) biphenyl (Aph-S), as corrosion inhibitors for mild steel (MS) in 0.5M HCl solution was studied by potentiodynamic polarization, linear polarization resistance (LP) and electrochemical impedance spectroscopy (EIS) techniques were applied to study the metal corrosion behaviour in the absence and presence of different concentrations of Aph and Aph-S [118]. In order to gain more information about adsorption mechanism the AC impedance technique was used to evaluate the potential of zero charge (PZC) from polarization resistance (Rp) versus voltage (E) plot. Potentiodynamic polarization measurements showed that Aph act as cathodic type inhibitor where as Aph-S act mixed type. The inhibition efficiency (IE %) increases with increasing concentration of compounds and reached 92.6 % for Aph and

97.2 % for Aph-S at 5×10^{-3}M. Double layer capacitance (C_{dl}) and polarization resistance (R_{p}) values are derived from Nyquist plots obtained from AC impedance studies. The experimental data fit Langmuir isotherm for both Aph and Aph-S, and from the adsorption isotherm some thermodynamic data for the adsorption processes are calculated and discussed. The effect of exposure time on the corrosion behaviour of mild steel in the absence and presence of inhibitor over 168 h was also studied.

The effect of temperature (15-65^{o}C) on the efficiency of succinic acid (SA), as an inhibitor, for the corrosion of a low cabon steel (LCS) electrode in aerated non-stirred 1M HCl solutions (pH 4) [119]. Weight loss, potentiodynamic polarization and EIS (electrochemical impedance spectroscopy) techniques were applied to study the metal corrosion behaviour in the absence and presence of different concentrations of SA in this temperature range.Results obtained showed that the inhibition efficiency decreases with increase in temperature, indicating that SA physisorbs on the electrode surface. Activation energies have been calculated in the absence and presence of various concentrations of SA by measuring the temperature dependence of the corrosion rate obtained from the three methods. The adsorptive behaviour of SA on the LCS surface follows Temkin-type isotherm. The standard free energies of adsorption are lower than 40 kJ mol^{-1}, confirming the physisorption of SA on the electrode surface. Surface analysis using EDX (energy dispersive X-ray) confirmed the results obtained from chemical and electrochemical measurements. All the results obtained from the methods employed are in reasonable agreement.

The inhibition effect of the Schiff bases $N,N^{\backslash}$-bis(salicylidene)-1,2-ethylenediamine (Salen), $N,N^{\backslash}$-bis(5-methoxysalicylidene)-1,2-ethylenediamine (MeO-Salen) and $N,N^{\backslash}$-bis(5-nitrosalicylidene)-1,2-ethylenediamine (NO2-Salen) on the corrosion of the mild steel in 1M HCl was studied by electrochemical impedance spectroscopy (EIS), linear Polarization resistance (LPR) and Tafel polarization measurements [120]. Maximum inhibition for MeO-Salen was obtained. Results showed that the inhibition efficiency have increased when the concentration of the Schiff bases have increased. Polarization curves revealed that the Schiff bases acted as anodic inhibitors. The surface adsorption of the Schiff bases has lead to a decrease in the double layer capacitance and to an increase in polarization resistance. The inhibitor performance depended strongly on the type of functional groups on benzene ring. The adsorption process is spontaneous one and follows Langmuir adsorption isotherm model. Scanning electron microscopy (SEM) has been applied to identify the surface morphology of the mild steel both in the absence and presence of the Schiff base molecules.

The inhibition effect of 2-(2-Hydroxybenzylideneamino)-2-methylpropane-1,3-diol(BAMP), 2-((2-hydroxynaphthalen-1-yl) methyleneamino)-2-methyl-propane-1,3-diol (NAMP), 2-((pyridin-2-ylimino) methyl) phenol (PMP) and N-(thiophen-2-ylmethylene)pyridin-2-amine (TMP) on the corrosion of mild steel in 2M HCl solution was studied by weight loss, polarization and electrochemical impedance spectroscopy techniques [121]. All measurements show that all compounds under study exhibit inhibitor properties for mild steel. Although the effect of molecular size on inhibition efficiency is observed from the results obtained between BAMP and NAMP, the introduction of heteroatoms into the structure is seen to be more pronounced eventhough the molecular size is diminished. TMP is seen to show the highest inhibitor efficiency of 97%.

