Introduction & Literature Survey

on the steel surface and also confirms the highest inhibition efficiency of the prepared surfactants at $1x10^{-2}$ M concentration.

Evaluating of the prepared surfactants as biocide against sulfate reducing bacteria, results showed that the synthesized cationic surfactants have antimicrobial activity against the tested microorganisms (SRB) and their activities depend on their chemical structures (mainly the hydrophobic chain length). The action mode of such cationic biocides on the bacterial strain is explained as an electrostatic interaction and physical disruption. However, ethoxylated-cationic surfactants showed weak antimicrobial activity against the tested microorganisms (SRB).

INTRODUCTION AND LITERATURE SURVEY

1.1. *Definition of surfactant*

Surfactants "Surface active agents" are substances that at low concentration are adsorbed at some or all of the interfaces in the system and significantly changes the amount of work required to expand those interfaces. Surfactants usually act to reduce interfacial free energy or surface tension (the work required to extend surface by unit area) rather than to increase it [1].

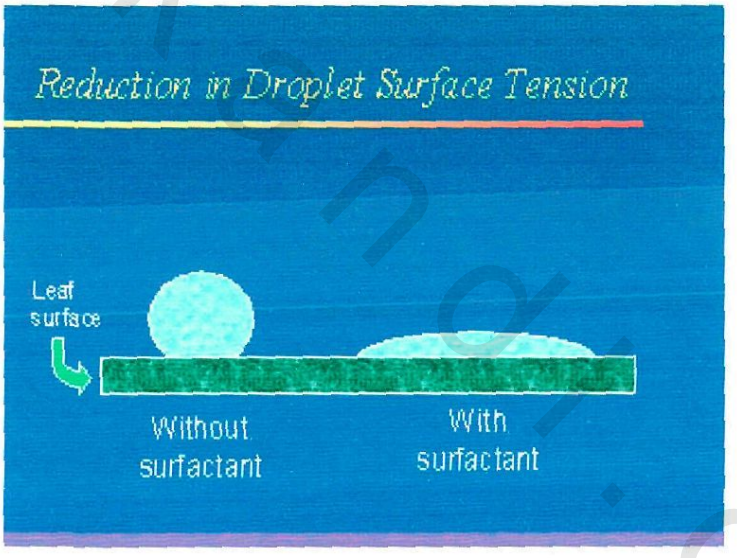


Fig. (1): Schematic illustration of reduction in droplet surface tension.

Surfactants are formed of large molecules consisting of two groups polar and non-polar groups which define the surfactant phase behavior. One of these groups is soluble in a specific fluid (the lyophilic part) and the other is insoluble (the lyophobic part). When the fluid is in water one usually talks about the hydrophilic and hydrophobic parts, respectively. The hydrophilic part is referred to the head group and the hydrophobic part as the tail [2, 3].

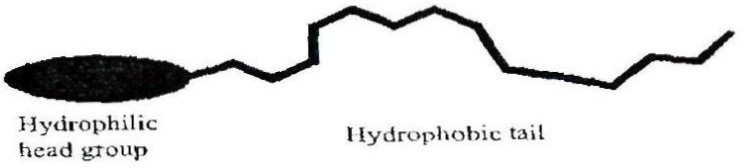


Fig. (2): Schematic illustration of a surfactant.

Generally, surfactants are organic substances which contain in their molecules hydrocarbon radicals (hydrophobic) with one or more of the active (polar) group (hydrophilic). The former is most often a long-chain hydrocarbon radical, from 8 to 16 carbon atoms, straight or branched saturated or not, possibly associated with paraffinic, isoparaffinic, naphthenic, aromatic, alkyl aromatic, alkyl naphtha aromatic hydrocarbons of different structures and molecular weights[4]. The latter is predominantly, sulphonate (SO_3H), sulphate (OSO_3H), nitro group (NO_2), carboxyl group (COOH), amine group (NH_2) or hydroxyl group (OH).

1.2. Types of surfactants

Depending on the hydrophilic group [5], surfactants are classified into two main categories:

1.2.1. Ionic surfactants

Ionic surfactants are dissociated into ions in the solution. They sub grouped into:

1.2.1.1. Cationic

The hydrophilic moiety of a cationic surfactant carries a positive charge when dissolved in aqueous media; the majority of cationic surfactants are based on the nitrogen atom carrying the positive charge. For example,

- Long chain fatty amines and their salts

  Fatty amines are derived from animals and vegetable fatty acids or derived from synthetic C_{12}–C_{16} primary, secondary or tertiary amines, which adsorb strongly onto most surface, that are usually negatively charged. They are very soluble and stable in strongly acidic solutions, sensitive to pH changes become uncharged and insoluble in water at pH above 7. Commercially, they are prepared by catalytic or electrolytic hydrogenation of the corresponding nitriles; the latter are usually prepared by heating the fatty acid with ammonia to 300-350 °C at atmospheric or elevated pressure [6]. This type can be used as corrosion inhibitors for metal surfaces and as anticaking agents.

- Fatty diamines, poly amines and their salts

  The main usage of this compound is adhesion promoters for asphalt coating of water damp road surface.

- Fatty quaternary ammonium salts

  These compounds are much soluble than the amine salts and retain their cationic nature in acidic, neutral and in alkaline solutions. This type can be used as corrosion inhibitors for metal surfaces and as bactericides.

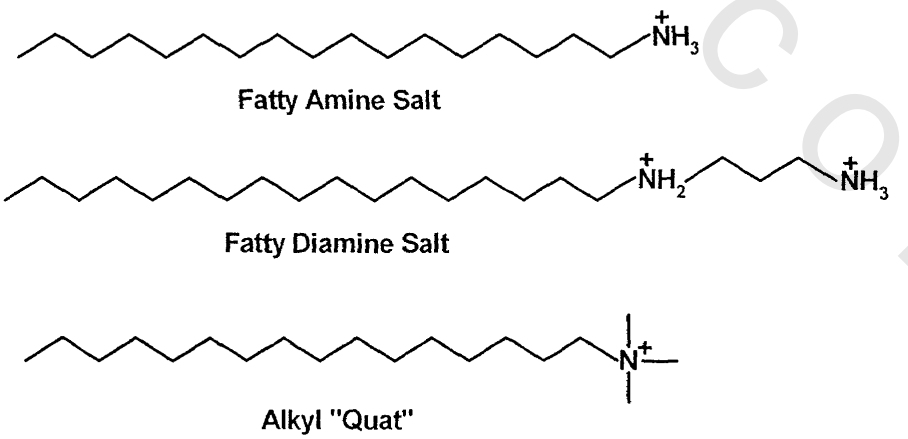


Fig. (3): Structures of some representative cationic surfactants.

- Polyoxyethylenated long chain amines

  These compounds are characterized by high water solubility. It is used in the production of xanthate rayon and as emulsifying agents for herbicides, insecticides, polishes and wax emulsion.

$$RN[(CH_2CH_2O)_xH]_2$$

- Quaternized Polyoxyethylenated long chain amines

  They are used as corrosion inhibitors for metal surfaces. They may also be used as textile antistatic agents and as dyeing levelers.

$$RN(CH_3)[(CH_2CH_2O)_xH]_2^+Cl^-$$

1.2.1.2. Anionic

The surface-active part of the molecules in aqueous solution is negatively charged. Carboxylate, sulfate, sulfonate and phosphate are the polar groups found in anionic surfactants [7]. For example:

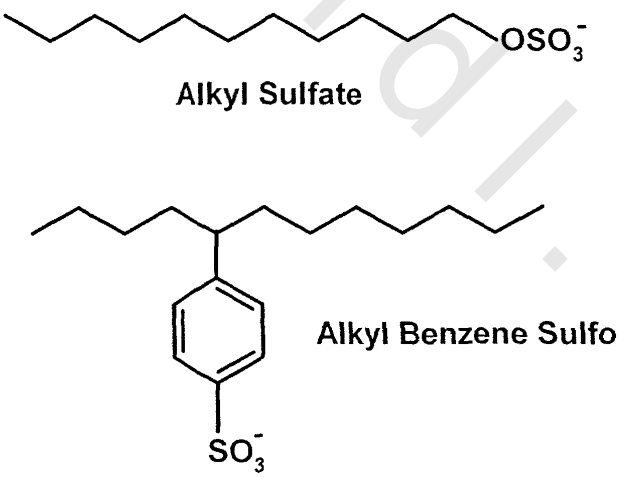


Fig. (4): Structures of some representative anionic surfactants.

1.2.1.3. Amphoteric

Both positive and negative charges may be present in the surface-active portion, for example, $RNH_2CH_2COO^-$ (long chain amino acid), $RN(CH_3)_2CH_2CH_2SO_3^-$ (sulfobetaine).

1.2.2. Nonionic

Unlike anionic or cationic surfactants, the molecules of this type of surfactants are not dissociated in aqueous solutions and they have complete surfactants properties. Their water solubility is generally caused by oxygen containing groups in the molecule with a higher affinity to water, i.e. hydrogen bond of the water molecules to the oxygen atoms of the hydrophilic molecule group[8]. Hydrogen bond provides solubilization in neutral and alkaline media. In strongly acid environment, oxygen atoms are protonated, providing a quasi-cationic character. Each oxygen atom makes a small contribution to water solubility. More than a single atom is therefore needed to solubilize a nonionic surfactant in water. With increasing temperature ethoxylates become less soluble as a result of decreasing hydration and increasing micellar size [9, 10]. The temperature, at which the appearance of a second phase is observable, is referred to as the cloud point. A small amount of admixed anionic surfactants may raise the cloud point by several degrees. Surface activity and performance efficiency of nonionics are usually the greatest at temperatures just below the cloud point.

