Introduction
&
Literature Survey

CHAPTER I

Introduction and Literature Survey

Surfactants "Surface active agents"

A surface active agent is a substance that at low concentration adsorbs 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.

Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group, together with a group that has strong attraction for the solvent, called the lyophilic group. This is known as an amphipathic structure [1]. Because of the presence of the hydrophilic group a surfactant is more or less readily soluble in water. However the hydrophobic group is repelled by water, so that there is a tendency for that portion of the molecule to leave the aqueous phase. This leads to a higher concentration at the surface of the solution at the air-water interface. The surfactants orient themselves with the hydrophilic groups in the water phase, the hydrophobic groups extending as far as possible in the other direction, still consistent with the molecular dimensions and geometry and with the intermolecular forces acting upon them. The result of this oriented surface film is the lowering of the surface tension of the water, and a greater tendency toward bubble and foam formation. In the presence of an immiscible liquid a similar layer tends to form at the liquid-liquid interface with the hydrophilic groups oriented toward the water, hydrophobic toward the other liquid. This promotes dispersion and emulsification as droplets. At liquid-solid interfaces a similar phenomenon occurs. In all of these cases an equilibrium exists between the surface molecules at the interface and the internal ones, with molecules constantly entering and leaving the two regions. The chemical structures of groups suitable as the lipophobic and lipophilic portions of

the surfactant molecule vary with the nature of the solvent and the conditions of use. In a highly polar solvent such as water, the lipophobic group may be hydrocarbon or fluorocarbon or siloxan chain of proper length. Whereas in a less polar solvent, only some of these may be suitable, e.g. fluorocarbon or siloxan chains in polypropylene glycol. In a polar solvent such as water, ionic **or** highly polar groups may act as lipophilic group. Whereas in a nonpolar solvent, such as heptane, they may act as lipophobic group. As the temperature and use conditions, e.g. presence of electrolyte or organic additive vary, modifications in the structure of the lipophobic and lipophilic groups may become necessary to maintain surface activity at a suitable level. Thus for surface activity in a particular system, the surfactant molecule must have a chemical structure that is amphipathic in that solvent under the used conditions. The hydrophobic group is usually a long chain hydrocarbon residue, less often a halogenated or oxygenated hydrocarbon of siloxan chain the hydrophilic group is an ionic or highly polar group. Depending on the nature of hydrophilic group, the surfactants are classified according to the charge of the hydrophilic group into:

Ionic Surfactants

Ionic surfactants are often represented schematically by (—O), a polar "head", (O), which is charged either positively or negatively, attached to a nonpolar "tail (—) [(2)]. Ionic surfactants usually are classified as follows:

a. Anionic Surfactants: are those which give negatively charged surfactant ions in aqueous solution. Anionic surfactants are usually contain sulfonate, sulfate, or carboxylate groups. Commercially these are very important and represent the major fraction of surfactants in use today. For the most part they are produced by sulfonation or sulfation of the desired hydrophobe.

$$RSO_3^-Na^+ + H_2O \rightarrow RSO_3^- + Na^+$$

b. Cationic Surfactants: are those which give a positively charged surfactant ion in aqueous solution, for example, quaternary ammonium derivatives.

$$RN^{+}(CH_3)_3Cl^{-} \rightarrow RN(CH_3)_3^{+} + Cl^{-}$$

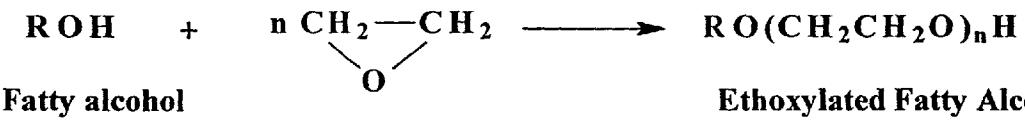
c. Amphoteric Surfactants: Both positive and negative charges may be present in the surface-active portion, for example, $RN^{+}H_2CH_2COO^{-}$ (long chain amino acid), $RN^{+}(CH_3)_2CH_2CH_2SO_3^{-}$ (sulfobetaine).

Nonionic Surfactants

When a molecule has no ionizable groups and the polarity in the surfactant molecule is not localized, but spread over a number of groups, the surfactants does not ionize in aqueous solution. It is then called a nonionic surfactant and is often represented schematically as (~~~). Here again we have a non-polar tail, but the head usually consists of a number of repeating groups such as oxyethylenes $-CH_2CH_2-O-$ or, less frequently, oxy-propylene $-CH(CH_3)OCH_2-$. The solubility of the surfactant in water increases with the number of such groups, typically from 8 to 30 oxyethylenes. The nature of the reaction between alkylene oxides and alkyl or aryl substances containing an active hydrogen atom such as –OH, $-NH_2$, -SH, -COOH, $-CONH_2$, is such that the polyethers obtained contain oxyalkylene chains varying in length according to a Poisson distribution. The distribution may vary with manufacturing conditions while the mean may be the same [3].

Condensation of Ethylene Oxide With Long Chain Fatty Alcohols

Ethylene oxide adds to alcohols to yield ether adducts:



Fatty alcohol **Ethoxylated Fatty Alcohol**

The hydrogen of the hydroxyl group of the starting material is less active than that present on the terminal hydroxyl groups of the glycol ethers. Quantitative yield of monoglycol ethers are not therefore obtained at first when reacting with ethylene oxide, but the higher homologous polymers start to form while the free alcohol is still present [4]. Consequently, the addition velocity is slower at the start and then increases gradually and becomes constant when

all the alcohol has been converted to the monoglycol ether. The activity of hydrogen differs from primary, secondary and tertiary alcohols. The length of the hydrophobic portion and its structure either straight or branched also has a similar effect.

