การศึกษาพฤติกรรมการกัดกร่อนของเหล็กกล้าไร้สนิม 304 ในสารละลายโซเดียมคลอไรด์ 0.9% โดยน้ำหนัก ที่มีการเติมโซเดียม 2-เอทิลเฮกซิลซัลเฟต

INFLUENCE OF SODIUM 2-ETHYLHEXYL SULFATE ON CORROSION BEHAVIOR OF 304 STAINLESS STEEL IN 0.9 wt.% SODIUM CHLORIDE

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SIRORAT THAWON
THIRAKORN MOKKAWES

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Project Title	Influence of Sodium 2-Ethylhexyl Sulfate on Corrosion Behavior of 304 Stainless Steel in 0.9 wt.% Sodium Chloride
Students	Miss Sirorat Thawon Student ID 56050621 Mr. Thirakorn Mokkawes Student ID 56050625
Degree	Bachelor of Science (Industrial Chemistry)
Department	Chemistry
Academic Year	2016
Advisor	Asst. Prof. Dr. Sutha Sutthiruangwong

Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, has approved this special project submitted in partial fulfillment of the requirement for the degree of Bachelor of Science in academic year 2016.

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Abstract

Stainless steel type 304 is one of the most favored materials used in many industries such as chemical plant, food production, and automobile manufacturing. Lifetime of stainless steel is reduced by corrosion. Corrosion protection technology such as surfactant corrosion inhibitor is interesting. In this research, the decrease of pitting corrosion resistance of 304 stainless steel in 0.9 wt.% NaCl solution was achieved when sodium 2-ethylhexyl sulfate was used as an inhibitor. The results suggested that critical micelle concentration (CMC) of sodium 2-ethylhexyl sulfate in 0.9 wt.% NaCl was found to be 3.550 mM by conductivity measurement. Various inhibitor concentrations in NaCl solution were studied (0.25xCMC, 0.5xCMC, 0.75xCMC, and 1xCMC). The results suggested that the corrosion potential (E_{corr}) was increased to more positive value after adding surfactant inhibitor. At 1xCMC of sodium 2-ethylhexyl sulfate concentration, pitting was completely inhibited.

Keywords : corrosion inhibitor, pitting corrosion, sodium 2-ethylhexyl sulfate, 304 stainless steel

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Sirorat Thawon
Thirakorn Mokkawes

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CHAPTER 1

INTRODUCTION

1.1 Motivation

The use of corrosion inhibitor is one of the most practical method for protection against corrosion in saline media. To be effective, an inhibitor must remove water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction, 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.

Surfactant inhibitors have many advantages, for example, high inhibition efficiency, low price, low toxicity, and easy production. Moreover, the investigation of surfactants adsorbed on metal surfaces is extremely important in electrochemical studies such as corrosion inhibition, adhesion, lubrication, and detergency. The effective type of corrosion inhibitors for these applications is film-forming inhibitors. The most important action of inhibition is the adsorption of the surfactant functional group on the metal surface [1]. This layer reduces or prevents corrosion of the metal in aggressive media. The ability of a surfactant molecule to adsorb is generally related to its ability to aggregate to form micelles. The degree of adsorption depends on the nature of the metal, surfactant and solution [2]. The corrosion inhibition of a metal may involve either physisorption or chemisorption of the inhibitor on the metal surface. 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 [3].

There are many research works about the corrosion of AISI 304 stainless steel, the effect of corrosion and how to prevent the corrosion in NaCl solution [4-6]. This is because the AISI 304 stainless steel is the main material in normal saline production. Normal saline solution is a mixture of 0.9 wt.% NaCl in water and has a number of uses in medicine [7, 8]. By applying to the affected area, it is used to clean wounds, help remove contact lenses, and help about the dry eyes. By injection into a vein it is used to treat dehydration such as from gastroenteritis and diabetic ketoacidosis. It is also used to dilute other medications to be given by injection. It is well known that chloride ion (Cl^-) concentration can have significant effect on the susceptibility of AISI 304 stainless steel to pitting corrosion.

The critical micelle concentration (CMC) of surfactants has been defined as the concentration of the surfactant solution at which the molecules completely adsorb on tested sample surface and enter the micellar state. The variation of the CMC with chemical and physical parameters provides a good insight into the nature of the surfactant self-association. For surfactants containing long chain alkyl groups the value of CMC is usually between 10^{-4} and 10^{-2} M [9]. In case of branched hydrocarbon chains, the CMC is not higher than in the straight chain. Since the decrease in free energy arising from the aggregation of branch chain molecules, is less than that obtained with linear molecules with the same number of carbon atoms.