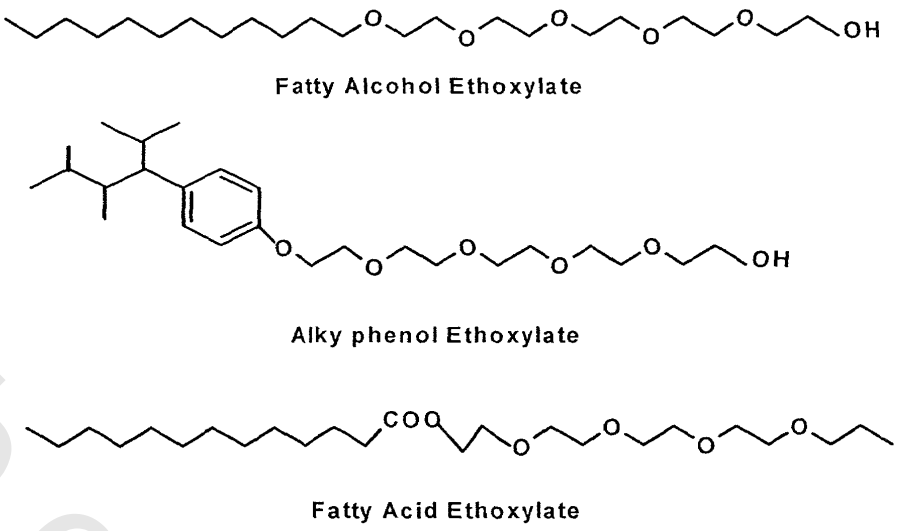


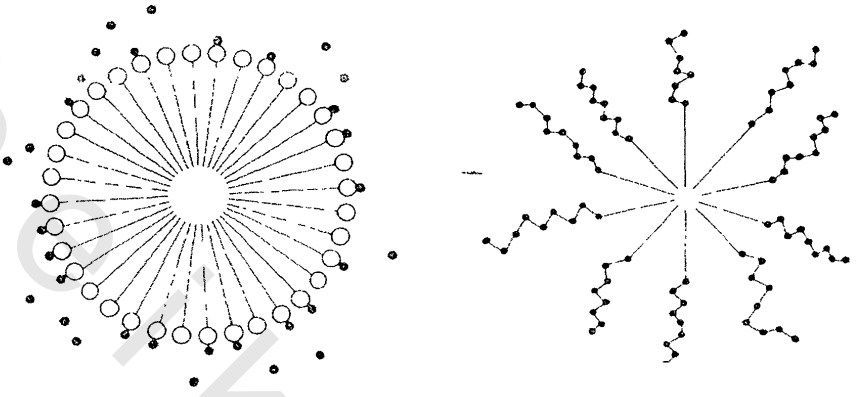
Fig. (5): Structures of some representative non-ionic surfactants.

Ethoxylated products can be produced from a polyoxyethylene group. They can easily be introduced by reaction of ethylene oxide with any organic molecule containing an active hydrogen atom, and a wide variety of structures that can be solubilized by ethoxylation[11].

1.3. Micelle formation

The micelle formation is the most vital point of view in the surfactant fundamental because it is the most effective geometric arrangement of the molecules at that desired concentration[12]. The surfactant molecules when dispersed in water tend to be adsorbed at the interface, leading to decrease in the surface tension of the surfactant solutions. Further increase in the concentration is followed by a gradual reduction of the surface tension until the surface of the solution becomes completely occupied by the surfactant molecules, after which the excess molecules tend to self aggregate in the bulk of the solution, thus forming micelles[13]. Further increments of surfactants concentration are leads to the formation of a critical micelle concentration, abbreviated CMC. The CMC is defined as the concentration of the surfactant at which decrease in the surface tension could be obtained upon addition of

any further amounts of surfactant in the solution. There is equilibrium between the singly adsorbed surfactant molecules at the interface and the micellized surfactant molecules. That equilibrium is occurs at the concentration of complete surface saturation (CMC) [14].



Ionic micelles **Nonionic micelles**

Fig. (6): Illustration of ionic and nonionic micelles.

1.4. Application of surfactants

Because of the characteristic behavior of surfactants to orient at surfaces and to form micelles, all surfactants perform certain basic functions. However, each surfactant excels in certain functions and has others in which it is deficient.

1.4.1. Corrosion inhibitor

Corrosion protection of steel in acidic media is great important both for industrial facilities and theoretical aspects [15]. The use of inhibitor is one of the most practical methods for protection of steel against corrosion in acidic media. Among all inhibitors, the most important are the organic ones, also called adsorption inhibitors [16]. They control corrosion, acting over the anodic or the cathodic surface or both. Most commercial acid inhibitors are organic compounds containing heteroatom such as nitrogen, oxygen, sulphur,

phosphor atoms, by which the inhibitor molecules are adsorbed on the metal surface in acidic media, thus resulting adsorption film acts as a barrier separating the metal from the corrosive medium and blocks the active site [17–22]. As a representative type of these organic inhibitors, quaternary ammonium salts have been demonstrated to be highly cost-effective and used widely in various industrial processing for preventing corrosion of iron and steel in acidic media [23–25].

Non-ionic surfactants are found to have a marked inhibiting efficiency on iron in acidic media by adsorption onto its surface.

1.4.2. Emulsifier

An emulsifier known as a surfactant from surface active material is a substance which stabilizes an emulsion. A wide variety of emulsifiers are used in pharmacy to prepare emulsions such as creams and lotions. Silicon Oil Emulsifier, Amino Oil Emulsifier, Paraffin Wax Emulsifier are name of some Emulsifiers. The selection of surfactant or surfactant system will depend on the materials to be used and the properties desired in the end product. An emulsion can be oil droplets suspended in water, oil in water (O/W) emulsion, water suspended in a continuous oil phase, water in oil (W/O) emulsion, or a mixed emulsion. Selection of surfactants, orders of addition and relative amounts of the two phases determine the class of emulsion. Each of these three functions is related to the surfactant adsorbing at a surface, either gas, liquid or solid with the hydrophilic ends of the molecules oriented to the water phase.

1.4.3. Coating

The surfactants form what amounts to a protective coating around the suspended material, and these hydrophilic ends associate with the

neighbouring water molecules. In addition to surfactant effects the stability of these suspensions is related to the particle size and density of the suspended material. Solubilization is a function closely related to emulsification. As the size of the emulsified droplet becomes smaller, a condition is reached where this droplet and the surfactant micelle are the same size. At this stage, an oil droplet can be imagined as being in solution in the hydrophobic tails of the surfactant and the term solubilization is used. Emulsions are milky in appearance and solubilized oils, for example are clear to the eye.

1.4.4. Detergent

Anionic surfactants are used in most detergent formulation and best detergency is obtained by using paraffin chains from 12 to 16 carbon atoms [(26)]. The counter ions mostly used are sodium, potassium, calcium and various protonated alkyl amines. The conventional detergent for those having a greasy skin is mainly a soap which contains an anionic surfactant having a high degreasing power (detergency). It also cleanses the whole object including non-greasy parts so that strong washing causes problems such as dry flaky skin or a stretched feeling after cleansing.

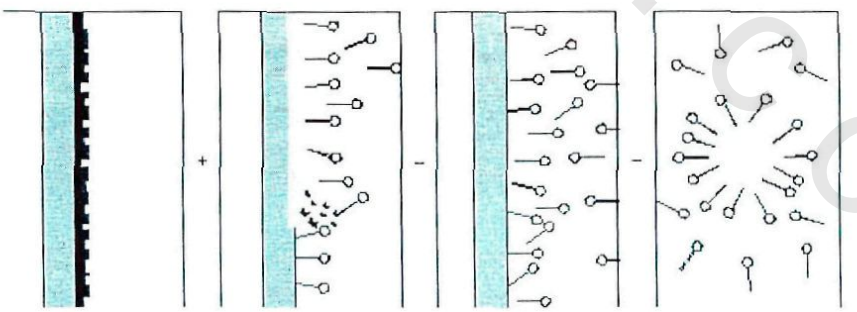


Fig. (7): Simplified illustration of detergency.

1.4.5. Foam stability

The role of surfactants in stabilizing the formation of bubbles in foams is studied using a phase-field model. In particular, it is concluded that the surfactant segregates to the interfaces, and that the prescription of the distribution of surfactant will dictate the locus of interfaces, which is in agreement with the experimental results.

1.4.6. Biocides

Surfactants have biocidal activity because of their ability of adsorption at the water/cell membrane interface. That adsorption increases the hydrophilicity of that membrane which, increase its permeability towards the media ingredients [27, 28]. This result in disturbing the biological reactions occurred within the cell cytoplasm.

The cationic surfactants have a unique ability of adsorption at interface due to their amphipathic structure, which acquires them a good biocidal activity towards micro-organisms [29, 30].

1.4.7. Flotation

Flotation process is one of the surfactant-based separation techniques. Originally it is used in the area of mineral processing. The concept of ore flotation is transferred into the waste paper recycling industry later. The application of flotation of ink from pulpwood was successfully introduced to waste paper mill in the 1980s. Both processes have the same concept, i.e., to control the surface hydrophobicity/hydrophilicity of disperse particles in water, but they have several differences in details.

1.4.8. Paints

The surfactant leaching is used to describe spots or streaks of sticky brown or colorless material that appears on the surface of freshly applied latex. Surfactant leaching, also known as water spotting, is a common paint problem that may occur with any brand of latex paint. The spots or streaks caused by

surfactant leaching, while unsightly, are not harmful and do not affect the performance of the paint. Surfactants are ingredients in paint that are critical to the performance properties of the paint such as its color, stability, flow, and leveling. These materials usually evaporate in good drying conditions, or they are locked into the paint film. The staining occurs when drying conditions cause the paint to dry too slowly, allowing the surfactants to rise to the surface of the paint.

1.5. Definition of corrosion

Corrosion can be defined as the destructive attack of metals or alloys by chemical or electrochemical reaction with their environment. Corrosion is the degradation of a metal by its environment. Most metals do not exist as a solid metal piece of material. In their natural state, they exist in the form of oxides. These metal oxides (or other metal compounds) must be refined to create the pure metals or alloys which become useful structural materials that can be used to build things.

Pure metals and alloys have a much higher energy state and there is a natural tendency to return to their lower energy state. Corrosion is the process nature uses to return metals to their original state. The rate of corrosion depends upon the environment and the type of material. It can be very rapid in a highly corrosive environment or take thousands of years in a slightly corrosive environment. Corrosion, whether in the atmosphere, underwater, or underground, is caused by the flow of electricity from one metal to another metal, or from one part of the surface of a piece of metal to another part of the same metal where conditions permit the flow of electricity. For this to occur there must be a moist conductor or electrolyte present for the flow of energy to take place.

Corrosion is a complex process and it can take on various forms depending on the properties of the material and the corrosive environment. Uniform corrosion refers to homogenous dissolution of materials, such as the corrosion of carbon steels in acidic solutions. The corrosion rate is almost the same every where and the corrosion can be monitored easily. Non uniform corrosion, however, is the inhomogeneous deterioration due to the heterogeneities of the material or the environment and it consists of various forms such as intergranular, selective and pitting corrosion [31].

