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Review

Anti-corrosion Ability of Surfactants: A Review

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The issue of the effects of corrosion on structural integrity of metal surfaces has been a question of concern for some time. The uses of chemical corrosion inhibitors are common in production and processing operations. Nevertheless, the challenge is to develop a new class of corrosion inhibitors to protect the materials, which are environment friendly under various conditions. Surfactants as corrosion inhibitors are environmentally acceptable and are very economical and easily available. The aim of this review article is to delineate the ability of surfactants to inhibit the corrosion on different metal surfaces. Various potential application and properties of different types surfactants have also been discussed. Various parameters like, effect of surfactant concentration, temperature and the mechanism of corrosion inhibition and mode of adsorption are also discussed in this review article.

Keywords: Corrosion inhibitors, critical micelle concentration, surfactants, aggregation, mechanism

1. INTRODUCTION

Corrosion of materials has continued to receive interest in the technological world. In the field of corrosion inhibition, scientists are persistent in seeking better and more efficient ways of combating the corrosion of metals. Addition of corrosion inhibitors to the corrosion environment with respect to the other methods of corrosion inhibition has been employed [1]. Corrosion inhibition of materials has been the focus of research for centuries and in many cases has been well analyzed and understood [2-4]. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media. To be effective, an inhibitor must also transfer water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reaction, and prevent transportation of water and corrosion-active species on the metal surface. Surfactant inhibitors can be divided into four types: (a) inorganic inhibitors, (b) organic inhibitors, (c) surfactant inhibitors and (d) mixed material inhibitors. Surfactants also called surface active agent are molecules composed of a polar hydrophilic group, the ‘‘head”, attached to a non-polar hydrophobic group, the ‘‘tail’’. In aqueous solution the inhibitory action of surfactant molecules may be due to the physical (electrostatic) adsorption or chemisorptions onto the metallic surface, depending on the charge of the solid surface and the free energy change of transferring a hydrocarbon chain from water to the solid surface.

Corrosion of materials usually takes place in the presence of oxygen and moisture and involves two electrochemical reactions, oxidation occurs at anodic site and reduction occurs at cathodic site [5]. Various scientific studies deal with the subject of corrosion inhibitors. Inhibitors are normally used to protect materials against deterioration from corrosion. The inhibitors, which reduce corrosion on metallic materials, are inorganic inhibitors, organic inhibitors, surfactant inhibitors and mixed material inhibitors. Organic compounds are well know acid inhibitors used in industry. These organic compounds have multiple bonds in their molecules that mainly contain nitrogen, sulphur, oxygen atoms through which they get adsorbed on the metal surface [6-13]. The use of ethoxylated fatty acid [14], ethoxylated fatty amines, [15] and propenethoxylated diol [16] had been used as corrosion inhibitors for steel and aluminum in acidic solutions. Effect of temperature on the inhibiting process is of enormous significance in industry [17]. Effective inhibitors are expected to perform under a wide range of conditions. The inhibition efficiency depends on the parameters of the system (temperature, pH, duration, and metal composition) and on the structure of the inhibitor molecule.

Surfactant inhibitors have many advantages, for example, high inhibition efficiency, low price, low toxicity, and easy production [2,5,18]. Moreover, the investigation of surfactants adsorbed on metal surfaces is extremely important in electrochemical studies such as corrosion inhibition, adhesion, lubrication, and detergency [18]. The effective type of corrosion inhibitors for these applications is film-forming inhibitors. Nowadays, surfactants are widely used and find a very large number of applications in the petroleum industry. This is attributed to their significant capability to influence the properties of surfaces and interfaces.

An important corrosion inhibition tool is the use of surfactant inhibitors, because of very little consideration towards this study. The most important action of inhibition is the adsorption of the surfactant functional group onto the metal surface [19], adsorption is critical to corrosion inhibition. The ability of a surfactant molecule to adsorb is generally related to its ability to aggregate to form micelles. Most acid inhibitors are organic compounds containing nitrogen, sulphur and/or oxygen atoms [20,21]. The concern of these materials arises from their significance in recent civilization. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The degree of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosion media [22]. The corrosion inhibition of a metal may involve either physisorption or chemisorption of the inhibitor on the metal surface. Electrostatic attraction between the charged hydrophilic groups and the charge active centres on the metal surface leads to physisorption. Various authors explained that most organic inhibitors are adsorbed on the metal surface by displacing water molecules from the surface and forming a compact barrier film on the metal surface. In this review, a brief overview of surfactants as corrosion inhibitors is provided.

2. SURFACTANT AND SURFACTANT MICELLES

The studies of chemical reactivity at interfaces occupy an important place in chemical sciences [23]. The domain of surface science is perhaps one of the most interdisciplinary areas of modern science and technology. During the last few decades, rapid advances in the understanding of surface phenomenon have taken place. However, the importance of surface science has been recognized for more than a century. A class of compounds called surface-active compounds (or surfactants) [24] that decrease prominently the interfacial tension or interfacial free energy of the interfaces [25,26]. Surfactant molecules are amphiphilic in character, i.e., they possess hydrophilic and hydrophobic regions [27,28] having a long hydrocarbon tail and a relatively small ionic or polar head group. Amphiphiles can be ionic (cationic, anionic), zwitterionic, or nonionic depending on the nature of their head groups. The surfactants have a tendency to accumulate at the interface of immiscible fluids with a marked influence resulting in decrease in free energy which is reflected in a corresponding lowering of interfacial tension that facilitates emulsification of the immiscible fluids and hence such compounds are also known as emulsifiers. A schematic diagram of a typical surfactant is shown in Figure (1).

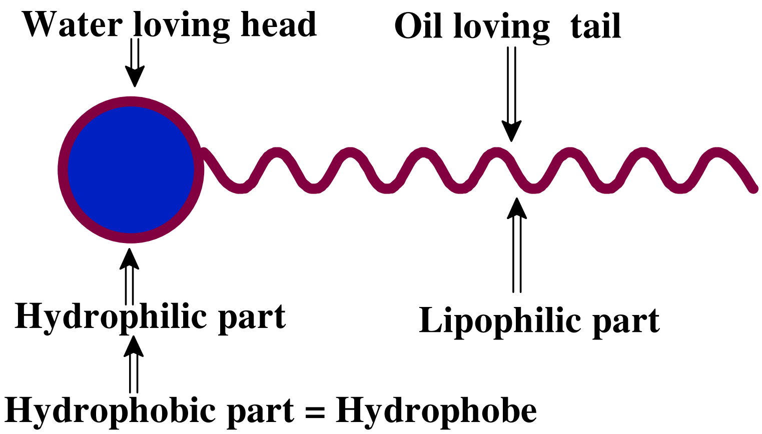


Figure 1. Schematic diagram of surface-active molecule.

Research on surfactants is a rapidly developing field due to their booming applications in many important practical and fundamental sciences like petroleum oil recovery, corrosion inhibition, water and environmental pollutions, understanding the mysterious role of biological membranes, biotechnology, and other systems. The behaviour of surfactants in solution were the subject of considerable interest because of its wide applications, in different industries, medical sciences, life sciences, analytical chemistry, pollution control and even in the fields of physics and engineering. Research on surfactant behaviour is completely multidisciplinary in nature.