This study aims to reduce pitting corrosion of AISI 304 stainless steel in 0.9 wt.% NaCl by adding Sodium 2-ethylhexyl sulfate (SEHS), which is alkyl branch chain surfactant. The effect of steric structure is expected to present lower CMC compare to straight chain and use less of surfactant inhibitor to get higher protection in pitting corrosion. The potentiodynamic polarization technique, which is widely used as a tool for corrosion study, was applied to investigate the corrosion behavior of 304 stainless steel in 0.9 wt.% NaCl solution with various concentrations of SEHS.

1.2 Objectives

1) To increase pitting potential in 0.9 wt.% NaCl solution using surfactant inhibitors of sodium 2-ethylhexyl sulfate on 304 stainless steel.
2) To study the influence of concentration of inhibitors above and below critical micelle concentration (CMC).

1.3 Scope of study

The scopes of this special project are as follows:

1) Study on application of SEHS with different concentration: 0.25, 0.50, 0.75, 1, 2×CMC in 0.9 wt.% NaCl solution and evaluate the surfactant inhibition activity by a three-electrode cell system with potentiodynamic polarization and chronoamperometry measurement at room temperature.

1.4 Expected results

The pitting resistance of 304 stainless steel can be increased with increasing SEHS concentration.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Basic principles of corrosion

2.1.1 Corrosion [10, 11]

Corrosion is defined as the destruction of metals and alloys because of a reaction with its reaction with its environment. Corrosive environments include moisture, oxygen, inorganic and organic acids, high pressure, temperature, and chlorides. During corrosion, metals tend to convert to more thermodynamically stable compounds such as oxides, hydroxides, salts, or carbonates. Recovering the original compounds (minerals and ores) from metals by spontaneous.

2.1.2 Mechanism of corrosion [10-14]

In general, corrosion can be classified into two major classes: direct chemical attack and electrochemical attack. In both cases, the metal is converted to oxide, hydroxide or sulfate compound. Corrosion process is described into distinct ranges depending on upon which of these reactions are the controlling one.

Direct chemical corrosion or dry corrosion, involves a direct exposure of a bare metal surface to medium and gets corroded by the direct attack of oxygen, sulfur dioxide and chlorine, etc. gases or the chemical reaction. Naturally, metals are oxidized and form a thin film of its oxides on the surface. This kinds of corrosion due to:

1) Oxidation corrosion
2) Corrosion by gases
3) Liquid metal corrosion

Electrochemical corrosion occurs when a metal is exposed to environment medium, this process is set by separation of anodic and cathodic areas within metal surface. A driving force is necessary to flowing electron between the anodes and the cathodes which difference in potential between both areas due to each oxidation or reduction reaction which associate with metal tendency.

Corrosion always occurs at the anodic area of the metal due to the oxidation process, as shown in Eq. (2.1), which electrons are liberated. The metal ions are formed during destruction of metal either dissolves in the medium or forms a thin film of oxide on the metal surface.

$$M \rightarrow M^{n+} + ne^- \qquad (2.1)$$

In addition, the cathodic area of metal is protected as a result of reduction reduction in Eq. (2.2). The electrons are released from anodic area and are consumed at the cathodic area by the following mechanisms.

$M^{n+} + ne^- \rightarrow M$ (2.2)

Corrosion process is described into distinct ranges depending on upon which of these reactions are the controlling one. Normally, the fundamental reaction in the corrosion of iron in neutral or alkaline solutions is described as shown in Eq. (2.3).

$2Fe + H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2\downarrow$ (2.3)

From Eq. (2.3), can be separated into anodic and cathodic reactions as shown in Eqs. (2.4) and (2.5).

$2Fe \rightarrow 2Fe^{2+} + 4e^-$ Anodic reaction (2.4)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ Cathodic reaction (2.5)

In anodic reaction, the iron gets oxidized into ferrous ions [Fe (II)] with the loss of two electrons. Asa cathodic reaction, the medium is contained with dissolved oxygen. Ferrous hydroxide which precipitates from overall corrosion reaction, is unstable compound in oxygenated solutions and is oxidized to the ferric salt [11, 14], presented in Eq. (2.6).

$2Fe(OH)_2 + H_2O + 1/2O_2 \rightarrow 2Fe(OH)_3$ (2.6)

In acidic medium hydrogen ions acquire electrons with the liberation of hydrogen gas in a cathodic reaction as shown in Eq. (2.7).

$4H^+ + 4e^- \rightarrow 2H_2$ (2.7)

2.1.3 Electrochemical polarization [15, 16]

The potential difference between the two electrodes in a cell provides the 'driving force' for the current, which determines the extent of corrosion at the anode. However, when the cell is operating, when current is flowing, the electromotive force of the cell is different from that theoretically predicted by taking the difference in potentials of the two metallic electrodes. Polarization occurs at both the anode and the cathode.