The nonionic surfactants derived from alcohols have excellent surfactant properties and chemical stability [5]. The principal alcohols used in making these surfactants include the naturally derived fatty and rosin alcohols, synthetic lipophilic alcohols and hydrophilic polyhydric alcohols.

The lipophilic alcohols derived from natural fats and oils were among the first materials used in making nonionic polyoxy-ethylene surfactants and they continue to present the largest segment of the aliphatic polyether class. These alcohols are made from esters by reduction with sodium or by catalytic hydrogenation. The fatty alcohols used in producing aliphatic polyoxyethylene ethers are lauryl, oleyl, tallow and hydroabietyle.

The aliphatic polyoxyethylene ethers exhibit excellent stability to acid and bases. Polyoxyethylene alkylethers are often preferred to other surfactants when using in raw wood scouring dye leveling, liquid dish washing detergents, improving the regenerative spinning of viscous fibers, kier boiling of cotton, mold release lubricants, detergent stabilizers, alkaline metal cleaners, secondary recovery in oil wells and foaming agents for air drilling and as emulsifiers for a variety of materials including silicon and polyethylene.

Other hydrophobic bases including linear propylene oxide polymers were described [6]. The polyoxypropylene ethoxylates are used in conjugation with other surfactants when highly efficient wetting or detergency is required.

Polymeric Surfactants

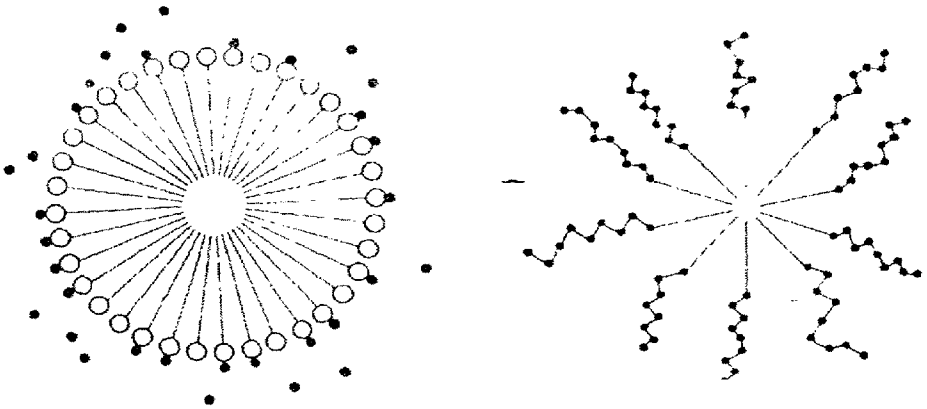
The growing interest in polymeric surfactants (or surface active polymers) can be said to emanate from two characteristic features [7] :

1. They have a very strong driving force to proceed to the interface and show a tendency to collect at the interface that is not as dependent on physical variable as for normal, low molecular weight surfactants. This means that:
    - The products are effective at low total concentrations,
    - The products show little sensitivity to salts, temperatures, etc.
2. They can have long polyoxyethylene (or polysaccharide) chains and still be retained at interface. (Low molecular weight surfactants with long hydrophilic chains tend to be desorbed from the interface and dissolve in the aqueous phase).

    It is known that differences in the nature of the hydrophobic groups are usually less pronounced than in the nature of the hydrophilic groups. Generally they may be long straight or branched alky group [8] , high molecular weight propylene oxides [9,10] or long fluoro-alkyl group [11].

Micelle Formation by Surfactants

Micelle formation is the most fundamental issue in surfactant technology because it is the most effective geometric arrangement of the molecules at a specific desired concentration. The surfactant molecules when dispersed in water tend to be adsorbed at the interface, leading to a 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 [12]. Further increments of surfactant concentration leads to the formation a critical micelle concentration, abbreviated CMC. The CMC is defined as the concentration of the surfactant at which a decrease in the surface tension could be obtained upon addition of any further amounts of surfactant in the solution. There is an equilibrium between the singly adsorbed surfactant molecules at the interface and the micellized surfactant molecules. This equilibrium occurs at the concentration of complete surface saturation.



Ionic micelles **Nonionic micelles**

Figure 1: Illustration of Ionic and Nonionic Micelles

Adsorption on the Liquid / Solid Interface

The adsorption of surfactants on the solid/liquid interface is strongly influenced by a number of factors:

- The nature of the structural groups on the solid surface. The surface can contain highly charged sites or essentially nonpolar groups that are defined by the nature of the atoms from which these sites or groups are constituted.
- The molecular structure of the surfactant being adsorbed. The surfactant can be ionic or nonionic and the hydrophobic group can be long or short, straight chain or branched and aliphatic or aromatic.
- The environment of the aqueous phase is also important, for example its pH, electrolyte content, the presence of any additives such as short chain polar solutes and temperature.

Together, these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption.

Mechanism of Adsorption

There are a number of mechanisms by which a surface active agent may adsorb onto a solid substrate from aqueous solution. In general, adsorption of surfactants involves single ions rather than micelles [13].

1- Ion exchange: involves replacement of counter-ions absorbed onto the substrate from the solution by similarly charged surfactant ions [14].

2- Ion pairing: adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counter-ions [15].

3- Adsorption by hydrogen bond formation between substrate and adsorbate [16].

4- Adsorption by polarization of π-electrons occurs when the adsorbate contains electron rich aromatic nuclei and the solid adsorbent has strongly positive sites. Attraction between electron-rich aromatic nuclei of the adsorbate and positive sites on the substrate results in adsorption.

5- Adsorption by dispersion forces occurs via London Van der Waals dispersion forces acting between adsorbent and adsorbate molecules. Adsorption by this mechanism generally increases with increase in the molecular weight of the adsorbate and is important not only as an independent mechanism but also as a supplementary mechanism in all other types. For example, it accounts in part for the pronounced ability of surfactant ions to displace equally charged simple inorganic ions from solid substrate by an ion exchange mechanism.