2.1. Classification of surfactants

Depending on the charge of head groups, the surfactants are classified as:

(i) *Anionics*: The anion is the surface-active species. Anionics are use in great volume than other surfactant class. A rough approximation of the worldwide surfactant production is 10 million tons per year, out of which approximately 60 % are anionics. Most important reason for their popularity is the ease and low cost of manufacture. Anionics are used mainly in detergent formulations and alkyl and alkylarye chains in the C_{12}–C_{18} range obtain the best detergency. The counterions most frequently used are sodium, potassium, ammonium, calcium and various protonated alkyl amines. Sodium and potassium impart water solubility, whereas calcium and magnesium promote oil solubility. Amine/alkanol amine gives both oil and water solubility. Soap is still the largest single type of surfactant. Sodium dodecyl sulfate (SDS) is by far the most important surfactant within this type.

(ii) *Nonionic*: Nonionic surfactants do not have any surface charge and have either a polyether or a polyhydroxyl unit as the non-polar group. In the vast of non-ionics, the polar group is a polyether consisting of oxyethylene unites, prepared by the polymerization of ethylene oxide. Strictly speaking, the prefix 'poly' is a misnomer. The classic number of oxyethylene unites in the polar chain is five to ten, although some surfactants, e,g. dispersants, often have much longer oxyethylene chains. The water- soluble moiety of this type can contain hydroxyl groups or a polyoxyethylene chain. This category continues to be dominated by ethylene oxide adducts of alkylphenols and fatty alcohols.

(iii) *Cationic*: In cationic surfactants, cation is the surface-active species. The quaternary ammonium salts are the main compounds in this class. The majority of cationic surfactants are based on the nitrogen atom carrying the cationic charge. Both amine and quaternary ammonium-based products are common. The amines only function as a surfactant in the protonated state; therefore, they cannot be used as high pH. Quaternary ammonium compounds, 'quats' on the other hand, are not pH sensitive. Non-quaternary cations are also much more sensitive to polyvalent anions.

(iv) *Zwitterionic*: Zwitterionic surfactants have two charged groups of different size. While the positive charge is almost in availably ammonium, the source of negative charge may vary, although carboxylate is by far the most common. Zwitterionics are often referred to as 'amphoterics'. An amorphic surfactant is one that changes from net cationic via zwitterionics to net anionic on going from low to high pH. Neither the acidic nor the basic site is permanently charged, i,e. the compound is only zwitterionic over a certain pH range. The change in the charge with pH of the truly amorphic surfactants naturally affects properties such as foaming, wetting, detergency, etc. All these properties strongly depend on the solution pH. Surfactants containing perfluorinated hydrophobic moieties are used in a wide variety of applications, ranging from fire extinguishing media to electroplating additives and water-repellent fiber coatings [29].

2.2. Micelles, micellar structure and properties

In polar solvents such as water, amphiphilic surfactant monomers assemble to form a micelle in such a way that their hydrocarbon tails huddle in the core of the micelle, and the polar head groups project outwards into the polar bulk solution and locate at the micelle-water interface such that the hydrophobic tails are shielded from water. Micelles often drawn as static structures of spherical aggregates of oriented surfactant molecules. However, micelles are in dynamic equilibrium with surfactant monomers in the bulk, which are frequently being exchanged with the surfactant molecule in the micelles. The equilibrium between monomer and aggregate is established within a few milliseconds. At equilibrium, the number of micelles disintegrated in the same time.

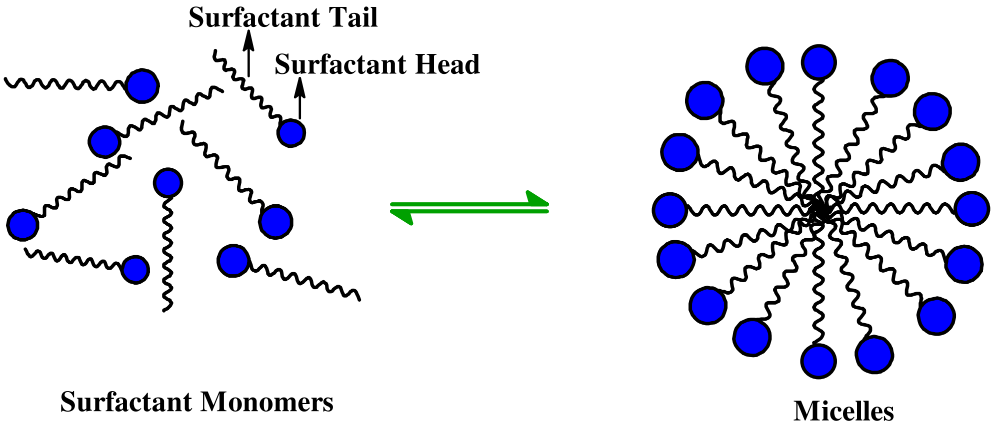


Figure 2. Schematic illustration of the reversible monomer-micelle thermodynamic equilibrium.

In addition, the micelles themselves have the property of constantly disintegrating and reforming. The surface layer of a micelle resembles a concentrated electrolyte solution with a dielectric constant lower than that of the bulk water. The micellar phase is less polar than water and the ionic micelles have polarity near to that of pure ethanol even at the stern layer [30,31]. A variety of properties like the number of monomers in a micelle, the aggregation number determines the size and geometry of the micelle and hence is an important quantity [32]. In aqueous solutions, the aggregation numbers for surfactants generally range between 10 and 100. The significant meaning of the aggregation number as per the corrosion point of view comes from the fact that its value is inversely proportional to the minimum surface area per molecule. Surface polarity decreases with an increase in the aggregation number [33]. The significant physical meaning of the value of Hydrophilic-Lipophilic Balance (HLB) for the surfactant is to find out the effectiveness of the surfactant as a corrosion inhibitor. A lower value of HLB suggests that the surfactant is more oil soluble, while a high value of HLB indicates that the surfactant is more water soluble [34,35].

Figure (3) represents that, the electric charge in ionic micelles is neutralized by counterions in the electrical double layer around it. The first layer immediately adjacent to its surface is called stern layer [36]. In this layer, the counterions are adsorbed so strongly that there is no thermal agitation and they migrate simultaneously with the colloidal micelle in an electrical field. According to the most widely accepted model, head groups of surfactant molecules are also located in this layer. The rest of the double layer is called the diffuse (Gouy-Chapman) layer since the ions are diffused into the bulk solution because of the thermal motion. The core radius is about the length of the fully extended alkyl chain of the amphiphile. The core is assumed to consist of two regions, namely the inner and outer core. The outer core contains approximately the first four methylene groups. There is also another defined region within micelles called palisade layer (mantle) which includes the head groups. Based on the Hartely model, the overall volume of a micelle is approximately twice that of the stern layer [37].