1.6. Why metals corrode?

Corrosion is the disintegration of metal through an unintentional chemical or electrochemical action, starting at its surface. All metals exhibit a tendency to be oxidized, some more easily than others. Tabulation of the relative strength of this tendency is called the galvanic series. Knowledge of a metal's location in the series is an important piece of information to have in making decisions about its potential usefulness for structural and other applications.

The driving force that causes metals to corrode is a natural consequence of their temporary existence in metallic form. To reach this metallic state from their occurrence in nature in the form of various chemical compounds (ores), it is necessary for them to absorb and store up for later return by corrosion. The thermodynamic or chemical energy stored in a metal or that is freed by its corrosion varies from metal to metal. It is relatively high for metals such as magnesium, aluminum, and iron, and relatively low for metals such as copper, silver and gold as shown in **Table (1).**

Table (1): Lists a few metals in order of diminishing amounts of energy required to convert them from their oxides to metal.

	Metal	Oxide	Energy (MJ Kg^{-1})
Highest energy	Li	Li_2O	40.94
	Al	Al_2O_3	29.44
	Mg	MgO	23.52
	Ti	TiO_2	18.66
	Cr	Cr_2O_3	10.24
	Na	Na_2O	8.32
	Fe	Fe_2O_3	6.71
	Zn	ZnO	4.93
	K	K_2O	4.17
	Ni	NiO	3.65
	Cu	Cu_2O	1.18
	Pb	PbO	0.92
	Pt	PtO_2	0.44
	Ag	Ag_2O	0.06
Lowest energy	Au	Au_2O_3	-0.18

1.7. Types of corrosion

1.7.1. Wet corrosion

Wet corrosion occurs when a liquid present. This usually involves aqueous solution or electrolytes and accounts for the greatest amount of corrosion. A common example is corrosion of steel by water. The corrosion process consists of an anodic and a cathodic reaction. In the anodic reaction (oxidation) the metal is dissolved and transferred to the solution as ions M^{2+}. The cathodic reaction is reduction of oxygen. It is seen that the process makes an electrical circuit without any accumulation of charges. The electrons released by the anodic reaction are conducted through the metal to the cathodic area where they are consumed in the cathodic reaction. A necessary condition for such a corrosion process is that the environment is a conducting liquid (an electrolyte) that is in contact with the metal. The electrical circuit is closed by ion conduction through the electrolyte. In accordance with the conditions this dissolution process is called wet corrosion, and the mechanism is typically electrochemical [32].

The anode, the anode corrodes by loss of electrons

$M = M^{z+} + ze^-$

Anode is anodic reaction, oxidation reaction and electron generation.

The cathode, the cathode does not corrode.

- (i) $pH < 7$ $\quad 2H^+ + 2e^- = H_2$
- (ii) $pH >= 7$ $\quad 2H_2O + O_2 + 4e^- = 4OH^-$

Cathode is cathodic reaction, reduction reaction and electron consumption.

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.

Wet corrosion is most efficient in waters 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.

1.7.2. 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. Zinc and zinc coatings carry a fairly protective zinc hydroxide or carbonate layer (zinc patina) which increases in thickness very slowly. Aluminum carries a thin, highly protective oxide layer [33].

1.8. Forms of corrosion

There are many forms of corrosion that can affect metals. They include general, pitting, galvanic, crevice, intergranular, stress, erosion and biological corrosion[34, 35].

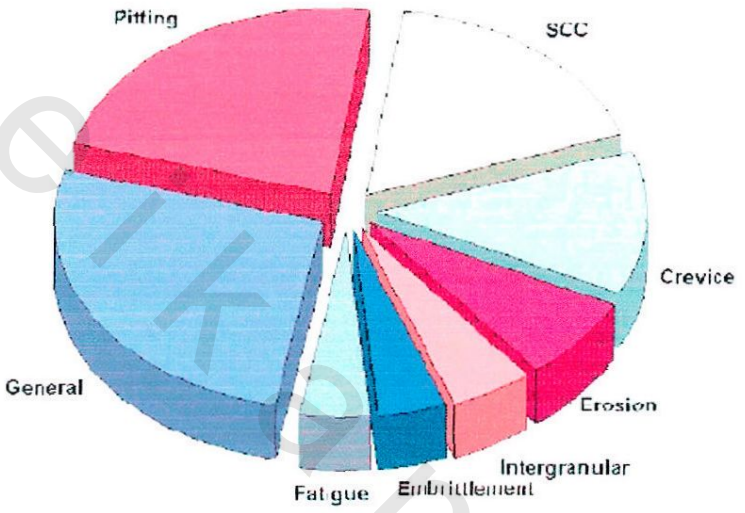


Fig. (8): Simplified illustration of the corrosion forms.

1.8.1. General or uniform corrosion

Uniform corrosion is the most common form of corrosion and is characterized by a chemical or electrochemical reaction which takes place uniformly over the entire exposed surface. Differences in the electrical potential occur on the surface of a piece of metal due to small differences in chemical composition, amount of cold work, etc. These differences set up small corrosion cells each with an anode and cathode. Corrosion continues until the metal is consumed or the film of rust formed on the surface sets up a barrier to the electrolyte.

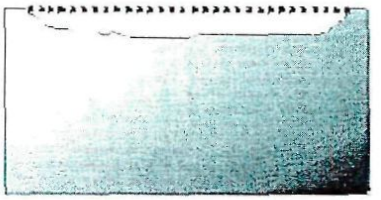


Fig. (9): Simplified illustration of uniform corrosion.

1.8.2. Pitting corrosion

Pitting corrosion is a form of extremely localized corrosion that leads to the creation of small holes in the metal. It is one of the most destructive and insidious forms of the corrosion. Pitting causes a small percent weight loss of the whole structure. The pitting corrosion rate is difficult to measure in laboratory test because of the varying number and depth of pits under identical conditions. Pitting attack usually requires several months or a year to show up in service. Pitting corrosion can be considered a unique type of anodic reaction and also a form of an autocatalytic process.

In passivated metal, or alloys that are exposed to solutions containing aggressive anions, primarily chloride, pitting corrosion results in local dissolution leading to the formation of cavities or (holes). The shape of the pits or cavities can vary from shallow to cylindrical holes, and the cavity is approximately hemispherical [36]. Pitting corrosion occurs mostly in solutions containing halides or oxyhalides, chlorides, bromides and hypochlorite are the most aggressive anions Fluoride, iodide and iodine containing anions were thought to be without pitting tendency. However, iodide ions were found to cause pitting corrosion in many cases [37]. Solutions of certain oxidizing actions produce the worst pitting reagents.

The driving power for pitting corrosion is the lack of oxygen around a small area. This area becomes anodic while the area with excess of oxygen becomes cathodic, leading to very localized galvanic corrosion. The corrosion penetrates the mass of the metal, with limited diffusion of ions, further pronouncing the localized lack of oxygen.

1.8.2.1. Mechanism of pitting corrosion

It is supposed by some that gravitation causes downward-oriented concentration gradient of the dissolved ions in the hole caused by the corrosion, as the concentrated solution is denser. The more conventional explanation is that the acidity inside the pit is maintained by the spatial separation of the cathodic and anodic half-reactions, which create a potential gradient and electro-migration of aggressive anions into the pit. This kind of corrosion is extremely insidious, as it causes little loss of material with small effect on its surface, while it damages the deep structures of the metal [38]. The pits on the surface are often obscured by corrosion products.

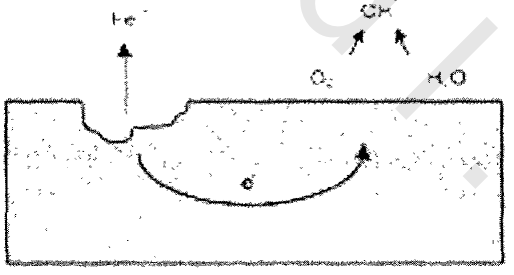


Fig. (10): Diagram showing a mechanism of localized corrosion developing on metal in a solution containing oxygen.

1.8.3. Galvanic corrosion

Galvanic corrosion (Also called ' dissimilar metal corrosion' or wrongly 'electrolysis') refers to corrosion damage induced when two dissimilar materials are coupled in a corrosive electrolyte. The figure below illustrates a

cell showing the corrosion process in its simplest form. This cell includes the following essential components. a metal anode, a metal cathode, a metallic conductor between the anode and the cathode and an electrolyte in contact with the anode and cathode, but not necessarily of the same composition at the two locations [39].

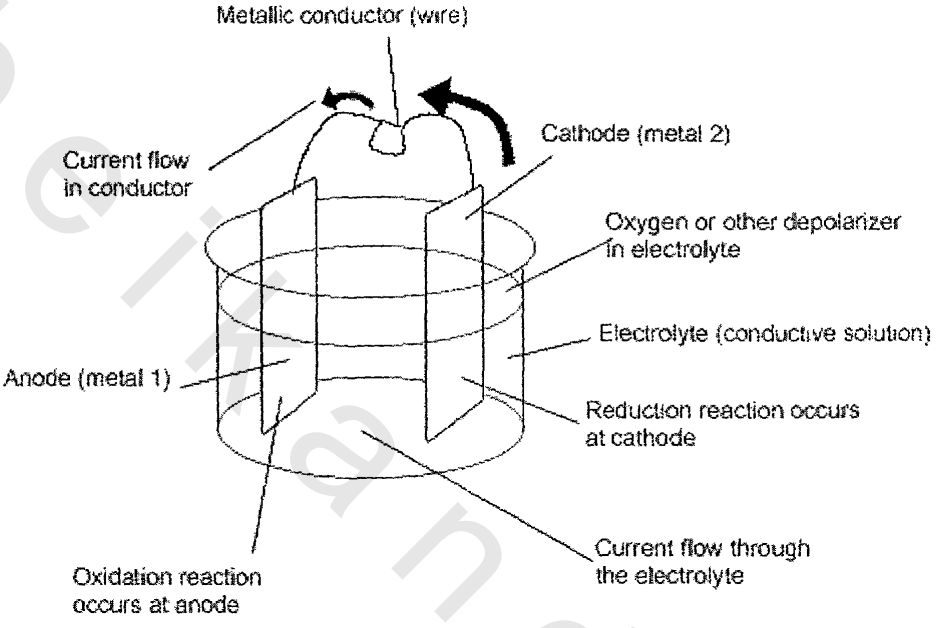


Fig. (11): Simplified illustration of galvanic corrosion.