6- Hydrophobic bonding occurs when the combination of mutual attraction between hydrophobic groups of the surfactant molecules and their tendency to escape from an aqueous environment becomes large enough to permit them to adsorb onto the solid adsorbent by aggregating their chains.

Al-Sabagh et al., [17] prepared nine novel nonionic polymeric surfactants based on ethoxylated aniline, 2-amino benzene thiol and benzene sulphonamide. The number of ethylene oxide units was 2, 10 and 20. The prepared surfactants were characterized by molecular weights

determination and elemental analysis. Surface tension as a function of concentration of the surfactants in the aqueous phase was measured at 25, 35, 45 and 55 °C using the drop volume tensiometer. From these measurements, the critical micelle concentration (CMC), the maximum surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}), the effectiveness of surface reduction and the efficiency (pc20) were calculated. The thermodynamic parameters of micellization (ΔG_{mic}, ΔH_{mic}, ΔS_{mic}) and of adsorption (ΔG_{ad}, ΔH_{ad}, ΔS_{ad}) for those surfactants were also calculated. Static light scattering was used to determine the aggregation number (N°), while dynamic light scattering provides the hydrodynamic radius of the micelle (R_H) and the diffusion coefficient at different surfactant concentrations. The values of R_H at different concentrations were used to determine the critical micelle concentration (CMC) giving results that are comparable to those obtained by the surface tension measurements.

Principles of Corrosion

Corrosion can be defined as the destructive attack of metals or alloys by chemical or electrochemical reaction with their environment. 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 everywhere 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 corrosion, selective corrosion and pitting corrosion.

Types of Corrosion:

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.

2- Pitting Corrosion

Pitting is a form of localized attack that causes localized penetration of the metal. It is one of the most destructive and insidious forms of corrosion. Pitting causes a small percent weight loss of the whole structure.

3- Intergranular Corrosion

Intergranular corrosion consists of localized attack at, and adjacent to, grain boundaries with relatively little corrosion of the grains, and results in disintegration of the alloy and loss of strength.

4- Galvanic Corrosion

Galvanic corrosion occurs when a potential difference exists between two dissimilar metals immersed in a corrosive solution. The potential difference produces a flow of electrons between the metals, the less corrosion resistant metal becomes the anode and the more corrosion resistant one the cathode.

5- Crevice Corrosion

Crevice corrosion is also known as deposit or gasket corrosion. Crevice corrosion occurs when there is a difference in ion or oxygen surroundings.

6- Corrosion Fatigue

Corrosion fatigue occurs due to the combined action of corrosion and cyclic stresses such as rapidly alternating tensile and compressive stresses.

7- 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 forms on contacting surfaces under load in atmospheric air.

8- 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.

9- Selective Leaching or Demetalification

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

10- Filiform Corrosion

Filiform corrosion appears as a network of corrosion trails of a worm like structure, particularly beneath thin organic salts containing chlorides, which have been left on the surface prior to coating [18].

Electrochemical Reactions of Aqueous Corrosion

Most metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte. Corrosion of metals requires the presence of two important processes: anodic and cathodic reactions. This can be written in the general form [19].

$$M \longrightarrow M^{*n+} + ne \qquad \textbf{[Anodic Reaction]}$$

There are several different cathodic reaction which are frequently encountered in metallic corrosion. The most common cathodic reactions which are:

- Hydrogen evolution

$$2H^+ + 2e \longrightarrow H_2 \qquad \textbf{[Acid solution]}$$

$$2H_2O + 2e \longrightarrow H_2 + 2^-OH \qquad \textbf{[Neutral or alkaline solution]}$$

- Oxygen reduction

$$O_2 + 4H^+ + 4\,e \longrightarrow 2H_2O \qquad \textbf{[Acid solution]}$$

$$O_2 + 2H_2O + 4\,e \longrightarrow 4^-OH \qquad \textbf{[Neutral or alkaline solution]}$$

- Metal ion reduction

$$M^{3+} + e \longrightarrow M^{2+}$$

- Metal deposition

$$M^{+} + e \longrightarrow M$$

Corrosion Prevention By Corrosion Inhibitors

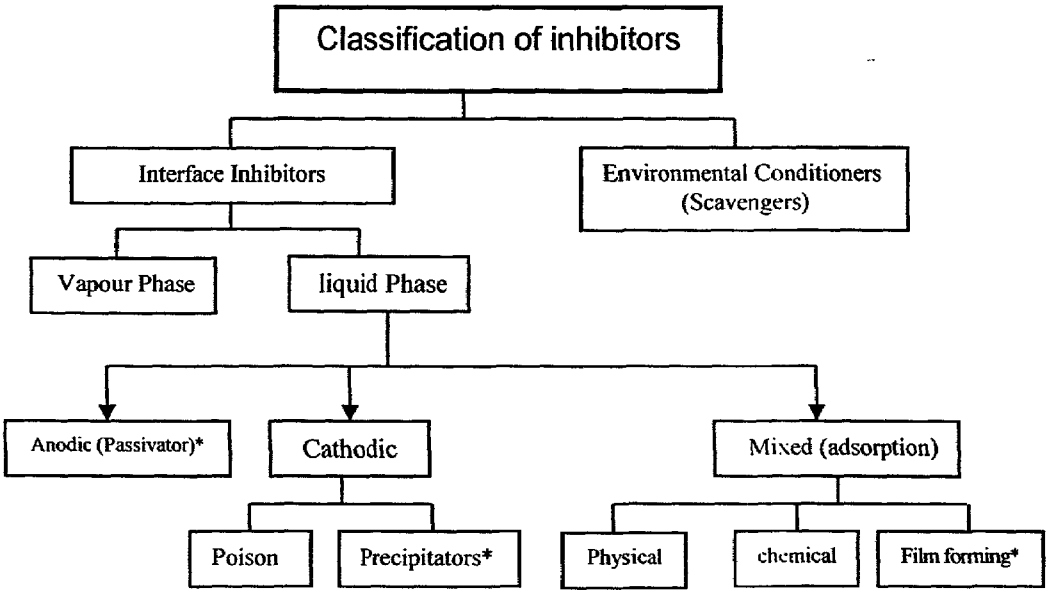
An inhibitor is a chemical substance which when added in small concentration to corrosive environment effectively decreases or prevents the reaction of the metal with the environment [20]. Corrosion inhibitors may be in liquid or powder form that effectively reduce the corrosion rate by adsorbing on the metal surface [21] 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.