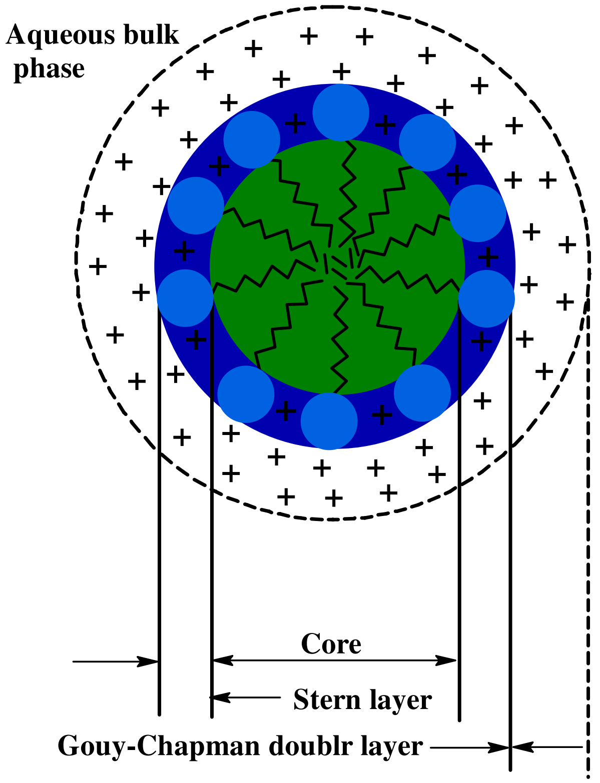
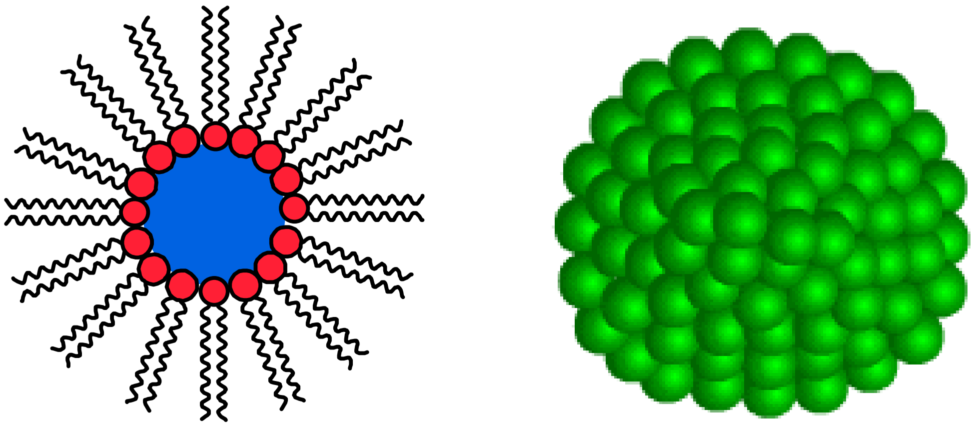


Figure 3. Model of a typical ionic micelle showing the location of Head group (●) surfactant chain (〰) and counter ions (+)

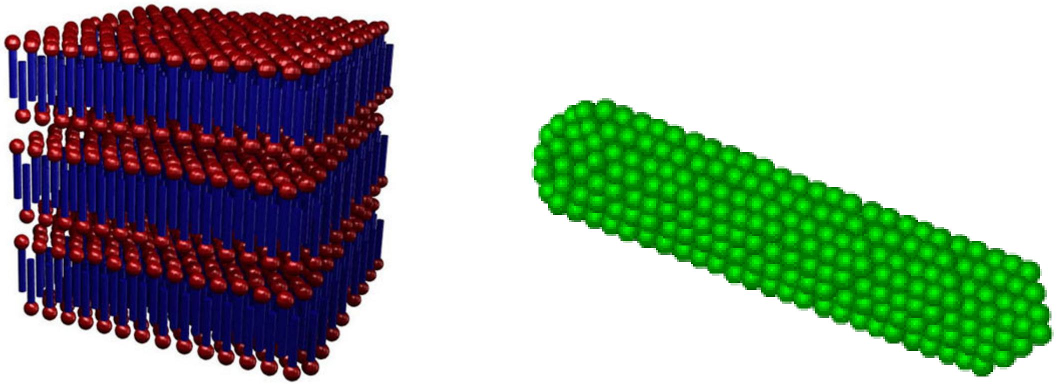
The shape and size of the micelle depends on the architecture of the surfactant molecules and the charge on the head group. There are different types of aggregates of surfactants that are formed depending upon the solution concentration and the molecular structure of the surfactant molecule. These consist of spherical micelle, cylindrical micelle, bilayers, vesicles, worm like micelle, rod-shaped micelle, reverse micelle (also called inverse micelle) etc. (Fig. 4).

2.3. Critical micelle concentration (cmc)

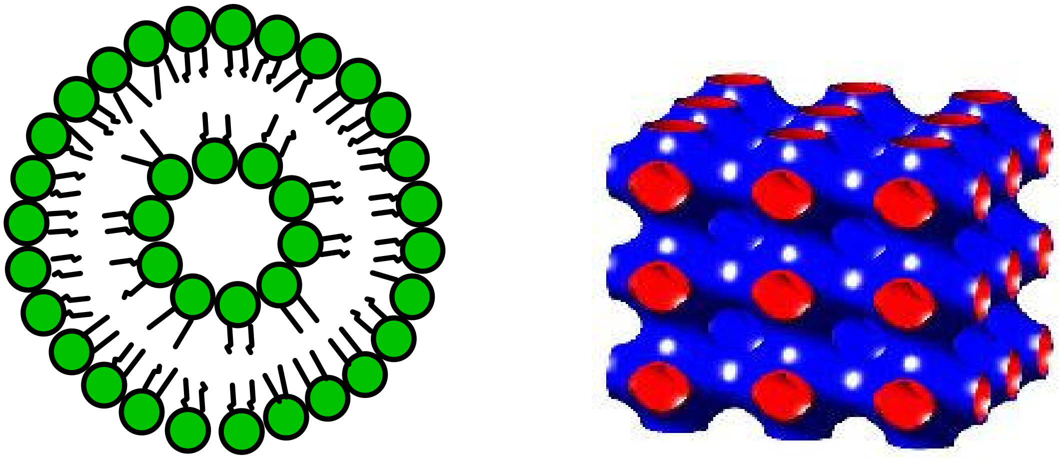
Surfactants or amphiphilic molecules contain both hydrophilic and hydrophobic parts. The hydrophilic part of the molecule prefers to interact with water while the hydrophobic part is repelled from water. Surface active molecules absorb at the air/water interface, decreasing surface tension. As the interface becomes saturated, the molecules start to form aggregates or micelles in the bulk of the liquid, with the surface tension remaining constant.



Reverse micelle Spherical micelle



Surfactant lamellar phase Rod shaped micelle



Vesicle Bicontinuous structure

Figure 4. Schematic representations of organized aggregates that may form in aqueous solution of surfactant depending on the concentration.

The amphiphile molecules exist in dilute solutions as individual species in the media with ideal physical and chemical properties. As the amphiphile concentration increases, these properties deviate gradually from ideality and at the concentration where aggregation of monomers into micelles occurs; an abrupt change is observed (Fig. 5). This concentration is called the critical micelle concentration (CMC). CMC is a key parameter for the optimization of surfactants in chemical formulations and home & beauty care products.

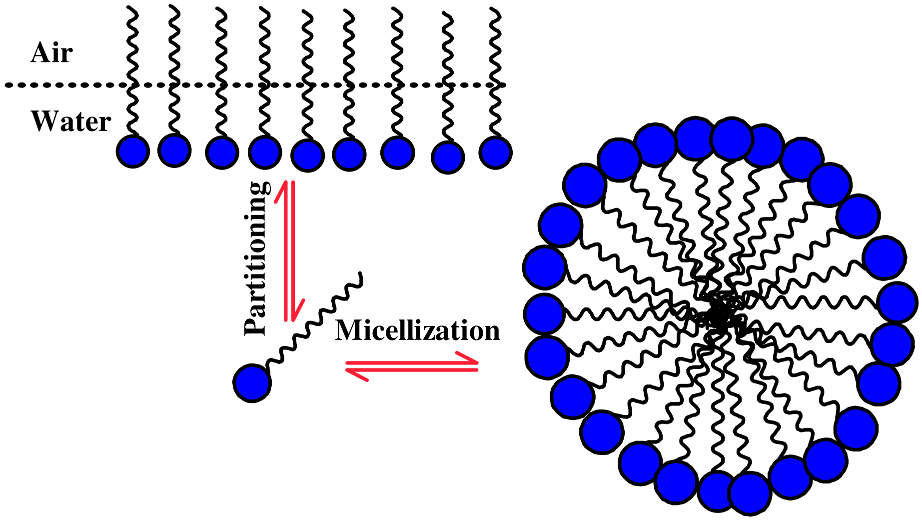


Figure 5. Representation of **c**hanges observed at critical micelle concentration.