Suppose that the anode is iron, the cathode is copper and the electrolyte is water containing mineral salts. The anode is negatively charged and the cathode is positively charged. This difference in charge (voltage) provides potential voltage, which is the driving force for current to flow in the cell. Since the iron in the test cell is negatively charged and the copper is positively charged, there is a potential voltage difference which causes a flow of electricity. The anode will give off iron ions in the form of rust (corrosion), while hydrogen gas would be produced at the cathode and no destruction will occur. Corrosion occurs only on the anode, the rate of corrosion in the cell

will be dependent upon the relative sizes of the anode, cathode and the potential difference between them [40].

If, for instance, the anode was very small and the cathode was large, the rate of corrosion would be very rapid. The opposite would be true if there was a very large anode compared to the cathode. If the anode was nickel and the cathode brass, there will be very little corrosion, because the voltage potential difference will be slight.

1.8.4. Crevice corrosion

Crevice corrosion is known as deposit or gasket corrosion. Crevice corrosion occurs when there is a difference in ion, or oxygen surroundings.
Crevice corrosion occurs at locations where crevices exist, such as threads, machining grooves, tears, metal lap joints, etc.

The illustration below shows how corrosion occurs at a crevice created by a lap joint. At the edge of the lap joint, movement of water (electrolyte) flushes away metal ions resulting in a lower metal ion concentration. The space between the two pieces of metal is stagnant and there is a higher concentration of metal ions, allowing corrosion to occur at the edge of the mechanical joint.

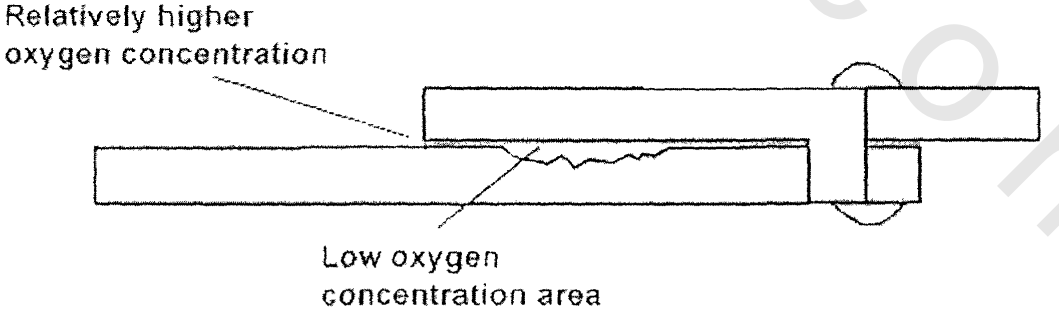


Fig. (12): Simplified illustration of crevice corrosion.

An oxygen concentration cell may also form if there is a depletion of oxygen in the dead space in the lap joint. If the material is stainless steel and there are high levels of chlorine in the water, the chlorine will attack metal in the dead space between the two pieces of metal, breaking down the passive film.

Since there isn't any oxygen available to regenerate the passive film, the stainless becomes active (anodic) in this cell and the rest of the stainless stays passive (cathodic) because the passive film remains intact. With this lap joint in water (electrolyte) conditions are right for current to flow and corrosion occurs in the crevices formed in the lap joint.

Concentration cells can form in any crevice in watering systems and corrosion is more likely to occur with the use of chlorine or hydrochloric acid. Corrosion may be accelerated if there are large amounts of organic material and very low levels of oxygen in the water along with the use of chlorine. Oxygen is necessary to maintain the passive film.

1.8.5. Intergranular corrosion

This type of corrosion may occur next to a weld if the carbon content of the stainless steel is too high. When stainless steel is welded, material next to the weld reaches a temperature of only 800-1500 °F. At these temperatures, the chromium and carbon form chromium carbides. Chromium carbides deplete the chromium at the weld interface and sensitize the material, making it subject to corrosion. If a weld interface is deficient, it cannot maintain the passive film. This area becomes anodic, while the rest of the material is cathodic. When the material is in water or moist air (the electrolyte), current will flow, resulting in corrosion (rusting) at the weld interface. By reducing the carbon content, we can prevent carbides from forming. For this reason,

Edstrom Industries uses 316L or 304L stainless steel when welding to avoid intergranular corrosion.

1.8.6. Stress corrosion cracking (SCC)

Stress corrosion cracking (SCC) is a process involving the initiation of cracks and their propagation, possibly up to complete failure of a component, due to the combined action of tensile mechanical loading and a corrosive medium. Indeed, it is the presence of tensile stresses that is dangerous, compressive stresses exerting a protective influence. SCC frequently occurs in media that are little or non-aggressive towards the metal or alloy concerned in the absence of tensile loading (e.g. austenitic stainless steels in high temperature water and steam). The associated weight losses are generally very small and even insignificant compared to the extent of the overall damage incurred. This form of corrosion is great practical importance and represents a permanent risk in numerous industrial installations, in terms of both the economic consequences and the safety considerations involved (equipment reliability and respect of the environment). The time necessary for a part to fail by SCC can vary from a few minutes to several years.

Means of reducing or preventing stress corrosion cracking are elimination of residual stresses by stress relieving heat treatments, purification of the medium, choice of the most appropriate material, improvement of the surface condition, avoid surface machining stresses, perform penning treatments on welds to induce surface compressive stresses, apply external protection methods (cathodic protection, inhibitors and organic or inorganic protective coatings).

1.8.7. Fatigue corrosion

Corrosion fatigue occurs due to the combined action of corrosion and cyclic stresses such as rapidly alternating tensile and compressive stresses. If the metal is simultaneously exposed to a corrosive environment, the failure can take place at even lower loads and after shorter time.

1.8.8. Fretting corrosion

Fretting is a wear phenomenon enhanced by corrosion. Fretting involves wear of a metal or alloy when in contact with another solid material in dry or humid air. Fretting is the result of abrasive wear of surface oxide film, which form on contacting surfaces under load in atmospheric air.

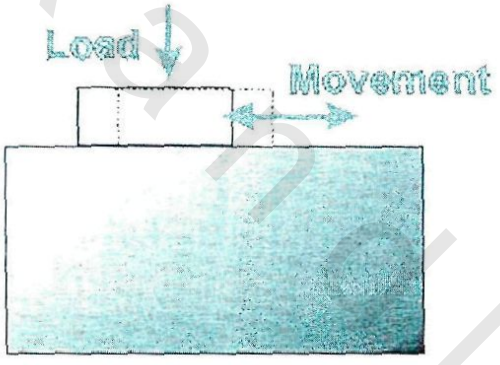


Fig. (13): Simplified illustration of fretting corrosion.

1.8.9. Filiform corrosion

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

1.8.10. Erosion corrosion

Erosion corrosion is the increase in the rate of attack of a metal because of relative movement between a corrosive medium and the metal surface.

1.8.11. Biological corrosion

When a metallic surface is immersed in water, a biofilm will begin to form if there are any bacteria in the water. A biofilm is a microbial mass composed of aquatic bacteria, algae, or other micro-organisms. Biofilm formation is inside the surface of a pipe. **Fig. (14)** showed a sketch of a biofilm formed on a metal surface in a pipe. The biofilm begins with the absorption of organic matter to the metal surface from the water. The flow of water transports microbes to the surface and the micro-organisms attach and then grow, using nutrients from the water [41].

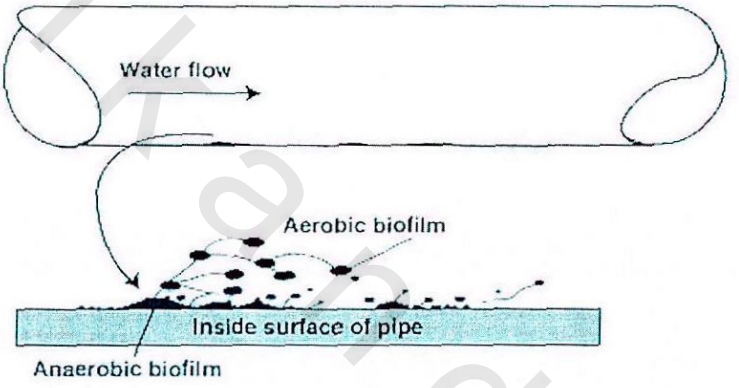


Fig. (14): Simplified illustration of biological corrosion.

When the micro-organisms grow, oxygen is excluded, which creates a place where the passive film may break down. With the breakdown of the passive film, the site becomes anodic with the likelihood of corrosion. Biofilm formation is most likely in spots where the flow of water is low, such as voids, crevices, and thread joints.

Steps in formation of biofilm.

(1) Formation is initiated when small organic molecules become attached to an inert surface.

(2) Microbiological cells are absorbed onto the resulting layer.

(3) The cells send out hairlike exopolymers to feed on organic matter and attach themselves to the surface.

(4) Adding to the coating.

(5) Flowing water detaches some of the formation producing an equilibrium layer.

1.9. Theory of corrosion

Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals. Metals will also corrode when exposed to gaseous materials like acid vapors, formaldehyde gas, ammonia gas, and sulfur containing gases. Corrosion specifically refers to any process involving the deterioration or degradation of metal components. The best known case is that of the rusting of steel. Corrosion processes are usually electrochemical in nature, having the essential features of a battery. When metal atoms are exposed to an environment containing water molecules they can give up electrons, becoming themselves positively charged ions provided an electrical circuit can be completed. The corrosion process (anodic reaction) of the metal dissolving as ions generates some electrons, as shown in the simple model, that are consumed by a secondary process (cathodic reaction). These two processes have to balance their charges. The sites hosting these two processes can be located close to each other on the metal's surface or far apart depending on the circumstances. This simple observation has a major impact in many aspects of corrosion prevention and control, for designing new corrosion monitoring techniques to avoiding the most insidious or localized forms of corrosion.

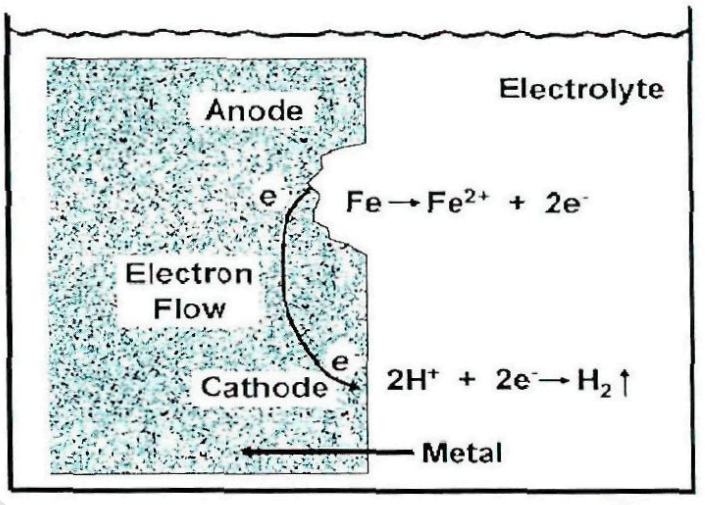


Fig. (15): Simplified illustration of theory of corrosion.