Structure of the Inhibitors

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 pairs 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 [22]. 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. Hence, with increasing electron density on the functional group a stronger coordinate bonding with metal surface is produced hence, greater adsorption.

Classification of Inhibitors

Inhibitor selection is based on the metal and the environment. A qualitative classification of inhibitors is presented in **Scheme 1.** Inhibitors can be classified into environmental conditioners and interface inhibitors.



Scheme 1: Classification of Inhibitors.

* Form three- dimensional layers at the interface, so they are classified collectively as interphase inhibitors.

Environmental Conditioners (Scavengers)

Corrosion can be controlled by removing the corrosive species in the medium with inhibitors that decrease corrosivity of the medium by scavenging. The aggressive substances are called environmental conditioners or scavengers. In near-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) [23].

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 which 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 serves as a cathodic inhibitor.

Cathodic inhibitors that form a visible film on the metal are generally not as efficient as anodic inhibitors and do not 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. The most common inhibitors of this category are the silicates and the phosphates. Organic inhibitors, on the other hand, are usually organic compounds which adsorb on the whole metal surface and simultaneously retard both the anodic and cathodic reactions. 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 their chemical composition, molecular structure and affinity for the metal surface. Because film formation is an adsorption process, the temperature of the system is an important factor.

Types of Adsorption

The adsorption of inhibitors is influenced by the nature and surface charge 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).

Physical Adsorption

Physical adsorption is the result of electrostatic attractive force between inhibiting organic ions or dipoles and the electrically charged surface of the metal. The surface charge can be defined by the position of the free corrosion potential (E_{corr}) of the metal with respect to its potential of zero charge (PZC) ($E_q = 0$) [24].

At the PZC, the net charge on the electrode is zero. At a potential more positive than the PZC, the electrode surface has a net positive charge, while at a potential more negative than the PZC, the electrode surface has a net negative charge. As a consequence, when the difference $E_{corr} - E_{q=0} = \xi$ is negative, the adsorption of cations is favored. On the contrary, the adsorption of anions is favored when ξ becomes positive. This behaviour is related not only to inorganic or organic ions with formal positive or negative charge, but also to dipoles whose orientation is determined by the value of the ξ potential [25].

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 [26].

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

$$\mathbf{Se > S > N > O}$$

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

Adsorption Isotherms

The relationships between concentration of inhibitor and corrosion rate or concentration of inhibitor and degree of inhibition respectively, were investigated [27] and resembled adsorption isotherms. Langmuir showed the classical relationship between the concentration of an adsorbate and the amount of adsorption. The fractional surface "θ", covered by adsorption is related to the concentration, "C" of the adsorbed species in solution by equation (1),

$$\theta = aC/(a + aC) \qquad (1)$$

Where "a" is a characteristic constant for the specific adsorbate. In the context of corrosion one can write "θ" as in equation (2),

$$\theta = k(m_o - m)/m_o \qquad (2)$$

Where m_o = the loss in mass per unit area in unit time in the absence of inhibitor, m = the loss in mass per unit area in unit time in the presence of an inhibitor and C is the concentration of the inhibitor. The above relation may be written as in equation (3),

$$M_o / (m_o - m) = A / (1/C) + B \qquad (3)$$

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

Three types of adsorption isotherm usually cover all the data relating to adsorption inhibitors. The three isotherms are the Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm. The plots are usually given as follows:

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

-Log θ versus log C Freundlich isotherms.

-θ versus log C for Temkin isotherms.

Industrial Applications of Corrosion Inhibitors

1- Petroleum Production

Corrosion in the hydrocarbon industries may be divided into two types, "wet corrosion" and "dry corrosion." At low temperature (i.e., below the boiling point or dew point of water), material corrodes due to the presence of an aqueous phase (wet corrosion). At higher temperature (above the boiling point of water), corrosion occurs in the absence of an aqueous phase (dry corrosion). Wet corrosion is influenced by pressure, temperature, and compositions of aqueous, gaseous, and oil phases. In refineries and petrochemical plants, the amount of water is usually small, but the corrosivity is high and is localized at regions where the aqueous phase contacts the metal. The water may contain dissolved hydrogen sulfide (H_2S), carbon dioxide (CO_2), and chloride ions (Cl^-). Corrosion may occur even when the water content is as low as 0.1%, or corrosion activity may not begin until after several years of production.

Refineries and petrochemical industries employ a variety of film-forming inhibitors to control wet corrosion. Most of the inhibitors are long-chain nitrogenous organic materials, including amines

and amides. Water-soluble and water-soluble oil-dispersible type inhibitors are continuously injected, or oil-soluble and oil-soluble-water-dispersible type inhibitors (batch inhibitors) are intermittently applied to control corrosion.. Film-forming inhibitors anchor to the metal through their polar group. The nonpolar tail protrudes out vertically. The physical adsorption of hydrocarbons (oils) on these nonpolar tails increases film thickness and the effectiveness of the hydrophobic barrier for corrosion inhibition [28]. Because inhibitors are interfacial in nature, they are active at liquid-liquid and/or liquid-gas interfaces and can lead to emulsification. As a result, foaming is sometimes experienced in the presence of inhibitors.