Various factors effects the CMC values e.g., temperature, the length of the hydrocarbon tail, the nature of the counterions and the existence of salts and organic additives; and thus amphiphiles have characteristic cmc values under given conditions [38, 39]. When micelles formation takes place, the head group repulsions are balanced by hydrophobic attractions and for ionic micelles, also by attractions between head groups and counter ions. Hydrogen bonds can also be formed between adjacent head groups [40, 41].

3. CORROSION OF MATERIALS

Corrosion is an electrochemical process that involves the rearrangement of electrons between metal surface and an aqueous electrolytic solution. Corrosion is considered as the destructive disintegration of a metal by electrochemical means in which a metal is destroyed by a chemical reaction. A very severe problem has economic implication costing billions of dollars each year. Much of this loss is because of the corrosion of iron and steel, although several other metals may corrode as well. The problem with iron as well as many other metals is that the oxide formed by oxidation does not firmly adhere to the surface of the metal and flakes off easily causing "pitting". Extensive pitting ultimately causes structural weakness and disintegration of the metal. It should be noted, however, that certain metals such as aluminum, form a very tough oxide coating which strongly bonds to the surface of the metal preventing the surface from further exposure to oxygen and corrosion. Corrosion can be atmospheric, underground/soil waste, acid, alkaline and combination of these [42]. Mostly corrosion of the materials takes place in acidic conditions and some times in alkaline or solvents media. Corrosion due to acids is central and expensive problem in the petroleum refining units and it represents a significant portion of loss because of lost production, inefficient operation, high maintenance, cost of corrosion control chemicals and serious damages caused by the metallic corrosion on piping and plant system [43]. Corrosion inhibitors can control, reduce, or prevent reactions between a metal and its surroundings when added to the medium in small quantities. For economy purpose, inhibitors should be effective in low concentrations. In industries like oil and gas exploration and production, petroleum refining, iron and steel industries chemical manufacturing units [42] corrosion program is vital. Corrosion is a major destructive process that results in destructive effects. Corrosion creates gaping hole or cracks in aircraft automobiles, boats, gutters screens, plumbing and many other things made up of metals. Corrosion is an ineffective phenomenon, which is tried to be reduced. The main concern is the stability of materials and structures, many studies have been carried out to develop an efficient means of corrosion control to extend service life of existing structures and minimize corrosion damage in new structures [44]. Even though corrosion inhibitors are considered as the most effective and flexible means of corrosion control. To select an appropriate inhibitor for a particular system is complicated process because of the specificity of inhibitors and great variety of corrosion related applications. Corrosion in metallic surfaces causes much concern with regard to material loss, especially in technological activities. In some areas, saline media are the main agents that lead to corrosion, a particular type of which is the localized pitting corrosion [45, 46]. The size, orientation, shape and electric charge on the molecule decide the degree of adsorption and hence the effectiveness of the inhibitor [47-56].

Many powerful techniques were offered to measure corrosion inhibition such as anodic or cathodic protection, coating layer on the metal, oxidizing or phosphatizing treatment, the application of inhibitors, etc have been used to reduce the corrosion of metal [57-70]. Different types of familiar corrosion forms, which damages the materials by different process are given below:

(1). Surface corrosion. Usually the surface corrosion is caused by the natural oxidation process of aluminum and its reaction to oxygen and external contaminants and obviously electron flow. The aluminum has ability to oxidize is the very thing that keeps it from rusting, and one of the most vital reasons for its use in airplane structures. If anybody has a metal polished airplane should remember that the beautiful shine of the plan is short-lived. Two or three days after polishing the airplane you can reject it with an aluminum polish rag will be black from oxidation that has built in that very short period. If we left it as unpolished surface will lose its luster and begin to develop a thin light grey haze, results the chalky powder on the surface after few months, which then becomes a crusty coating. Later on, it will begin to pit and erode the aluminum if left for indefinite time. Surface corrosion is very sensitive to moisture, for instance humidity and polluted rainwater. When certain impurities mix with water, water behaves as an electrolyte that increases the electron flow results corrosion faster. I case of stainless steel long-standing impact of water/humidity causes the surface corrosion. This is a common situation, especially in airplanes that are stored in a humid environment. Surface corrosion is not

limited to the airframe. Over the years, we have seen several severely corroded seat structures caused by the improper flame proofing of upholstery materials. The flame-proofing chemical that is applied to finish materials contains a bromide salt. If it is improperly applied or applied in too great a concentration, this salt, if exposed to high humidity or water, will mix with the moisture and create an electrolytic vapor or water solution that causes severe corrosion in aluminum or steel. The seat frame shown here was so severely corroded by a phenomenon that it had to be replaced.

(2). Filliform corrosion. This corrosion develops beneath a coating such as paint. It is usually caused by contaminants that were left on the surface or trapped between two mating surfaces before the primers and paint were applied. Once trapped by the paint, the corrosion develops and has the appearance of a spidery growth or a lake bed pattern under the painted surface.

(3). Fretting corrosion. This type of corrosion results from the normal causes of corrosion exacerbated by friction when two surfaces scrape against one another. It is common to see this type of corrosion where cowlings vibrate against airframes, doors rub against doorjambs, etc. The oxides form a powder that accelerates the corrosion of the material as the parts rub together, mechanically forcing the corrosive oxides into the metal.

(4). Inner granular corrosion. This corrosion is not caused by surface contaminants but is caused primarily by differential metal content of the alloy or a contaminant that became imbedded in the alloy during the manufacturing process. These dissimilar materials cause a very high level of inner electron flow (galvanic action) in the metal, resulting in the formation of internal corrosion and oxidation, and eventually making the metal swell as the pressure from the inner granular corrosion oxides try to push the molecules apart. At a very advanced stage, the metal begins to crack and split open, revealing the presence of powdery gray oxide.

4. SURFACTANTS AS CORROSION INHIBITORS

The promising potential application of surfactants as corrosion inhibitors has been studied widely from last few years. It is well known that surfactant have a tendency to associate with one another at interfaces and in solution to form aggregates [71]. The adsorption is critical to corrosion inhibition and the primary action of the surfactant functional group is to be adsorbed on the metal surface. Adsorption of the surfactant molecules onto metal surface was found to be responsible for the corrosion inhibition of the metal and is in general directly related to its capability to aggregate to form micelles [72-77]. Consequently, a better understanding of the relation between the adsorption of surfactant molecules onto metal surface and corrosion inhibition is of great importance for both theoretical and experimental reasons. To neutralize the corrosion, inhibitors should be injected constantly through the system [78]. A number of researches reduce the steel corrosion in acidic media [79-89] by means of the surfactants. Addition of surfactants to acidic media is an efficient and quite cheap method for rust protection of metal surfaces. The capability of surfactants to solubilize organic compounds and control various electrochemical reactions in aqueous media was supported in early 1950s. In past 20 years, research has focused on the scheming electrochemical reactions with surfactants as well as aggregate description through electrochemical methods. These studies guide to control the electrochemical catalysis through their microstructures. Various studies reveal that columbic and hydrophobic interactions with surfactants can stabilize different electrochemically produced ion radicals [90]. Surfactants were introduces in this research field to give a novel and useful dimension to these investigations. Very few investigations were found on the role of surfactants in surface modification of electrodes. Very recently, researchers were engaged in field of surfactants adsorbed from micellar solutions have paid attention on elucidating or utilizing, aggregate structures formed on the electrode. Surfactant molecules usually adsorb at the interface between two bulk phases such as air and water, oil and water or electrode and solution. Adsorption of surfactants on electrodes can have a deep influence on electrochemistry in fluids.