The corrosion inhibition of cold rolled steel in 0.5 mol L^{-1} H_2SO_4 was studied by a quaternary ammonium gemini surfactant, l,3-propane-bis (dimethyldodecylammonium bromide) (designated as 12-3-12), in the absence and presence of chloride ions at different temperatures [55]. The results revealed significant synergistic effect between gemini 12-3-12 and chloride ions for the corrosion protection of cold rolled steel in H_2SO_4, and that the novel composite inhibitor system containing cationic gemini surfactant and chloride ions was efficient and low-cost for steel corrosion inhibition in H_2SO_4 medium, even when concentration of 12-3-12 was as low as $1x10^{-6}$mol L^{-1}. By fitting the obtained experimental data with Langmuir adsorption model and Arrhenius equation, some thermodynamic and kinetic parameters such as adsorption free energy, the apparent activation energy, and the pre-exponential factor were estimated. The adsorption mechanism of the gemini surfactant onto steel surface in acid medium in the absence and presence of chloride ions was also discussed, respectively.

The effect of sodium carboxymethyl cellulose (Na-CMC) on the corrosion behavior of mild steel in 1.0 mol·L^{-1} HCl solution was studied by weight loss measurement, potentiodynamic polarization, linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS) methods [122]. These results showed that the inhibition efficiency of Na-CMC increased with increasing the inhibitor concentration. Potentiodynamic polarization studies revealed that the Na-CMC was a mixed type inhibitor in 1 mol·L^{-1} HCl. The adsorption of the inhibitor on mild steel surface has been found to obey the Langmuir isotherm. The effect of temperature on the corrosion behavior of mild steel in 1mol·L^{-1} HCl with addition of 0.04% of Na-CMC has been studied in the temperature range of 298–328 K. The associated apparent activation energy (E_a) of corrosion reaction has been determined. Scanning electron microscopy (SEM) has been applied to investigate the surface morphology of mild steel in the absence and presence of the inhibitor molecules.

Abdel Rehim et al [123] studied the influence of the concentration of adenine (AD), as a safe inhibitor, on the corrosion of low carbon steel (LCS) in aerated 4M H_2SO_4 solutions. The investigations involved weight loss, potentiodynamic polarization, impedance and electrochemical frequency modulation (EFM) methods. Variations of (OCP) as a function of time till steady-state potentials were also studied. Measurements were conducted under the influence of various experimental conditions complemented with ex situ EDX examinations of the electrode surface. By using EFM measurements, corrosion current density was determined without prior knowledge of Tafel slopes. Results obtained revealed that together with iodide ion, AD is an effective corrosion inhibitor for LCS corrosion in H_2SO_4 solutions. Synergism between iodide ion and AD was proposed. Potentiodynamic polarization studies showed that AD alone and the mixture of AD and iodide ions act as mixed-type inhibitors for the corrosion of LCS in 4M H_2SO_4 solution. The inhibition mechanism involves the electrostatic adsorption of protonated AD molecules on the LCS surface charged with a negative layer of chemisorbed I^- ions. An adherent layer of inhibitor is postulated to account for the protective effect. EDX examinations of the electrode surface confirmed the existence of such adherent layer on the electrode surface. The inhibition efficiency increases with increase in the concentration of AD and immersion time. The potential of zero charge (PZC) of the LCS electrode was determined in 4M H_2SO_4 solutions in the absence and presence of 0.001 M KI, and the mechanism of adsorption was discussed. The results obtained from chemical and electrochemical measurements were in good agreement.

Abd El-Rehim et al [124] studied the inhibiting effect of 4-amino pyrine [AAP] toward corrosion of mild steel in 2M H_2SO_4 solution using weight loss measurements and potentiodynamic polarization technique.

The inhibition efficiency increases with the inhibitor concentration, but decreases with temperature. The inhibition of AAP is due to its adsorbance and blocking the active sites on the metal surface without affecting the corrosion mechanism. AAP behaves mainly as an anodic inhibitor. The Flory-Huggins isotherm and the kinetic model of El-Awdy et al fit the experimental results well.