2- Internal Corrosion of Steel Pipelines

Gathering pipelines, operating between oil and gas wells and processing plants, have corrosion problems similar to those in refineries and petrochemical plants. The flow regimes of multiphase fluids in pipelines influence the corrosion rate. At high flow rates, flow-induced corrosion and erosion-corrosion may occur, whereas at low flow rates, pitting corrosion is more common. High-velocity flow tends to sweep sediments out of the pipeline, whereas low velocity allows sediments to settle at the bottom, providing sites for pitting corrosion. Internal corrosion of pipelines is controlled by cleaning the pipeline (pigging) and by adding continuous and /or batch inhibitors [29].

3- Acids

Acids are widely used in pickling, in cleaning of oil refinery equipment and heat exchangers, and in oil well acidizing. Mixed inhibitors are widely used to control acid corrosion [30].

Other Factors in Applying Inhibitors

Some factors to be considered in applying inhibitors are discussed in the following paragraphs.

Application Techniques

A frequent cause of ineffective inhibition is loss of the inhibitor before it either contacts the metal surface or changes the environment to the extent required. If the inhibitor is continuously

applied in a multiphase system, it should partition into the corrosive phase, usually the aqueous phase. This partitioning is especially important when using water-soluble, oil-dispersible inhibitors. In batch treatment, the frequency of treatment depends on the film persistency. It is important that the corrosion rates are measured frequently to ensure that a safe level of inhibition is maintained. It is also important that the inhibitor contacts the entire metal surface and forms a continuous persistent film. When using volatile inhibitors, care must be taken in packaging to prevent the loss of inhibitor to the outside atmosphere. Inhibitors are added to the primers used in paint coatings. When moisture contacts the paint, some inhibitor is leached from the primer to protect the metal. The inhibitor should be incorporated in such a way that it protects the areas where potential corrosion can take place, and not leach completely from the primer during the service life.

Temperature Effects

Organic molecules decompose at elevated temperatures. In general, film-forming inhibitors that depend on physical adsorption become less effective at elevated temperatures, so that larger treatment dosages may be required to maintain protective films. Chemisorption, on the other hand, increases with temperature due to the strengthening of chemical bonds. As a result, inhibitor efficiency increases with temperature up to the temperature at which decomposition of the inhibitor occurs.

Secondary Inhibition

The nature of the inhibitor initially present in acid solutions may change with time as a consequence of chemical or electrochemical reactions. Inhibition due to the reaction products is called secondary inhibition. Depending on the effectiveness of the reaction products, secondary inhibition may be higher or lower than primary inhibition. For example, diphenyl sulfoxide undergoes electrochemical reaction at the metal surface to produce diphenyl sulfide, which is more effective than the primary compound [31]. On the contrary, the reduction of thiourea and its alkyl (e.g., methyl, ethyl) derivatives gives rise to HS^- which accelerates corrosion.

Green Inhibitors

Environmental concerns worldwide are increasing and are likely to influence the choice of corrosion inhibitors in the future. Environmental requirements are still being developed, but some elements have been established.

Biodegradation, or biological oxygen demand (BOD), should be at least 60%, and inhibitors should be nontoxic [32,33]. The BOD is a measure of how long the inhibitor will persist in the environment. There is a growing demand for corrosion inhibitors that are less toxic and more biodegradable compared to current formulations. Green inhibitors displaying substantially improved environmental properties will be the inhibitors most widely used in the future [34].

Surfactant as Corrosion Inhibitors

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 [35]. 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. Jeyaprabha et al., [36] studied the inhibition of corrosion of pure iron in 0.5 M H_2SO_4 by ethanolamines such as mono-, di- and triethanolamines using by both dc polarization and ac impedance techniques. The results showed that a strong dependence of inhibitor performance with concentration in addition to the structural effects of amine molecules.

Wombacher et el., [37] presented new results and sum up the behavior of aminoalcohol based mixed corrosion inhibitors. These organic and mixed (organic/inorganic) inhibitors can be used 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. Apart 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. The effect of organic molecules containing heteroatoms such as nitrogen and sulphur on the corrosion behavior of iron has been investigated by Lgamri [38]. Electrochemical studies of the iron samples were performed in an aerated solution of 1M HCl by means of electrochemical impedance spectroscopy as well as polarization curves. The recorded electrochemical data showed that the corrosion resistance was greatly enhanced in the presence of an inhibitor that acts at the same time on the anodic and cathodic electrochemical processes and its effect depends on its concentration.

Alsabagh et al., [39] 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).

Corrosion inhibition of carbon steel in acid chloride solution using ethoxylated fatty alkyl amine surfactants has been studied [40] using gravimetric, open circuit potential and potentiostatic polarization techniques. It was found 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.

Osman, et al., [41] synthesized three water-soluble surfactants based on maleic anhydride-oleic acid adduct (MO). The inhibitive efficiency of corrosion on mild steel in 1M H_2SO_4 for these surfactants was measured by potentiodynamic technique. The surface and thermodynamic properties of the surfactants were also investigated.

Principles of Demulsification

Chemical Composition of Crude Oil

Due to the complex composition of crude oils, characterization by the individual molecular types is not possible, and elemental analysis is unattractive because it gives only limited information about the constitution of petroleum due to the constancy of elemental composition. Instead, hydrocarbon group type analysis is commonly employed [42,43]. Knowledge of the distribution of major structural classes of hydrocarbons in crude oils is needed in various fields in the petroleum industry. Examples are studies related to reservoir evaluation, migration and maturity, degradation processes, processing, and environmental effects [44].