Surfactants have a wide range of applications as emulsifiers and dispersants. Miscellaneous and specific uses of surfactants are well described in literature [91,92]. J.H. Fendler and E.J. Fendler have comprehensively described the catalysis of organic reactions in micellar and macromolecular systems [93]. Surfactant aggregates results the solubilization of organic compounds is a well-known phenomenon, in electrochemistry. Gelatin and Triton X-100 were commonly used in electroanalytical chemistry to suppress the so-called streaming maxima at DME, shortly after the invention of polarography by Heyrovsky [94]. Early landmark papers featuring effects of surfactants also appeared in the literature of organic electrochemistry. Sodium dodecyl sulfate (SDS) was found to be an effective corrosion inhibitor for copper in acidic solution. The investigation performed by polarization technique revealed that SDS was a good anodic inhibitor at low anodic overvoltage and the adsorption of the inhibitor followed the Langmuir isotherm [95, 96]. From weight loss measurement, SDS was also found to be an effective inhibitor for nickel in acidic solution. The inhibition efficiency of surfactant for nickel increased with the increase of SDS concentration [97]. The adsorption of the anionic surfactants such as SDS on an aluminum surface has been found to be the main reason to provide better corrosion inhibition [98].

Cationic micelles of long-chain quaternary ammonium bromides (e.g. CTAB) are reported to act as inhibitors of corrosion of steel, and the inhibitory effect of the surfactant increases with alkyl chain length at concentrations above their CMC [99]. Very recently, Kim et al. [100] observed the beneficial effects of CTAB on the electrochemical film formation. They explained the CTAB-promoted film led to an increased energy conversion efficiency of the dye-sensitized solar cells. In figure 6 (a) and (b), the plain-view scanning electron microscopy (SEM) images of annealed TiO_2 in absence and presence of CTAB, respectively, and reveals that each film has clusters of near spherical, non-oriented, randomly connected, and loosely packed particles. In contrast, rod-shaped particles are usually obtained when films are grown by precipitation from hydrolyzed $TiCl_4$ solutions [101]. Irrespective of the precursor, i.e., $TiCl_3$ or $TiCl_4$, almost the same plain-view SEM images were obtained. The co-presence of CTAB, however, increased the film thickness significantly, as can be judged from Fig. 6 (c) and (d), suggesting a favorable effect of the surfactant on the electro deposition.

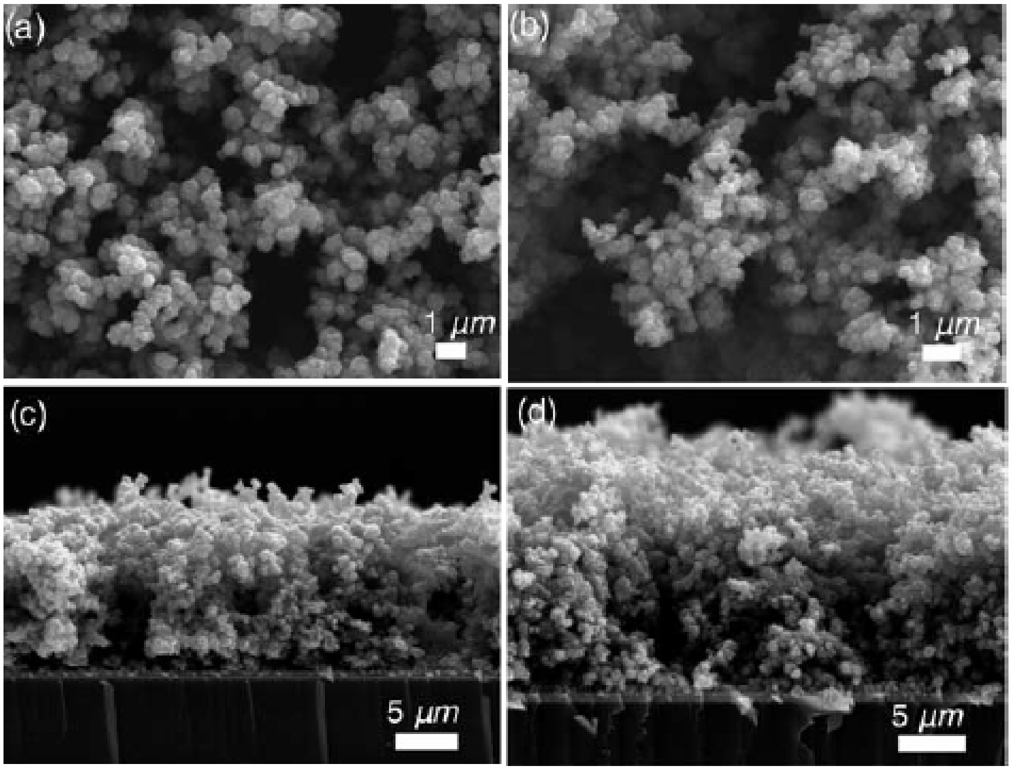


Figure 6. Plain and cross-sectional views of FE-SEM images of electrodeposited and annealed TiO2 film, prepared from TiCl4: (a, c) without and (b, d) with CTAB.

Atia and Saleh have reported that the cationic surfactant cetylpyridinium chloride (CPC) showed high inhibition efficiency for the corrosion of low carbon steel in 1 M H_2SO_4 and that protection efficiencies of up to 97 % were measured [102]. El Achouri et al. have synthesized gemini surfactants of the type 1,2-ethanediyl bis-(dimethylalkylammonium bromide) and studied their inhibitive effect on the corrosion of iron in hydrochloric acid, and concluded that these compounds are good inhibitors of iron corrosion and reach their maximum inhibition efficiency near their CMC [103]. Adding surfactants to acidic media is often the only efficient and rather cheap method of rust protection of metals. The general mechanism of corrosion inhibitors lies in the fact that they form an adsorbed film on the metal to be protected [104]. Liu et al. have shown that undoped polyaniline-4-dodecyl-phenol complex (PANI-DDPH) is an effective corrosion inhibitor, and that the surfactant improves the wet adhesion property between the coating and the metal surface [105].

Recently, gemini surfactants received great attention, because of two hydrophilic groups and two hydrophobic groups in the molecule, separated by a rigid or flexible spacer, rather than one hydrophilic group and one hydrophobic group for conventional surfactants, and they are more efficient at reducing surface tension and forming micelles than conventional surfactants. Gemini surfactants show many unique properties as compared with single chain conventional surfactants, such as lower CMC(s), better wetting properties and more effective in lowering the surface tension of water [106-108]. Farhat and his coworkers [109] studied three gemini surfactants, N-hexane-diyl-1,2-ethane-bis ammonium bromide (HEAB), N-dodecane-diyl-1,2-ethane-bis ammonium bromide (DDEAB), N-hexadecane-diyl-1,2-ethane-bis ammonium bromide (HDEAB), were developed as novel corrosion inhibitors for mild steel in 20% formic acid. The inhibition effectiveness of these gemini surfactants has been evaluated by electrochemical studies. The surface adsorption phenomena were investigated by scanning electron microscopy (SEM). The scanning electron microscopy (SEM) in Fig. 6 shows that, all gemini surfactants showed good performance as corrosion inhibitors for mild steel. Their inhibition efficiency is concordant to their order of CMC(s).