Rusting of iron consists of the formation of hydrated oxide, $Fe(OH)_3$, FeO(OH), or even $Fe_2O_3.H_2O$. It is an electrochemical process which requires the presence of water, oxygen and an electrolyte. In the absence of any one of these rusting does not occur to any significant extent. In air, a relative humidity of over 50 % provides the necessary amount of water and at 80 % or above corrosion of bare steel is worse. When a droplet of water was containing a little dissolved oxygen falls on a steel pipe, the solid iron or Fe(s) under the droplet oxides.

$$\mathbf{Fe(s) \dashrightarrow Fe^{2+}(aq) + 2e^-} \qquad (1)$$

The electrons are quickly consumed by hydrogen ions from water (H_2O) and dissolved oxygen or O_2(aq) at the edge of the droplet to produce water.

$$\mathbf{4e^- + 4H^+(aq) + O_2(aq) \dashrightarrow 2H_2O} \qquad (2)$$

More acidic water increases corrosion. If the pH is very low the hydrogen ions will consume the electrons anyway, making hydrogen gas instead of water.

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad (3)$$

Hydrogen ions are being consumed by the process. As the iron corrodes, the pH in the droplet rises. Hydroxide ions (OH^-) appear in water as the hydrogen ion concentration falls. They react with the iron (II) ions to produce insoluble iron (II) hydroxides or green rust.

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) \quad (4)$$

The iron (II) ions also react with hydrogen ions and oxygen to produce iron (III) ions.

$$4Fe^{2+}(aq) + 4H^+(aq) + O_2(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O \quad (5)$$

The iron (III) ions react with hydroxide ions to produce hydrated iron (III) oxides (also known as iron (III) hydroxides).

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s) \quad (6)$$

$Fe(OH)_3$ can slowly transform into a crystallized form was written as $Fe_2O_3.H_2O$ the familiar red-brown stuff that is called "rust". Since these processes involve hydrogen ions or hydroxide ions, they will be affected by change in pH. With limited O_2, magnetite is formed (Fe_3O_4).

1.10. Factors influencing corrosion reactions

In considering the group of three typical reactions involved in corrosion, we shall denote as primary factors those which determine the tendency of the metal to corrode and thus influence its initial rate of solution and as secondary factors those which influence the rate of the subsequent reactions. In fact, by influencing the nature and distribution of the final corrosion products, they usually determine the rate of corrosion, and the useful life of the metal, in

each environment. In the general case, some one or two of the many factors involved exert outstanding influence upon the ultimate rate of corrosion; these term controlling or dominant factors. In general, the primary factors have to do with the metal (or alloy) itself, the secondary factors more with the specific environment. It is convenient to divide them in this way, although no sharp distinction can be made. Accordingly on this basis we list below some of the more important factors.

1.10.1. Factors associated mainly with the metal

(1) Effective electrode potential of a metal in a solution.

(2) Overvoltage of hydrogen on the metal.

(3) Chemical and physical homogeneity of the metal surface.

(4) Inherent ability to form an insoluble protective film.

1.10.2. Factors which vary mainly with the environment

(1) Hydrogen-ion concentration (pH) in the solution.

(2) Influence of oxygen in solution adjacent to the metal.

(3) Specific nature and concentration of other ions in solution.

(4) Rate of flow of the solution in contact with the metal.

(5) Ability of environment to form a protective deposit on the metal.

(6) Temperature.

(7) Cyclic stress (corrosion fatigue).

(8) Contact between dissimilar metals or other materials as affecting localized corrosion.

1.11. Corrosion protection

The corrosion control methods that were considered include protective coatings, corrosion resistant metals and alloys, corrosion inhibitors, anodic and cathodic protection.

1.11.1. Protective coating

Both organic and metallic coatings are used to provide protection against corrosion of metallic substrates. These metallic substrates, mostly carbon steel will corrode in the absence of the coating, resulting in the reduction of the service life of the steel part or component.

1.11.2. Metals & alloys

Corrosion-resistant alloys are used where corrosive conditions prohibit the use of carbon steels and protective coatings provide insufficient protection or economically not feasible. Examples of these alloys include stainless steels, nickel-base alloys and titanium alloys.

1.11.3. Corrosion inhibitors

An inhibitor is a chemical substance which when added in small concentration to corrosive environment effectively decreases or prevents the reaction of the metal with the environment[42], corrosion inhibitors may be liquids or powder form that effectively reduce the corrosion rate by adsorbing on the metal surface[43] and protect it by forming an isolating film. Electrochemical inhibitors slow the corrosion process by increasing the anodic or cathodic polarization behavior, reducing the movement or diffusion of aggressive ions to the metallic surface or by increasing 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.

1.11.3.1. Structure of the inhibitor

Some inhibitors can form a co-ordinate type of link with the metal by electron transfer to the metal. Inorganic compounds, of functional groups containing elements of group V and VI of the periodic table, having suitable lone pair of electrons occur in these functional groups for coordinate bonding. The tendency to stronger coordinate bond formation and hence, stronger adsorption by these elements increases with increasing the electro-negativity in the order O < N < S < Se [44]. It depends also on the nature of the functional group and the rest of the molecule, since; they affect the electron density on the functional group, which is generally thought to increase the efficiency of the inhibitor as it increases. So, with increasing electron density on the functional group a stronger coordinate bonding with metal surface is produced hence, greater adsorption.

1.11.3.2. Classification of inhibitors

Inhibitor selection is based on the metal and the environment. A quantitative classification of inhibitors is presented in **Fig. (16)**. Inhibitors can be classified into environmental conditioners and interface inhibitors.

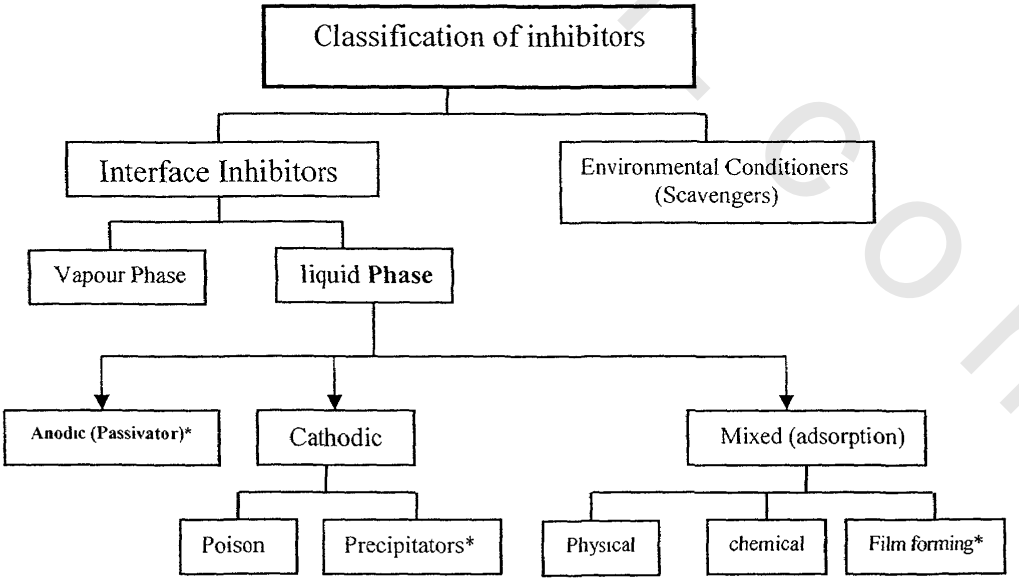


Fig. (16): Classification of inhibitors.

1.11.3.2.1. Environmental conditioners (scavengers)

Corrosion can be controlled by removing the corrosive species in the medium inhibitors that decrease corrosivity of the medium by scavenging. The aggressive substances are called environmental conditioners or scavengers. In neutral and alkaline solutions, oxygen reduction is a common cathodic reaction. In such situations, corrosion can be controlled by decreasing the oxygen content using scavengers (e.g., hydrazine) [45].

1.11.3.2.2. Interface inhibitors

Interface inhibitors control corrosion by forming a film at the metal/environment interface. Interface inhibitors, can be classified into liquid and vapor-phase inhibitors.

Liquid-phase inhibitors

Liquid phase inhibitors are classified as anodic, cathodic, or mixed inhibitors, depending on whether they inhibit the anodic, cathodic, or both electrochemical reactions.

a. Anodic inhibitors

Passivating inhibitors (passivators) or anodic inhibitors are families of inhibitors that act by preventing the anodic reaction. The inhibitors are incorporated into the oxide film on the metal, thereby stabilizing it and preventing further dissolution.

There is often no change in the appearance of the metal although it carries a very thin film that may be isolated by the use of special technique. There are two types of passivating inhibitors:

- Oxidizing anions, such as chromate and nitrite that can passivate steel in the absence of oxygen.
- Non oxidizing ions such as phosphate, tungestate and molybdate that require the presence of oxygen to passivate steel.

These inhibitors are the most effective and consequently the most widely used. When the concentration of anodic inhibitors is not sufficient, corrosion may be accelerated rather than inhibited. The critical concentration above with inhibitors are effective depends on the nature and concentration of the aggressive ions.

b. Cathodic inhibitors

Cathodic inhibitors stifle the cathodic reaction either by restricting the access of oxygen or by poisoning sites favorable for cathodic hydrogen evolution. Cathodic inhibitors that decrease the corrosive action of aqueous solution on steel include salts of magnesium, manganese, zinc and nickel. The increase in alkalinity near the vessel walls by reduction of oxygen to OH^- leads to the precipitation of the hydroxides of these metals as a reasonably adherent porous deposit that retards the diffusion of oxygen to the steel.

The presence of calcium carbonate in water gives a general precipitate of calcium carbonate if the water is supersaturated or gives a local deposit on or near cathodic areas where the pH is high. The additions of lime to water increase the pH and serve as a cathodic inhibitor.

Cathodic inhibitor forms a visible film on the metal are generally not as sufficient as anodic inhibitors, and doesn't completely prevent attack. On the other hand, cathodic inhibitors are less likely than anodic inhibitors to intensify attack if added in sufficient amounts.

c. Mixed inhibitors

About 80 % of inhibitors are organic compounds that cannot be designated specifically as anodic or cathodic and are known as mixed inhibitors. Precipitation inducing inhibitors are films forming compounds that have a general action over the metal surface, blocking both anodic and cathodic sites indirectly. This organic compound has multiple bonds in their molecules that mainly contain nitrogen, sulphur and oxygen atoms [46, 47].