The crude oils are classified into four main chemical classes based on differences in solubility and polarity. The four fractions are the saturates (S), aromatics (A), resins (R), and the asphaltenes (A).

Saturates

The saturates (aliphatics) are non-polar hydrocarbons, without double bonds, but including straight-chain and branched alkanes, as well as cycloalkanes (naphthenes). Cycloalkanes contain one or more ring, which may have several alkyl side chains.

The proportion of saturates in a crude oil normally decreases with increasing molecular weight fractions, thus the saturates generally are the lightest fraction of the crude oil. Wax is a sub-class of the saturates, consisting primarily of straight-chain alkanes, mainly ranging from C20 to C30. Wax precipitates as a particulate solid at low temperatures, and is known to affect emulsion stability properties of crude oil systems [45].

Aromatics

The term aromatics refer to benzene and its structural derivates. Aromatics are common to all petroleum, and by far the majority of the aromatics contain alkyl chains and cycloalkane rings, along with additional aromatic rings. Aromatics are often classified as mono-, di-, and tri-

aromatics depending on the number of aromatic rings present in the molecule. Polar, high molecular weight aromatics may fall in the resin or asphaltene fraction [46].

Resins

This fraction is comprised of polar molecules often containing heteroatoms such as nitrogen, oxygen or sulphur. The resin fraction is operationally defined, and one common definition of resins is the fraction soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane [47]. Since the resins are defined as a solubility class, overlap between both the aromatic and the asphaltene fraction is expected. Naphthenic acids are commonly regarded as a part of the resin fraction [48].

Asphaltenes

The asphaltene fraction, like the resins, is defined as a solubility class, namely the fraction of the crude oil precipitating in light alkanes like pentane, hexane or heptane. This precipitate is soluble in aromatic solvents like toluene and benzene. The asphaltene fraction contains the largest percentage of heteroatoms (O, S, and N) and organometallic constituents (Ni, V, Fe) in the crude oil. The structure of the asphaltenes has been the subject of several investigations, but is now believed to consist of polycyclic aromatic clusters, substituted with varying alkyl side chains. The breaking of a crude oil emulsion is a necessity for several reasons. Obviously the quality of the crude oil is highly dependent on residual contents of water and water soluble contaminants present. Even a small amount of these components can cause unwanted effects in pipes and refineries. Therefore, different methods to solve the emulsion problem have emerged [49].

Emulsion

An emulsion is a "significantly stable" suspension of particles of liquid of a certain size within a second, immiscible liquid. The term significantly stable means relative to the intended use and may range from a few minutes to a few years. Two types of emulsions based on the size of the dispersed particles are recognized: macro and microemulsions. The particles of the usual

type of emulsion (now sometimes called a macroemulsion) range from 0.2 to 50 micrometers (μm) in size and are easily visible under the microscope.The other type of emulsion is called a microemulsions and has particles from 0.01 to 0.20 μm (10-200nm) in size [50].

Two immiscible, pure liquids cannot form an emulsion. For a suspension of one liquid in another to be stable enough to be classified as an emulsion, a third component must be present to stabilize the system. The third component is called the "emulsifying agent" and it is usually a surface-active agent, although not necessarily of the type that is usually considered a surface-active agent (finely divided solids, for example, may act as emulsifying agents).The emulsifying agent, if of the conventional type, need not be an individual substance, and, in fact, the most effective emulsifying agents are usually mixtures of two or more substances, as we shall see subsequently.

Types of Emulsions

Emulsions are of two types, based on the nature of the dispersed phase : oil-in-water (O/W) and water-in-oil (W/O).

a-The Oil-in-Water (O/W)

is a dispersion of a water-immiscible liquid (always called the oil, regardless of its actual nature) in an aqueous phase. The oil is, in this case, the " discontinuous" (inner) phase; the aqueous phase is the "continuous" (outer) phase.

b-The Water-in-Oil (W/O)

is a dispersion of water or an aqueous solution in a water-immiscible liquid.

The type of emulsion formed by the water and the oil depends primarily on the nature of the emulsifying agent and, to a minor extent, on the process used in preparing the emulsion and the relative proportions of "oil" and "water" present. In general, O/W emulsions are produced by emulsifying agents that are more soluble in the "water" than in the "oil" phase, whereas W/O

emulsion are produced by emulsifying agents that are more soluble in the "oil" than in the "water". This is known as the Bancroft rule [51].

Emulsion Stability

In the formation of emulsions, one of the two immiscible liquids is broken up into particles that are dispersed in the second liquid. Since the interfacial tension between two immiscible pure liquids is always greater than zero, this dispersion of the inner liquid, which produces a tremendous increase in the area of the interface between them, results in a correspondingly large increase in the interfacial free energy of the system. The emulsion produced is consequently highly unstable thermodynamically, relative to the two bulk separated by a minimum area interface. It is for this reason that two immiscible liquids, when pure, cannot form an emulsion. The function of the emulsifying agent is to stabilize this basically unstable system for a sufficient time so that it can perform a desired function. This the emulsifying agent does by adsorption at the liquid / liquid interface as an oriented interfacial film. This oriented film performs a number of functions:

1- It reduces the interfacial tension between the two liquids and consequently the thermodynamic instability of the system resulting from the increase in the interfacial area between the two phases

2- It decreases the rate of coalescence of the dispersed liquid particles by forming mechanical, steric, and/or electrical barriers around them. The steric and electrical barriers inhibit the close approach of one particle to another. The mechanical barrier increases the resistance of the dispersed particles to mechanical shock and prevents them from coalescing when they do collide.