The effect of three new Schiff bases, viz., N,N-ethylen-bis (salicylidenimine) [S1], N,N$^{\backslash}$-isopropylien-bis (salicylidenimine) [S2], and N-acetylacetoneimine, N-(2-hydroxybenzophenoneimine) orthophenylen [S3] as corrosion inhibitors for mild steel in 0.5M H_2SO_4 was studied using Tafel polarization and (EIS) [125]. The three Schiff bases function as good inhibitors reaching inhibition efficiencies of 97–98% at 300 ppm concentration. The fraction (Θ) of the metal surface covered by the inhibitor is found to increase with inhibitor concentration. Of the three Schiff bases, the S2 shows better efficiency than the other two Schiff bases. The adsorption of the inhibitor follows Langmuir isortherm. Thermodynamic calculations indicate the adsorption to be physical in nature.

Deyab [126] studied the corrosion behavior of carbon steel (CS) in formation water associated crude oil from Egyptian western desert at various concentrations of dodecyl dimethyl ammonium chloride (CS) as a cationic surfactant. Polarization curves indicate that CS has good inhibition efficiency for carbon steel in formation water and behaves as cathodic inhibitor. The inhibition efficiency was found to increase with increase in CS concentration until reaches a maximum constant value corresponding to the critical micelle concentration of CS and decrease with increase in solution temperature. The adsorption of CS follows the kinetic thermodynamic model and Flory–Huggins isotherm. Thermodynamic parameters obtained indicate that that the presence of the

CS increases the activation energy. Polarization and impedance measurements indicate that the addition of KI has a significant synergistic effect with CS and results in increase the inhibition efficiency of CS in formation water.

The inhibitive effect of the synthesized two gemini surfactants, 1,4/1,6-Bis(α-ctylpyridinium) butane /hexane dibromide for A3 steel in 20% HCl solution medium was studied by mass loss, Tafel extrapolation method and electrochemical impedance spectroscopy [56]. The result of mass loss indicated that the inhibitive efficiency of the surfactants increases with the rise of concentration; decreases with the rise of temperature and is up to the highest at a concentration of surfactants much less than their critical micelle concentration. Polarization data indicates that these compounds act as very good inhibitors of iron in 20% HCl both for cathode and anode. Electrochemical impedance spectroscopy has the same trend of inhibitive effect as that of the polarization data, which indicate the formation of a protective layer on the iron surface by the adsorption of surfactants molecules.

Abdallah et al [127] studied the effect of some aminopyrimidine derivatives on the corrosion of 1018 carbon steel in 0.05M HNO_3 solution using weight loss and polarization techniques. The percentage inhibition efficiency was found to increase with increasing concentration of inhibitor and with decreasing temperature. The addition of KI to aminopyrimidine derivatives enhanced the inhibition efficiency due to synergistic effect. The inhibitors are adsorbed on the steel surface according to Temkin isotherm. Some thermodynamic functions were computed and discussed. It was found that the aminopyrimidine derivatives provide a good protection to steel against pitting corrosion in chloride containing solutions.

The inhibiting action of a Schiff base 4-[(4-hydroxy-3-hydroxymethyl-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (phv), derived from 4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one (phz) and 4-hydroxy-3-methoxy-benzaldehyde (vn), towards the corrosion behavior of steel in 2M HCl solution was studied by weight loss, polarization and electrochemical impedance spectroscopy (EIS) techniques [128]. Although vn and phz were found to retard the corrosion rate of steel, the compound synthesized from vn and phz was seen to retard the corrosion rate even more. At constant temperature, the corrosion rate decreases with increasing inhibitor concentration. However, at any inhibitor concentration the increase in temperature leads to an increase in the corrosion rate of steel. The activations energy, ΔE_a, as well as other thermodynamic parameters ($\Delta G°_{ads}$, $\Delta H°_{ads}$) for the inhibitor process was calculated. The inhibitor efficiencies calculated from all the applied methods were in agreement and were found to be in the order: phv > phz > vn.