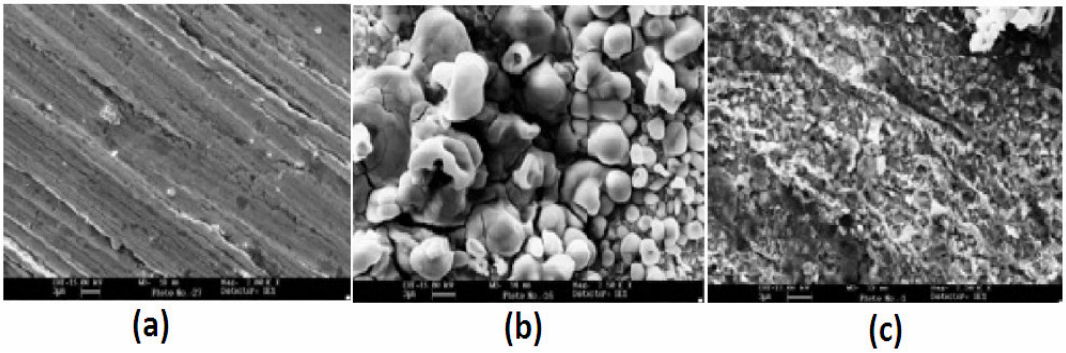


Figure 7. Mode of adsorption of gemini surfactants on mild steel surface.

Electrochemical studies showed that the inhibitors adsorb on the air-water interface and form a film on the metal surface. Infact all of the above-mentioned inhibitors, inhibit the corrosion by adsorption mechanism and the adsorption of these compounds follow Langmuir's adsorption isotherm. Moreover, scanning electron microscopy (SEM) shows smoother surface of inhibited metal surfaces than uninhibited metal surfaces due to the formation of a film on inhibited metal surfaces.

Min et al. [110] studied the corrosion inhibition behaviour of green surfactant Alkylpolyglucoside (APG) in 907 carbon steel in natural seawater by potential polarization curves measurements and weight-loss trials, respectively. The results show that, the green surfactant APG can inhibit the corrosion of 907 carbon steel in quiescent, natural seawater. When APG is combined with calcium gluconate and zinc sulfate, the corrosion inhibition rate was improved greatly, although the dosage of APG had been reduced largely [110]. The distinct synergistic effect was found among APG, calcium gluconate and zinc sulfate. The corrosion inhibitor was found to control both the anodic and cathodic processes, suggesting that the corrosion inhibitor is of a mixed-type. This corrosion inhibitor could form an adsorbent and deposited film on the surface of the metal. However, the adsorbent film acted primarily. Brij 56, a nonionic surfactant, or pluranic P123, a triblock copolymer, also a surfactant, was used to template the electrodeposition of mesoporous nickel films onto foamed nickel electrodes. The method was found to produce a 30- to 35-fold increase in surface area of the three-dimensional electrodes, which is beneficial for various applications including electrochemical detectors, batteries, and fuel cells [111]. Metallic nickel was electrodeposited from aqueous nickel(II) acetate dissolved in the liquid crystalline templating mixture Brij 56 and Brij 78, and the electrochemically accessible surface area of this film has been estimated to be 100 times greater than samples grown without a templating electrolyte [112]. Very recently, Tantay [113] studied a new cationic surfactant compound (di dodecyl benzyl tri ethyl ammonium chloride) (CS), which gives a good corrosion inhibition for the carbon steel. Barbara et al. [114] observed the effect of surfactants in electroplating to clean metal surfaces and to accelerate hydrogen evolution at the cathode. Fatty alcohol ethoxylates and sulphates are often used, and in some cases also alkyl benzene sulfonates. Adavntageous effects of fluorosurfactants in electroplating were particularly useful because of their chemical stability. Surfactants were used for electroplating venture because of the various beneficial effects [115]. They can modify the crystal size of the deposited metal, so that the brightness of the resulting plate improves, and reduces the surface tension of the electroplating solution. Due to the reduced surface tension, detachment of gas bubbles from the cathode is facilitated, pitting and pin holing are avoided, and cleaning of the metal surface as a preparatory step to plating, e.g., in nickel-plating baths. Best deposits are obtained at the lowest surface tension, which is brought forth by the addition of surface-active agents.

Uchida and co-workers have patented an invention which relates to a non-cyanide based Au–Sn alloy plating bath comprising a solution of gold salt, a solution of tin salt etc., wherein the polymeric cationic surfactant or agent is contained for enhancing the luster and reflow properties [116]. In plating silver, gold and copper from alkaline solution of the double cyanides, surfactants shorten or eliminate the buffing operation (grinding a surface to remove extrusions or to expose underlying metal), which is otherwise required to produce a bright polished surface [117]. Surfactants influence the depolarization of an electroplated coating and the efficiency of plating operations. The effects of surfactants include changing the polarization potentials at the cathode [117] and altering the smoothness of the plate, the grain size, rate of grain growth and adhesion of the grains to the substrate and to each other [118]. Yoshida et al. have developed a new electroplating technology using nonionic surfactants to prepare high quality nickel films with higher uniformity, smaller grain size (sub-100 nm) and higher vickers hardness, compared to those of the films obtained by conventional electroplating method without using surfactant [119]. Surfactants solutions play a role in electrodes, which are coated with clay films. Natural clays are layered aluminosilicate cation exchangers. They adsorb cation surfactants, which form bilayer or hemimicelle coatings on the clay surface. Surfactant treated clay colloids can adsorb nonpolar reactants [120,121]. Clay-modified electrodes (CMEs) have been made by depositing colloidal sodium bentonite (ca. 500 nm thickness) on pyrolytic graphite (PG) [122]. Tris (2,2V-bipyridyl) cobalt (II) dication was taken up by the CMEs in the absence and presence of CTAB micelles [122]. It gave separate CV reduction peaks for Co(II) at -1.2 V and Co(I) at -1.5 V. Films of tetraalkylammonium surfactant bilayers, intercalated between colloidal clay layers, were prepared by Okahata and Shimizu [123] as membranes with controlled permeability.

Zhao and Mu [124] observed the effect of anionic surfactants such as dodecyl sulphonic acid sodium salt (DSASS), dodecyl benzene sulfonic acid sodium salt (DBSASS) and sodium dodecyl sulfate (SDS) on the aluminium surfaces. They showed that surfactants are the main reason to cause the corrosion inhibition. When the concentration of surfactants is close to that of its CMC, aluminum will obtain its greatest adsorption amount, least weight loss and strongest corrosion resisting property. In addition, adsorption rules conform to the Langmuir formula by taking the straight adsorption mode with hydrophilic group facing the aluminum surface and the hydrophilic group facing the medium. Several surfactants that functions as corrosion inhibitors have biocidal properties [125-128]. Houyi Ma et al. [129] have investigated the inhibitive action of CTAB, SDS, sodium oleate and polyoxyethylene sorbitan monooleate on the corrosion behaviour of Cu by electron impedance spectroscopy. CTAB was found to be the most efficient inhibitor due to the synergistic effect between bromide anions and the positive quaternary ammonium ions. Suguna et al. [130] have determined the corrosion rates of carbon steel in the absence and presence of sodium dodecyl sulfate and Zn^{2+} in aqueous solutions. Rong Guo [131] has studied the effects of sodium dodecylsulphate (SDS) and some alcohols (ethanol / n-butanol) on the inhibition of the corrosion of Ni. Abd-El-Rehim et al. [132] have reported that the inhibition of corrosion of Al alloy in 1 M HCl in the temperature range 10-60º C occurs through the adsorption of the anionic surfactant SDS on the metal surface without modifying the mechanism of the corrosion process.