Organic inhibitors, on the other hand, are usually organic compounds which adsorb on the whole metal surface and simultaneously retard both the anodic and cathodic reactions. But, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors usually designated as "film-forming" and protect the metal by forming a hydrophobic film on the metal surface. The effectiveness of these inhibitors depends on the chemical composition, their molecular structure and their affinities for the metal surface because film formation is an adsorption process; the temperature of the system is an important factor.

1.11.4. Cathodic protection

Cathodic protection is a technique to control the corrosion of a metal surface by making it work as a cathode of an electrochemical cell. This is achieved by placing in contact with the metal to be protected another more easily corroded metal to act as the anode of the electrochemical cell. Cathodic protection systems are most commonly used to protect steel, water or fuel pipelines and storage tanks, steel pier-piles, ships, offshore oil platforms and onshore oil well casings. Cathodic protection can be, in some cases, an effective method of preventing stress corrosion cracking [48].

A side effect of improperly performed cathodic protection may be production of hydrogen ions, leading to its absorption in the protected metal and subsequent hydrogen embrittlement of welds and materials with high hardness. Under normal conditions, the ionic hydrogen will combine at the metal surface to create hydrogen gas, which cannot penetrate the metal. Hydrogen ions, however, are small enough to pass through the crystalline steel structure, and they can in some cases lead to hydrogen embrittlement [49].

Effectiveness of cathodic protection systems on steel pipelines is often nullified by the use of solid film backed corrosion coatings such as polyethylene tapes, shrinkable pipeline sleeves, and factory applied single or multiple solid film coatings. This phenomenon occurs because of the property of high electrical resistivity which solid film backings exhibit. Protective electrical current from the cathodic protection system is blocked by the highly resistive film backing, and cannot reach the steel pipeline surface.

1.11.5. 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. anodic protection is more suitable than cathodic protection for certain metals such as stainless steel specially in extremely corrosive environments, as in the handling and storage of concentrated sulfuric (sulphuric) acid. This method, however, requires careful monitoring and control otherwise it may instead hasten the corrosion process.

1.12. Types of adsorption

The adsorption of inhibitors is influenced by the nature and surface change of the metal, by the type of aggressive electrolyte and by the chemical structure of the inhibitor. The principle types of interaction between an organic inhibitor and a metal surface are physical (electrostatic, coulombic) adsorption and chemisorption (contact adsorption).

1.12.1. Physical adsorption

Physical adsorption is the result of electrostatic attractive forces between inhibiting organic ions or dipoles and the eclectrically charged surface of the metal. The surface charge of the metal is due to the electric field at the outer

Helmholtz plane of the electrical double layer existing at the metal/ solution interface. The surface charge can be defined by the potential of the metal (E_{corr}) vs. its zero-charge potential (zcp) (E_q=o) [50].

When the difference E_{corr} - $E_{q=0} = \xi$ is negative, cation adsorption is favored. Adsorption of anions is favored when ξ becomes positive. This behavior is related not only to compounds with formal positive or negative charge, but also to dipoles whose orientation is determined by the value of the ξ potential [51].

The position of the PZC can be useful in interpreting the positive synergistic effect observed in the corrosion inhibition of iron in sulfuric acid solution by quaternary ammonium cations in the presence of halide ions, such as chlorides [52]. In this case, the degree of inhibition in the presence of both absorbable anion and inhibitor cations is higher than the sum of the individual effect. At the free corrosion potential of iron in sulfuric acid solution, the surface charge of the metal is positive (E_{corr} about -0.2 V_H; PZC about -0.37 V_H). In this situation, only very poor adsorption of organic cations can occur. If chloride ions are present in the sulfuric acid solution, they are adsorbed on the metal surface and the creation of dipoles oriented to the surface takes place. As a consequence, the PZC shifts to more positive values. If the PZC is more positive than the free corrosion potential, the adsorption of inhibitor cations will occur. This effect can also explain the higher inhibiting efficiency of various organic cations on iron corrosion in hydrochloric acid solutions compared to sulfuric acid solutions.

1.12.2. Chemisorption

The most important type of interaction between an inhibitor and metal surface is chemisorption. In this type of adsorption, the adsorbed species actually come in contact with the metal surface. It is generally assumed that the

chemisorption process involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond. According to Bockris, there is not necessarily a chemical bond between the contact adsorbed species and the metal [53].

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

Chemisorption is specific for certain metals and is not completely reversible. The bonding occurring with electron transfer clearly depends on the nature of the metal and the nature of the organic inhibitor. In fact, electron transfer is typical for transition metals, having vacant and low-energy electron orbitals. Concerning inhibitors, electron transfer can be expected with molecules having relatively loosely bound electrons. This situation may arise because of the presence in the inhibitor molecule of multiple bonds or aromatic rings, whose electrons have a π character. Clearly, the presence of heteroatoms with lone-pair electrons in the inhibitor molecule will favor the electron transfer.

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

$$Se > S > N > O$$

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

1.13. Literature Survey

R.F. Godec, investigated the effectiveness of cationic surfactants of the N-alkyl quaternary ammonium salt type, i.e. myristyltrimethylammonium chloride (MTACl), cetyldimethylbenzylammonium chloride (CDBACl), andtrioctylmethylammonium chloride (TOMACl), as corrosion inhibitors for type X4Cr13 ferritic stainless steel in 2M H_2SO_4 solution. He used potentiodynamic polarization measurement showed that these surfactants hinder both anodic and cathodic processes, i.e. act as mixed type inhibitors. He found that the adsorption of the N-alkyl ammonium ion in 2M H_2SO_4 solution follows the Langmuir adsorption isotherm. He plotted log [θ/ (1- θ)] versus log C_{inh} yielded straight lines with a slope, which changed drastically at the critical micelle concentration (CMC) of the surfactants studied. He showed that the CMC could be accurately determined from these measurements. He noted that the calculated values of the free energy of adsorption ΔG_{ads} are, in cases when the charge on the metal surface is negative with respect to the PZC, relatively high what is characteristically for the chemisorptions. On other hand, for positive metal surfaces it is assumed that SO_4^{-2} anions are adsorbed first, so the cationic species would be limited by the surface concentration of anions. Accordingly ΔG_{ads} values were lower in this case and the adsorption is due to merely electrostatic attraction, which is characteristically of physisorption [54].

G. Gao, synthesized some tertiary amines in the series of 1, 3-di-amino-propan-2-ol, referred as 1,3-di-morpholin-4-yl-propan-2-ol (DMP) and 1,3-bis-diethylamino-propan-2-ol (DEAP), by alkylation's reaction. They checked these compounds by MS, IR, ^{1}HNMR and CNMR. They investigated the electrochemical performance of these products through potentiodynamic polarization measurement and electrochemical impedance spectroscopy (EIS) under thin electrolyte layer with thickness of 100 μm. They measured the

inhibition efficiencies by using gravimetric method. They noted that, these compounds retarding the anodic dissolution of iron by the protective layer bonding on the metal surface were anodic inhibitors under thin electrolyte layer. They noted that, polarization data indicated that the inhibitive performance of DMP for carbon steel was improved with the increasing of concentration, whereas DEAP showed a maximum inhibiting power at 2.5×10^{-2} M. The values of the charge transfer resistance, obtained from impedance plots of carbon steel, showed that DEAP was a promising inhibitor. The gravimetric results showed that the inhibition efficiency of DEAP at 2.5×10^{-2} M was 95 %. The adsorption on the carbon steel surface followed Langmuir isotherm model. They used the Fourier transform spectroscopy (FTIR) to analyze the surface adsorbed film [55].

A.A. Atia et al., studied the adsorption of dodecylbenzensulfonate (DBS) and cetylpyridinium bromide (CPBr) at liquid/air and bentonite/liquid interfaces. They calculated the surface excess concentration as well as the area occupied by each adsorbed surfactant molecule at liquid/air interface. They found that, the cationic surfactant (CPBr) was adsorbing on bentonite surface to a higher extent compared with anionic surfactant (DBS). The adsorption of CPBr exceeded the CMC of bentonite and they assumed to proceed via action exchange and to be enhanced by the mutual hydrophobic interaction among the hydrocarbon chains. On the other hand, they explained the adsorption of DBS to proceed due to specific adsorption. They were found that both surfactants to follow the pseudo second order kinetic indicating that the rate of the adsorption is controlled by both the concentration of surfactant as well as the surface properties of bentonite. They noted that, the thermodynamic parameter indicated that the adsorption of both DBS and CPBr is of physical nature [56].

C. Jeyaprabha et al., investigated the inhibition of corrosion of pure iron in 0.5M H_2SO_4 by ethanolamines such as mono-, di- and triethanol amines by dc polarization and ac impedance techniques. The result showed that a strong dependence of inhibitor performance with concentration in addition to the structural effects of amine molecules. From impedance data it is found that the corrosion of iron is controlled by charge transfer process at all concentrations of inhibitors. All the three inhibitors are found to hinder the formation of passive film on iron [57].

W. Wang et al., used surfactants as corrosion inhibitors in different applications. They developed methodology and formula to predict mild steel corrosion inhibition by alkyl pyridinium chloride and alkyl trimethyl ammonium bromide compounds. By utilizing different surfactants of varying chain lengths in different acidic media, they can evaluate the relationship between surfactant concentration, surfactant hydrocarbon chain length, and surfactant critical micelle concentration and corrosion inhibition. The results from this study can be used to improve relevant industrial uses of surfactants for corrosion inhibition [58].

M.T. Saeed et al., prepared variety of bisquaternary ammonium salts for first time by reacting N,N,N',N'–tetraallyl-1, 6-hexanediamine with allyl chloride, and 1-bromododecane in excellent yields (> 90 %). They were determined gravimetrically the inhibition efficiency for different concentrations of the synthesized compounds for the inhibition of corrosion of carbon steel in 1M HCl exposed for 6 h at 60° C. They were noted that the bisquaternary salts exhibited excellent inhibition efficiencies (97-99 %) in the acidic solution containing 400 ppm of the inhibitor. They were obtained comparable results by the electrochemical method using Tafel plots for the inhibition efficiency of the synthesized compounds. They were found the adsorption of these compounds on carbon steel surface obey Temkin's

adsorption isotherm. The work marked the beginning of constituting an important class of new inhibitors containing multiple adsorption centers of positive nitrogen as well as Π-donor moieties [59].