Factors Determining Emulsion Stability

The term stability, when applied to emulsions used for practical applications, usually refers to the resistance of emulsions to the coalescence of their dispersed droplets. The mere rising or settling of the droplet (creaming) because of a difference in density between them and

the continuous phase is usually not considered instability. The rate of coalescence of the droplets in an emulsion is stated to be the only quantitative measure of emulsion stability [52]. It can be measured by counting the number of droplets per unit volume of the emulsion as a function of time in a haemocytometer under a microscope [53] or by means of a Coulter centrifugal photosedimentomerter [54]. The rate at which the droplets of a macroemulsion coalesce to form larger droplets and eventually "break" has been found to depend on a number of factors: (1) the physical nature of the interfacial film, (2) the viscosity of the continuous phase, (3) the size distribution of the droplets, (4) phase volume ratio and (5) the temperature.

Demulsification

One third or more of the crude oil being produced in the world comes to the surface associated with appreciable proportions of water in emulsified form. Even where the percentage of emulsion in total production is very low, storage tanks tend, eventually, to accumulate significant volumes of emulsion. Demulsification is, therefore, an important element in handling crude oil from the time it is produced until it enters the refining process [55].

Demulsification Techniques

In the early days, the general practice was to fill a tank with emulsified oil, introduce the reagent, agitate the mixture by means of gas or air or even by hand, best it by circulation through a heater as required, and then allow the water to settle. Current practice is to employ a continuous process "flow-line treatment", introducing the reagent continuously into the well "down-the-hole", heating the mixture during passage through the flow-line, if required, and then settling the water in a settling tank. When continuous or flow-line treatment is used, the demulsifier may be injected at the desired point to the flow-sheep. It is usually injected as near as possible to the wellhead, to take advantage of the natural heat and of agitation arising from the turbulence of flow in the system [56].

Mechanism of Demulsification

Demulsification is believed to be accompanied by inversion followed by coagulation. It is important to note that the coagulation of the disperse phase occurs as two-stage process, flocculation and coalescence. In the second stage, termed coalescence, each aggregate combines to form a single drop. This is an irreversible process, leading to a decrease in the number of water droplets and finally to complete demulsification [57].

Flocculation

In the first stage, flocculation, the droplets of the dispersed phase form aggregates in which the drops have not entirely lost their identity; such aggregation is often reversible. This aggregation of droplets is due to the attraction of Van der Waal forces. This process involves, in some sense, overcoming of the repulsion effect of the double layer.

To enhance the flocculation process, a common practice is to use chemical demulsifiers that are believed to:

- Promote the flocculation of the droplets by weakening the repulsive forces that stabilize the emulsion.
- Enhance the drainage of the interfacial film between the flocculated droplets.

Coalescence

The coagulated droplets combine with each other and become bigger droplets [58]. During this process, the oil in the liquid film between the droplets drains out, thereby thinning the film and finally rupturing it. The faster the film thins, the greater is the demulsification effectiveness. The chemical counteracts the emulsifying agents, allowing the dispersed droplets of the emulsion to coaslesce into larger drop and settle out of the matrix [59] . This is an irreversible process, leading to a decrease in the number of water droplets and finally to complete demulsification. The coalescence is favored by the fastest adsorption of demulsifier molecules, which is achieved when the average interactions of the surface active species are equilibrated with oil and water [60].

Methods of Demulsification

The problem of resolving water-in-oil emulsions has been attacked in a number of ways over the past several years and a great deal of progress has been made in developing and utilizing methods for demulsification [61]. Seven basic methods have been listed by which emulsion may be denatured: (a) settling (b) heating or distilling at atmospheric pressure (c) heating or distilling at elevated pressure (d) use of chemicals and (e) centrifuging. Recently, some studies have discovered new techniques used in demulsification process such as, (f) high electrostatic fields [62] and (g) freeze/ thaw method [63]. All of these methods and combinations of these methods are used extensively at the present time. However, the chemical demulsification process is by far the most widely used method in petroleum industry.

Chemical Demulsification

Chemical demulsification is a process in which the film-thinning rate is enhanced and stability of the film is reduced by chemical demulsifiers. Demulsifiers are a class of chemicals used to aid the separation of emulsions (water in oil). They are commonly used in the processing of crude oil, which is typically produced along with significant quantities of saline water. This water (and salt) must be removed from the crude oil prior to refining, otherwise significant corrosion problems can occur in the refining process. Demulsifiers are typically based on the following chemistry:

- Acid catalysed phenol-formaldehyde resins
- Base catalysed phenol-formaldehyde resins
- Polyamines
- Di-epoxides
- Polyols

The above are usually ethoxylated (and/or propoxylated) to provide the desired degree of water/oil solubility. The addition of Ethylene Oxide increases water solubility, Propylene Oxide decreases it. A surface-active agent (or surfactant) is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to marked degree the surface or interfacial free energies of those surfaces (or interfaces). Surfactants may be applied or encountered at all stages in the petroleum recovery and processing industry, from oil well drilling, reservoir injection, oil well production, and surface plant processes, to pipeline, seagoing transportation of petroleum emulsions. Demulsifiers as a class of surfactants are often used to maximize the cost-effectiveness of petroleum production and refining processes and to achieve required quality parameters of oil, water and crude oil contaminations [64]. Most commercial chemical demulsifiers that are used to breakup water-in-oil (w/o) emulsions are oil soluble. The interfacial activity of these oil-soluble demulsifier molecules is controlled by the rate of the bulk diffusion process from the bulk phase to the interface and the adsorption barrier at w/o interface [65]. Usually commercial chemical demulsifiers are blended mixtures of several components with various chemical structures polymeric materials, as well as a wide molecular weight distribution [66]. In this case, each component of the demulsifier possesses a different partitioning ability and a different interfacial activity due to various chemical structures or types.