The effect of SDS on Copper corrosion has been studied in the absence and presence of benzotriazole using electrochemical impedance and surface tension measurements [133,134]. Rajendran et al. [130] have evaluated the inhibition efficiency of SDS in controlling the corrosion of carbon steel immersed in 60 ppm of aqueous NaCl in the absence and presence of Zn^{2+}. FTIR spectrum has revealed the presence of a film containing iron-SDS complex and $Zn(OH)_2$.

Monticelli et al. [135] have investigated the corrosion inhibition of Al alloy (AA 6351) in 0.01 M NaCl using inhibitors such as sodium salts of N- dodecanoyl-N-methylglycine (NLS), dodecyl sulfate (LS), N-dodecanoyl-N-methyltaurine (NLT) and dodecylbenzene sulfonate (DBS). The existence of synergism and antagonism in mild steel corrosion inhibition by sodium dodecylbenzene sulfonate and hexamethylenetetramine has been ascribed to the formation of hemi-micellar aggregation that provokes inhibitor desorption from the metal/solution interface at higher concentration [136]. Rajendran et al. [137] have reported the mutual influence of HEDP and SDS on the corrosion inhibition of carbon steel immersed in rainwater in the presence of Zn^{2+}. They carry out this work (i) to evaluate the inhibition efficiency and the biocidal efficiency of SDS - Zn^{2+} system for the corrosion of the carbon steel in 120 ppm chloride solution; (ii) to study the biocidal efficiency of N-cetyl-N,N,N-trimethylammonium bromide [CTAB] and N-cetyl pyridinium chloride [CPC] in the presence of the inhibitor system and their influence on the IE of SDS-Zn^{2+} system; (iii) to analyze the protective film on carbon steel by FTIR spectra and UV spectra; (iv) to understand the mechanistic aspects of corrosion inhibition by AC impedance analysis and potentiodynamic polarization studies; (v) to propose a suitable mechanism for corrosion inhibition.

5. CMC IN CORROSION INHIBITION

It is well known that surfactants are characterized by critical micelle concentrations (so called CMCs). The CMC is the concentration where surfactants in solution change their initial molecular solvated state. Most of the physical and chemical properties of surfactant solutions undergo an abrupt variation at this concentration. The CMC is influenced by a number of factors that are dependent on the nature of the surfactant and the aqueous environment. The ionic strength of the solution is one of these influential factors, being responsible for the shift of the CMC value with respect to its primary value in pure water [138-141].

Consequently, the critical micelle concentration (CMC) is a key indicator in determining the effectiveness of surfactants as corrosion inhibitors. Below the CMC, individual surfactant molecules or monomers tend to adsorb on exposed interfaces, so interfacial aggregation reduces surface tension and is related to corrosion inhibition. Above the cmc, the surface becomes covered with more than one monolayer (Fig. 8) and forms a protection layer on the metal surface. Thus, any additional surfactant added to the solution above the cmc will lead to the formation of micelles or multiple adsorbed layers on surfaces. Consequently, the surface tension and corrosion current density are not altered significantly above the CMC. Therefore, an excellent surfactant inhibitor is one that aggregates or adsorbs at low concentrations. In other words, surfactants with low cmc values are desirable, because they adsorb at low concentrations.

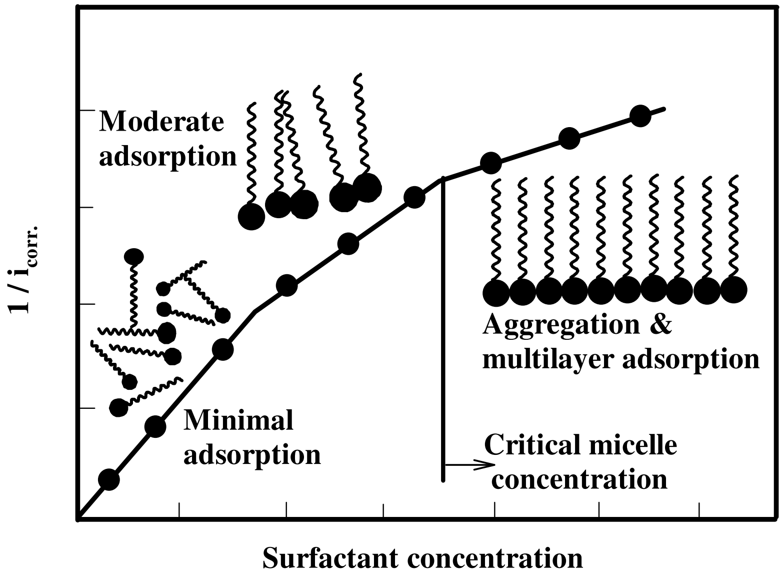


Figure 8. Effect of surfactant concentration on corrosion inhibition.

Corrosion inhibition by surfactant molecules are related to the surfactant's ability to aggregate at interfaces and in solution. Understanding the factors that affect aggregation as well as the state of aggregation of surfactant molecules on metal surfaces is, therefore, an important prerequisite to understanding corrosion inhibition by surfactant molecules. It is well known that surfactant molecules have a tendency to associate with one another at interfaces and in solution. Surfactant aggregation can be measured by decreasing surface tension at the air-water interface. The effect of temperature on a chemical reaction is an important parameter in both practical and theoretical aspects. Similar to the most of chemical reactions, the corrosion rate of iron and steel increases with increase in temperature, especially in media in which evolution of hydrogen accompanies corrosion, e.g. during corrosion of steel in acids. It has been reported that, the effect of temperature on the corrosion behavior of Al in the absence and presence of different concentrations of anionic surfactants in acidic media at different temperatures has been studied [104]. It is apparent that corrosion efficiency increases with increasing the concentration of surfactants and decreases with increasing the temperature. This concludes that the increase of temperature led to the reduction of the corrosion inhibitor adsorption on the metal surface and then the acceleration of the dissolution process [142]

6. MECHANISM

Corrosion inhibition has complex mechanism and depends on the formation of mono- or multi-dimensional protective layers on the metal surface. The protective nature of the surface layer depends on many factors: interaction between inhibitors and substrate, incorporation of the inhibitor in the surface layer, chemical reactions, electrode potentials, concentration of the inhibitor, temperature and properties of the corresponding surface, etc. The first stage in the action mechanism of the surfactants as corrosion inhibitors in aggressive media is adsorption of the surfactant molecules onto the metal surface. The adsorption process is influenced by the nature and the surface charge of the metal, the chemical structure of the surfactant, and the nature of the aggressive electrolyte. Adsorption of the surfactant molecules on the metal surface can be expressed according to the following equation:

$$\text{Surfactant}_{(\text{sol.})} + n\text{H}_2\text{O}_{(\text{ads.})} = \text{Surfactant}_{(\text{ads.})} + n\text{H}_2\text{O}_{(\text{sol.})}$$

where n is the number of water molecules removed from the metal surface for each molecule of surfactant adsorbed. It is clear that the value of n depends on the cross sectional area of the surfactant molecule with respect to that of the water molecule. Adsorption of the surfactant molecules occurs because the interaction energy between the surfactant molecules and the metal surface is higher than that between water molecules and the metal surface. So the inhibition effect by surfactants is attributed to the adsorption of the surfactant molecules via their functional groups onto the metal surface. The adsorption rate is usually rapid and hence the reactive metal is shielded from the aggressive environment. Corrosion inhibition depends on the adsorption ability of the surfactant molecules on the corroding surface, which is directly related to the capacity of the surfactant to aggregate to form clusters (micelles). The critical micelle concentration, CMC, is a key factor in determining the effectiveness of a corrosion inhibitor. Below CMC as the surfactant concentration increases, the molecules tend to aggregate at the interface, and this interfacial aggregation reduces the surface tension. Above CMC the metal surface is covered with a monolayer of surfactant molecules and the additional molecules combine to form micelles or multiple layers. This, consequently, does not alter the surface tension and the corrosion rate.