G. Bereket et al., studied the potentiodynamic polarization on the inhibition of low carbon steel in 0.1M hydrochloric acid solution over the temperature range 20-60 °C at different inhibitor concentrations by various quaternary ammonium salts and cationic surfactants. The inhibitors examined were tetraethylammonium chloride, tetrabutylammonium chloride, benzyl trimethylammonium chloride, benzyltriethylammonium chloride, benzyltri-butylammonium chloride, phenyltrimethylammonium chloride, alkylbenzyl-dimethylammonium chloride, tetradecyltrimethylammonium bromide and cetyltrimethylammonium bromide. They were found that the maximum inhibition efficiencies of cationic surfactants observed around and above critical micelle concentration (cmc), while the inhibition efficiencies of the quaternary ammonium salts increase with the increase in their concentrations. The degree of shift in E_{corr} value, together with change in anodic and cathodic Tafel slopes ($ß_a$, $ß_c$), revealed that cationic surfactants behave as an anodic inhibitor, while quaternary ammonium salts behave as mixed type inhibitors. Inhibition efficiencies of studied inhibitors seem to be closely related with the chain length of the alkyl group as well as the presence of benzene ring in quaternary ammonium compounds. They were calculated thermodynamic and kinetic parameters for dissolution and adsorption [60].

A. Kumar, studied the inhibiting effect of Cetyl pyridinium chloride (CPC) on mild steel in 1M Hydrochloric acid by using three techniques namely weight loss, electrochemical polarization and metallurgical research microscopic techniques. He was noted that the results obtained reveal that CPC is good inhibitor and shows very good corrosion inhibition efficiency (IE). He was found the IE varied with concentration of inhibitor and

temperature. The electrochemical polarization result revealed that CPC is anodic in nature [61].

R.F. Godec, performed the electrochemical measurements to investigate the effectiveness of cationic surfactants of the N-alkylquaternaryammonium salt type with different counter ions and different chain lengths, as corrosion inhibitors for ferritic stainless steel type X4Cr13 in 2M H_2SO_4 solution. Tow of them was single-chained surfactants and the other two were composed of three C_8 alkyl-chains. The chosen cationic surfactants were myristyltrimethyl-ammonium chloride (MTACl), myristyltrimethylammonium bromide (MTABr), trioctylmethylammonium chloride (TOMACl), trioctylmethyl-ammonium bromide (TOMABr). Potentiodynamic polarization measurements showed that these surfactants hinder both anodic and cathodic processes; they act as mixed type inhibitors. He was found that, the adsorption of the n-alkyl ammonium ion in 2M H_2SO_4 solution is in accordance with the Langmuir adsorption isotherm. Plots of log [θ/ (1- θ)] versus log C_{inh} yielded straight lines with a slope, which changed drastically at the critical micelle concentration (CMC) of the surfactants studied. The plot of log θ vs. $\log_{inh}$ confirms the four-region reverse orientation model of adsorption, suggested by Somasundaran and Fuerstenau. In region IV where is progress in the formation of a multilayer. He was supposed that two different multilayer formed on metal surface in the case of TOMABr and MTABr. The influence of added-CH_2 groups (chain length) on the inhibition efficiency is greater than the influence of different counterions [62].

Z. A. Chikh et al., showed that 1, 12-bis (1, 2, 4-triazolyl) dodecane (dTC12) is an excellent corrosion inhibitor for carbon steel in 1M HCl solution. They were used in this work electrochemical and analytical techniques the inhibition study of corrosion on carbon steel in acidic medium. They were attributed the carbon steel corrosion inhibition of dTC12 to show

the synergistic effect between chloride anion and quaternary ammonium ion. The protective efficiency of the film was higher than 90 %, indicating that corrosion of carbon steel in 1M HCl is reduced by dTC12. They were investigated the effect of dissolved oxygen on the inhibition efficiency. The result show that the inhibition efficiency increases in early stage and decreases for along immersion time [63].

M. Hosseini et al., studied the inhibition effects of sodium dodecylbenzensulphonate (SDBS) and hexamethylenetetramine (HA) on the corrosion of mild steel in sulphuric acid solution by using weight loss, electrochemical impedance and Tafel polarization measurements. For HA, monotonous inhibition efficiency increasing is observed as a function of concentration. For SDBS, however, an optimum in the inhibition efficiency is observed as a concentration close to 250 ppm, which is ascribed to the formation of hemi-micellar aggregates that provoke inhibitor adsorption from the metal/solution interface at higher concentrations. Upon mixing HA and SDBS, concentration regions showing synergistic and antagonistic inhibition behavior are identified, and it is concluded that electrostatic interactions between adsorbate ions are likely responsible for both phenomena. They were used Langmuir and Frumkin isotherms for tested the relevance in describing the adsorption behavior of both HA and SDBS [64].

S.T. Keera et al., studied the effect of adding some organic surfactants, cocamide diethanol amine as a nonionic surfactant (NS), cetrimonium chloride as a cationic surfactant (CS), and cocamidopropyl betaine as an amphoteric surfactant (AmS), on the electrochemical behaviour of carbon steel in formation water was investigated by using a potentiodynamic and impedance techniques. Results reported in this study show that the addition of these surfactants inhibits the corrosion of carbon steel and the extent of inhibition depends upon the type and concentration of the surfactant [65].

A.M. Alsabagh et al., studied the reactivity of polyester aliphatic amine surfactants as corrosion inhibitors for carbon steel in formation water (deep well water). These surfactants exhibit different levels of inhibition particularly at high concentration (200 ppm). These compounds function via adsorption on reactive sites on the corroding surface reducing the corrosion rate of the metal. It was revealed that the adsorption of these surfactants obey Langmuir adsorption isotherm. The inhibition effectiveness increases with the length of the aliphatic hydrocarbon chain, being a maximum in the presence of surfactant IV (96 % efficiency) [66].

H.H. Hassan, studied The corrosion behavior of mild steel in 0.1M HCl solution without and with 5-amino-1,2,4-triazole (5-ATA), 5-amino-3-mercapto-1,2,4-triazole (5-AMT), 5-amino-3-methylthio-1,2,4-triazole (5-AMeTT) or 1-amino-3-methylthio-1,2,4-triazole (1-AMeTT) as a function of the immersion time and the solution temperature. He was used in this study potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Results obtained showed that the inhibition efficiency (IE%) increases with increasing the immersion time reaching its maximum value after 1 h, IE% slightly decreased and subsisted at reasonable values at least during the studied 20 h. The adsorptive behavior of the investigated inhibitors on the steel surface followed Langmiur isotherm. He found that, the increasing temperature was greatly enhance IE% till arriving plateau at about 80 % for 5-ATA and more than 90 % for the other compounds between 323 and 348 ^{o}K. The polarization and impedance measurements were in good agreement. These results indicate the suitability of the use of the investigated inhibitors in the cooling systems. The plots of ln K versus 1/T for the four studied inhibitors showed non-linear behavior. The standard enthalpy, ΔH^{o}_{ads}, entropy, ΔS^{o}_{ads} and free energy changes of adsorption $\Delta G^{o}_{ads.}$ were evaluated using a proposed quadratic equation based on an inverse square dependence

of the heat capacity on temperature. The calculated values of ΔG°_{ads} were negative while those for ΔH°_{ads} and ΔS°_{ads} were positive. The values of the three thermodynamic functions of adsorption for the four investigated inhibitors were decreased with increasing the solution temperature. All the above results are suggestive of chemisorption of inhibitor molecules on the steel surface [67].

F. Wombacher et al., presented new results and sum up the behavior of aminoalcohol based mixed corrosion inhibitors. They were used these organic and mixed (organic/inorganic) inhibitors as concrete admixtures or in repair products to delay the onset of corrosion or to reduce the rate of corrosion of reinforcing steel in concrete structures. The inhibitors delay the onset of corrosion and reduce the rate of corrosion. A part from their application as concrete admixture, they can be used as surface-applied inhibitors on existing concrete structures, in repair mortars or in grouts for rock bolts and anchors [68].

M.A. Migahed et al., studied the corrosion inhibition of carbon steel in acid chloride solution using ethoxylated fatty alkyl amine surfactants. They were using gravimetric, open circuit potential and potentiostatic polarization techniques. They were showed that the adsorption of the surfactants on carbon steel followed the Langmuir adsorption isotherm. Potentiostatic polarization data indicated that these surfactants act as mixed type inhibitors [69].

A.K. Satpati et al., studied the mechanism and efficiency of corrosion inhibition using 1,2,3-benzotriazole (BTAH) as the inhibitor on stainless steel corrosion in sulphuric acide. They were used electrochemical impedance spectroscopy (EIS) as well as the potentiodynamic polarization for the quantification of inhibition efficiency and determination of the mechanism of interaction of the metal surface with the inhibitor molecule. They were found that, under the present experimental condition 1,2,3- benzotriazole was

an efficient inhibitor for the acid corrosion of austenitic stainless steel and the inhibition efficiency of up to 97 % was obtained. They were observed that, in presence of inhibitor there is a diffusional contribution on the mechanism of the corrosion process in impedance measurements at low frequency region. They were studied the effect of temperature on the mechanism and also on the efficiency of the corrosion inhibition process by using the Arrhenius approximation of the rate law. Polarization experiments were performed at different solution temperatures. Thermodynamic parameters for the corrosion process were obtained and interpreted. The adsorption of the inhibitor, BTAH, on the stainless steel surface in the acid medium (0.1M H_2SO_4) obeyed the Langmuir adsorption isotherm. Present results were discussed and compared with the similar results reported by some other groups [70].

B. Gao et al., prepared quaternized polyethyleneimine (QPEI) via two procedures of macromolecular reactions, tertiary amination reaction and quaterisation, and its chemical structure which characterized by infrared and UV spectra. They were mainly investigated the corrosion inhibition property of QPEI for low carbon steel (A_3 steel) in H_2SO_4 solution by using weight loss method, electrochemical technique (potentiodynamic polarization curves) and scanning electron microscopy (SEM) investigation. They were also fully explored the corrosion inhibition mechanism of QPEI. The experiment results show that as a polymeric quaternary ammonium salt, QPEI is quite an excellent corrosive inhibitor, it possesses outstanding inhibition action for low carbon steel, and only with 5 mg L^{-1} QPEI concentration, the inhibition efficiency can reach to 92 % in 0.5M H_2SO_4 solution for 72 h of immersing time. The inhibition efficiency increases with the increase of QPEL concentration, and the inhibition efficiency also increases with the enhancement of the cationic degree (quaternized agree) of QPEI. QPEI acted as a mixed type inhibitor with anodic predominance. QPEI possesses function

of double filming, adsorption filming and polymer filming, with the cooperation of the two filming effects, QPEI can form a compact barrier film on A_3 steel surface, and prevent metal dissolution and retard H^+ discharging. They were found that, the adsorption of QPEI on A_3 steel surface follow the Langmuir isotherm equation [71].