Surfactants as Demulsifier

Alsabagh et al., [67] prepared three polymeric surfatants to be used as demulsifiers; polyalkyl phenol formaldehyde monoethanol amine ethoylate, polyalkylphenol formaldehyde diethanolamine ethoylate and polyalkyl phenol formaldhyde triethanolamine ethoylate. Their demulsification potency in breaking water-in-crude oil emulsions was investigated. The data revealed that the resolution of water away from crude emulsions was easier than from an asphaltenic crude emulsion. The demulsification efficiency increased with increasing demulsifier

concentrations contact time and temperature. The interfacial tension (IFT) at the crude oil-water interface was measured. It was found that the increasing of demulsifier concentration decreases the IFT, hence increasing the maximum demulsification efficiency.

They also prepared six demulsifiers based on oleic acid-maleic anhydride adduct (OM) [68]. The adducts were ethoxylated with triethanol amine (E(10)OMTEA); ethoxylated OM-cetyl amine (E(10)OMCA); ethoxylated OM-triethanol amine-lauryl alcohol (E(10)OMTEA-LA); ethoxylated OM-triglycerol (E(10)OMT); ethoxylated OM (E(32)OM) and ethoxylated OM-polyoxyethylene-polyoxypropylene block co-polymer (E(54)OMBP5). Their efficiency to break water-in-oil emulsion was investigated. The surface and interfacial tension were measured between their solutions and the crude oil used. The rheological properties for water-in-oil emulsion with and without demulsifiers were determined. The relation between demulsification efficiency surface properties and rheology was discussed on the light of the chemical structure of the demulsifiers. From the data obtained, it was concluded that the demulsifier which exhibited a high demulsification efficiency causes the greatest reduction of surface and interfacial tension, furthermore, it enhanced the flow properties of emulsion to facilities complete demulsification.

Another set of adducts based on four maleic anhydride-oleic acid compounds were prepared by Alsabagh et al. [69]. The first of them was hexaglycerol MO (HGMO) and the other three different compounds were ethoxylated MO adducts (n = 30, 45, and 60) namely; E(30)MO, E(45)MO, and E(60)MO. The later three demulsifiers were based on polyethylene-polypropylene oxide co-polymer and maleic anhydride-oleic acid adducts at different molecular weights of copolymer. The surface tension at 30, 40, 50, and 60 °C of their solutions was measured. The critical micelle concentration (CMC) of these demulsifiers was determined by the surface tension and the dynamic light scattering. From the obtained data, it was found that, the CMC values of the two methods are very closed. Further calculations were made to obtain the surface active properties and thermodynamic parameters of micellization and adsorption. The

demulsification efficiency of these demulsifiers was determined on the basis of the time taken for complete water separation of emulsion.

Wanli Kang et al., [70] studied the demulsification of a synthetic water-in-oil (W/O) crude oil emulsion by measuring water-oil interfacial properties such as life time and thinning rate of oil film in the presence of various demulsifiers. The results indicated that the interfacial elasticity decreased both the strength and the life time of oil film and film thickness when adding the demulsifiers. The oil film broke when film thickness reached a critical level. As for a demulsifier, the interfacial elasticity was decreased with demulsifier concentration increase, and stayed constant above a critical demulsifier concentration. The rate of dewatering is related to interfacial elasticity. When different demulsifiers were compared, the more the interfacial elasticity was lowered, the more efficient was the dewatering. The mechanism of the different types of demulsifiers was discussed based on the experimental results. The demulsifiers partially replaced the emulsifiers, which led to the interfacial elasticity decreased. The effect of chemical structure of the demulsifiers on water–oil interfacial film was studied.

Jiangying et al.,[71] investigated the properties and the performance of 20 blocked copolymers from four surfactant families and three pairs isomeric compounds were compared. The results showed that different positions of the ethylene oxide (EO) and propylene oxide (PO) in block copolymers lead to different hydrophile–lipophile balances (HLB) of surfactant. The sequential block copolymer is more hydrophilic than the reverse-sequential one with similar chemical composition. The greater the molecular weight, the greater the difference between the (HLB) of the two surfactant types. Generally, the demulsification performance of sequential copolymers is better than that of reverse-sequential copolymers.

Hafiz et al., [72] synthesized a series of diethanolamine polyethers via condensation of 3–7 or 9 mol of diethanolamine. IR and MS confirmed the chemical structures. The demulsifiers were used for treatment of pollution in the refinery waste water with or without $FeCl_3$. The flocculation efficiency of the synthesized demulsifiers was determined by turbidity measurement

of the treated and untreated O/W emulsion in the Cairo Oil Refinery Company. The critical flocculation concentration (CFC) and charge density of the synthesized demulsifiers were determined. Biodegradation of diethanolamine polyethers was measured in river water within 7–8 days.

Faul et al., [73] described the preparation of a copolymer, which is useful as a demulsifier for petroleum emulsions by condensing a polyether polyol, e.g., ethylene oxide-propylene oxide block copolymer with an unsaturated acid, such as acrylic acid. The demulsifier was found to give a petroleum phase with low water content. Polyesterification of adipic acid with ethylene glycol, 1,4-butane diol and 1,6-hexane diol in the absence and presence of p-toluene sulphonic acid, as a catalyst, was carried out under constant reaction temperatures of 140-180 °C and at ratio of diol to diacid of 0.9867: 3.5880.

Abendroth, et al., [74] synthesized oligomeric esters, which were very effective as mineral oil demulsifiers. They were synthesized by reaction of dibutylmaleate and dibutyl phthalate with polyalkyleneglycols and block copolymeric polyether alcohols with alkali catalysts at 10-120°C.

Sjoblom et al., [75] found that medium chain alcohols (1-butanol and benzyl alcohol) and amines are spreading up the separation of water from water in crude oil emulsions. The destabilization mechanisms seem to be fundamentally different.