The adsorption behavior of gemini surfactants on metal surface is more complicated than that of conventional surfactants because the gemini surfactants contain two hydrophilic groups and two hydrophobic groups. Figure 9(a) shows the mode of adsorption of the surfactant as individual molecules at very low concentration of the inhibitor. Figure 9(b) shows the mode of adsorption of the surfactant as hemi-micelles at moderate concentration. The hemi-micelle phase in the surfactant solution means the start point to collect the surfactant in duplet, triplet, or quadrate before forming the complete micelles.

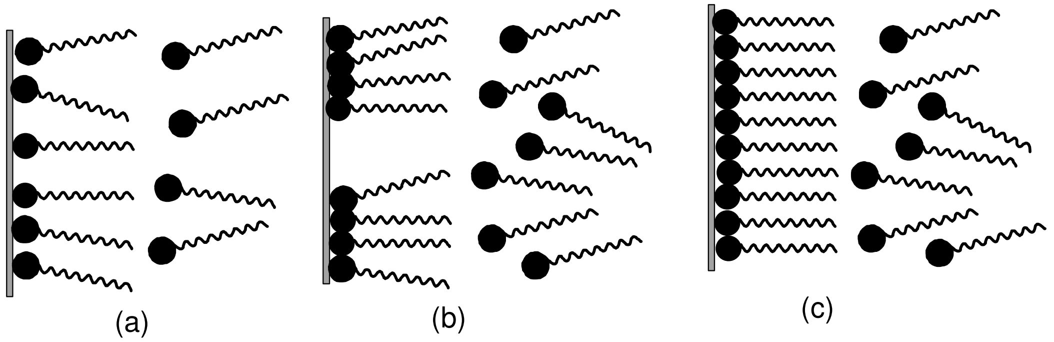


Figure 9. Schematic representations for adsorption process of surfactant molecules on steel surface: (a) adsorption of single molecule at low concentration, (b) hemi-micelle formation at higher concentration, (c) formation of multilayers at very high concentration of inhibitor.

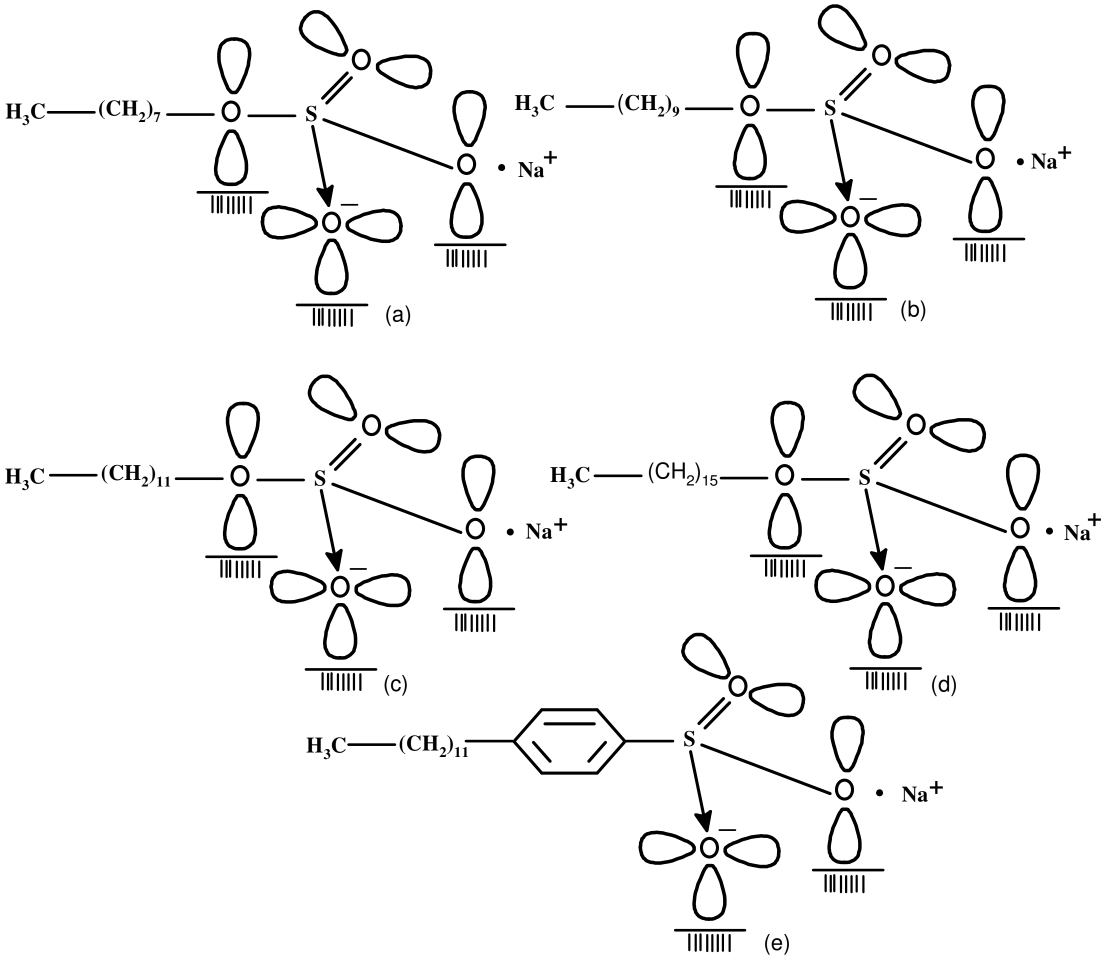


Figure 10. Schematic representation of the mode of adsorption of anionic surfactants.

The mode of adsorption of some anion surfactants ((a) octyl sulphate sodium salt, (b) decyl sulphate sadium salt, (c) dodecyl sulphate sodium salt, (d) hexadecyl sulphate sodium salt and (e) dodecyl benzene sulfonate, respectively) is shown in Figure (10) [104]. The order of decreasing inhibition efficiency of these anionic surfactants is (a) < (b) < (c) < (d) < (e). Higher molecular size and high electron density on the adsorption centers may be responsible for high corrosion efficiency.

5. CONCLUSIONS

Surfactants are proved to be one of the best eco friendly anti-corrosion substances to protect the materials from corrosion. The high affinity of surfactant molecules to adsorb onto interfaces to form micelles is responsible for their applications in several interfacial systems have make them very attractive to be used as corrosion inhibitors in metallic surfaces. Novel anticorrosion ability of different types of surfactants can be potentially used in the industry as good options to solve the problems of corrosion on metallic surfaces to prevent the material and economic loss.

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