R.F. Godec, studied the corrosion inhibition characteristics of mixtures of cationic/zwitterionic types of surfactant (Myristyltrimethyammonium bromide/Palmitylsulfobetaineas), and non-ionic surfactant TRITON-X-405 mixed with 1mM of KBr, as corrosion inhibitors for stainless steel (SS) (type X4Cr13) in aqueous solutions of 2M H_2SO_4. He was investigated this compounds by using potentiodynamic polarisation measurements. The polarization data showed that mixtures of the surfactants used in this study acted as mixed inhibitors, adsorbing on the stainless steel surface in agreement with the Flory–Huggins adsorption isotherm. The tensiometric results of this study suggest the existence of a second state of aggregation for zwitterionic/cationic surfactant mixtures. From these values of the free energy of adsorption, which in both mixtures decreased with respect to a single surfactant, we concluded that the adsorption in mixtures was stronger. The mixtures studied here showed good inhibition properties for ferritic stainless steel type X4Cr13 in 2M H2SO4 solution [72].

M.Z.A. Rafiquee et al., studied the corrosion inhibition characteristics of 2-aminophenyl-5-mercapto-1-oxa-3,4-diazole (AMOD) on mild steel in HCl solution by weight loss studies and potentiodynamic polarization. AMOD is a good corrosion inhibitor in HCl solution and its inhibition efficiency increased markedly in presence of surfactants (SDS, CTAB, TX-100). TX-100 is found to be most effective among the tested surfactants. Weight loss measurements showed that the inhibition efficiency increased with the increasing surfactant concentration and attained a maximum value

around 0.2 mol dm^{-3}. In presence of surfactant, the adsorption of AMOD on the mild steel surface obeyed Langmuir's adsorption isotherm. They were investigated the influence of inhibitor concentration, solution temperature and acid concentration on the corrosion rate of mild steel. The deduced thermodynamic parameters for adsorption reveal a strong interaction between the inhibitor and mild steel surface. The negative values of G_{ads} indicate the spontaneous adsorption of inhibitors on the mild steel surface. Potentiodynamic polarization studies show that these surfactants are mixed inhibitors [73].

R. Solmaz et al., studied the adsorption of 2-amino-5-mercapto-1,3,4-thiadiazole (2A5MT) on mild steel (MS) surface in 0.5M HCl solution and its corrosion inhibition effect in both short and long immersion times (over 120 h). For this purpose, they were utilized a series of techniques, such as potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR), thermogravimetric analysis (TGA), surface photographs, hydrogen evolution (V_{H2}-t) and change of open circuit potential with immersion time (E_{ocp}–t). They were calculated and discussed the values of activation energy for MS corrosion and the thermodynamic parameters, such as adsorption equilibrium constant (K_{ads}), free energy of adsorption (G_{ads}), adsorption heat (H_{ads}) and adsorption entropy (S_{ads}) values. They were studied the potential of zero charge (E_{pzc}) of MS in inhibited solution both after short and long immersion times by EIS method, and a mechanism of adsorption process was proposed. Results showed that 2A5MT performed excellent inhibiting effect for the corrosion of MS in 0.5M HCl solutions and inhibition efficiency is higher than 99 % after 120 h at 1.0×10^{-2} M. They were discussed the high inhibition efficiency in terms of strongly adsorption of inhibitor molecules on the metal surface and forming a protective film. Surface photographs showed a good surface coverage on the

metal surface. TGA results indicated that, the surface inhibitor film has relatively good thermal stability [74].

O.A. El-Seoud et al., synthesized a series of surface-active ionic liquids, RMeImCl, by the reaction of purified 1-methylimidazole and 1-chloroalkanes, RCl, R = C10, C12, C14 and C16, respectively. They were studied adsorption and aggregation of these surfactants in water by surface tension measurement. Additionally, they have employed solution conductivity, electromotive force, fluorescence quenching of micelle-solubilized pyrene, and static light scattering to investigate micelle formation. The following changes resulted from an increase in the length of R: an increase of micelle aggregation number; a decrease of minimum area/surfactant molecule at solution/air interface; critical micelle concentration and degree of counter-ion dissociation. Theoretically, they were calculated aggregation numbers and those based on quenching of pyrene are in good agreement. Gibbs free energies of adsorption at solution/air interface, ΔG^{o}_{ads}, and micelle formation in water, ΔG^{o}_{mic}, were calculated, and compared to those of three surfactant series, alkylpyridinium chlorides, RPyCl, alkylbenzyldimethylammonium chlorides, $RBzMe_2Cl$, and benzyl(3-acylaminoethyl)dimethylammonium chlorides, $RAEtBzMe_2Cl$, respectively. Contributions to the above mentioned Gibbs free energies from surfactant methylene groups (in the hydrophobic tail) and the head-group were calculated. For RMeImCl, the former energy is similar to that of other cationic surfactants. The corresponding free energy contribution of the head-group to ΔG^{o}_{mic} showed the following order: RPyCl >$RBzMe_2Cl$ >RMeImCl >$RAEtBzMe_2Cl$. The head-groups of the first two surfactant series are more hydrophobic than the imidazolium ring of RMeImCl, this should favor their aggregation. Micellization of RMeImCl, however, is driven by a relatively strong hydrogen-bonding between the chloride ion and the hydrogens in the

imidazolium ring, in particular the relatively acidic H_2. This interaction more than compensates for the relative hydrophilic character of the diazolium ring. As indicated by the corresponding ΔG^{o}_{mic}, micellization of $RAEtBzMe_2Cl$ is more favorable than that of RMeImCl because the –CONH– group of the former surfactant series forms hydrogen bonds to both the counter-ion and the neighboring molecules in the micelle [75].

M.A. Migahed, studied the effect of non-ionic surfactant, namely N,N-di(polyoxyethylene) amino lauryl amide, on the corrosion rate of carbon steel in produced water and has investigated by various corrosion monitoring techniques. The strong adsorption ability of the surfactant molecules leads to formation of a mono-layer, which isolates the surface from the environment and thereby reduces the corrosion attack on the surface. He was found that, the adsorption process obeyed Langmuir adsorption isotherm. The potentiostatic polarization results clearly revealed that the inhibitor behaves as a mixed type. The maximum percentage inhibition efficiency (η%) approached 94.87 % in presence of 250 ppm of the inhibitor molecules. He was studied the effect of temperature on the corrosion rate of carbon steel in the temperature range from 30 to 70 °C. Finally, he was used scanning electron microscopy to examine the surface morphology of carbon steel samples in absence and presence of the inhibitor [76].

S.A. El-Maksoud, investigated the effect of hexadecylpyridinium bromide (HPB) and hexadecyltrimethylammonium bromide (HTAB) on the corrosion behavior of iron and copper in hydrochloric and sulphuric acid solutions by potentiodynamic polarization and Tafel extrapolation methods. The polarization curves indicate that the two compounds behave as mixed inhibitors, but the cathode is more inhibited. HPB is more effective than HTAB in both acids; this is explained on the basis of the charge located on the nitrogen atom on the two compounds. They were investigated the

inhibition efficiency of the compounds is more effective for iron and copper metals in HCl than in H_2SO_4, which is explained on the basis of the potential of zero charge of the metal surface and the adsorption ability of both Cl^- and SO_4^{2-} on the metal surface [77].

J. Harkot et al., studied the surface tension measurements for aqueous solutions of two cationic surfactants: Dodecylethyldimethylammonium bromide (C_{12}(EDMAB)) and benzyldimethyldodecylammonium bromide (BDDAB). They were determined isotherms and thermodynamic adsorption parameters from the surface tension data. Firstly, they were determined the surface excess concentration in the adsorbed monolayer and the total concentration of the surfactants, then the standard free energy of adsorption was calculated by different methods. In the calculations, different orientations of the surfactants at the adsorbed monolayer were also taken into account. From the experimental and calculated data it results that the difference in the structure of the two cationic surfactants by changing the methyl group for aryl one in their heads causes an increase of the efficiency and a decrease of the effectiveness of adsorption at water/air interface, and that the standard free energy of adsorption can be predicted from the surface tension of the surfactants assuming the aryl group to be equivalent to 3.5 methylene groups. The experimentally obtained difference between the standard free energy of adsorption of the C_{12}(EDMAB) and BDDAB was in good agreement with that theoretically accounted, corresponding to the standard free energy of adsorption of the aryl group. However, the best correlation between the values was obtained when a parallel orientation of the surfactant molecules at the adsorbed monolayer was taken into account [78].

P.C. Okafor et al., investigated the inhibition behavior of 2-undecyl-1-ethylamino-1-methylbenzyl quaternary imidazoline (2UMQI) and KI on mild steel in 1M H_2SO_4 solutions at 25 ^oC using electrochemical methods. The

results indicated that 2UMQI inhibited the corrosion of mild steel and the extent of inhibition increased with 2UMQI concentrations. The inhibition action in the presence of 2UMQI is due to physical adsorption of 2UMQI. A mixed inhibition mechanism is proposed for the inhibitive effects of 2UMQI. They were enhanced the inhibition efficiency of 2UMQI by the addition of iodide ions. In the presence of KI, the potentials of unpolarization, E_u was observed and increased with KI concentration [79].

H. Tavakoli et al., studied the inhibition effects of sodium dodecylbenzenesulphonate (SDBS) and 2-mercaptobenzoxazole (2-MBO) on corrosion of copper in sulphuric acid solution by using electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements. They were observed for 2-MBO, a monotonous increase in inhibition efficiency as a function of concentration. For SDBS, however, an optimum in the inhibition efficiency was observed for a certain concentration, which is ascribed to the formation of hemi-micellar aggregates that provoke inhibitor desorption from the metal/solution interface at higher concentrations. Upon mixing 2-MBO and SDBS inhibitors, concentrations range showing synergistic inhibition behavior were identified, and it is concluded that electrostatic interactions between the adsorbed ions. They were tested different adsorption isotherms for describing the adsorption behavior of both 2-MBO and SDBS [80].