Polarization, sometimes termed overpotential or overvoltage, can be defined as the difference of the potential of an electrode from its equilibrium or steady-state potential. This can be considered in terms of the energy required to cause a reaction to proceed. An analogy would be the initial energy required to push a car on a level path. Once the car is moving, less energy is required, but if a slope is reached the energy required on the level is not sufficient to push it up the slope, so it tends to slow down and eventually stops.

Once the cell is operating, changes occur in the cell; ions tend to collect near the anode and reactants tend to surround the cathode. The net result is reduction in the potential difference between the electrodes.

2.1.4 Type of corrosion

In this study, corrosion process is described in specific type as uniform corrosion and pitting corrosion.

2.1.4.1 Uniform corrosion

Uniform corrosion is assumed to be the most common form of corrosion and particularly responsible for most of the material loss which characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the total area, without any localized attack. Corrosion does not penetrate very deep inside, and the most familiar example is the rusting of steel in air. Consequently, it leads to a relatively uniform thickness reduction as shown in Fig. **2.1**. Homogeneous materials without a significant passivation tendency in the actual environment are liable to this form of corrosion. Traditionally, however it is not recognized as dangerous form of corrosion, because prediction of thickness reduction rate can by means of simple tests and available protection methods are usually so efficient that the corrosion rate is reduced to an acceptable level.

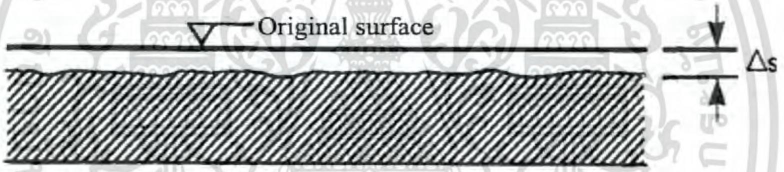


Fig. 2.1. Uniform corrosion [11].

2.1.4.2 Pitting corrosion

This form of corrosion is characterized by narrow pits with a radius of the same order of magnitude as, or less than, the depth. The pits may be of different shape, but a common feature is the sharp boundary, represented in Fig. **2.2**. Pitting is a dangerous form of corrosion since the material in many cases may be penetrated without a clear warning, because the pits often are narrow and covered, and the pit growth is difficult to predict. This is connected to the fact that the extent and the intensity of pitting corrosion is difficult to measure because the number and size of pits (diameter and depth) vary from region to region and within each region. Short-term testing in the laboratory for determination of pit growth is also problematic because, under realistic conditions, it may take long time, e.g. many months, before the pits become visible. Another problem is that the critical size, the maximum pit depth, increases with increasing surface area.

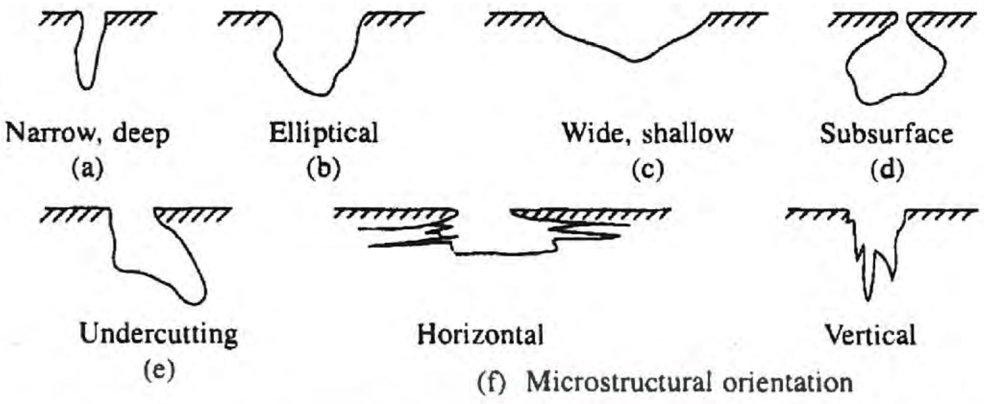


Fig. 2.2 Variations in the cross-sectional shapes of pits observed during pitting attack [12].

2.1.5 Influence of environment

Environment could be regarded as the greatest sources of corrosion, since all materials must exist in one environment or the other. The environmental constituents such as the presence of salt sprays, acids bases and corrosives are potential sources of corrosion. In the following section, some environmental variables are considered to determine the performance of materials and to evaluate mitigation techniques.

2.1.5.1 pH

pH is defined as a measure of concentration of hydrogen ions [17], when there is an excess of H^+ ions, the solution is acidic. When the pH is decreasing (acidity increase), the corrosion rate and is increasing as shown in Fig. 2.3. This is because the low pH solutions accelerate corrosion by providing hydrogen ions and will raise the redox potential of the aqueous solution with a consequent increase in rate as shown in Eq. (2.7) [18].

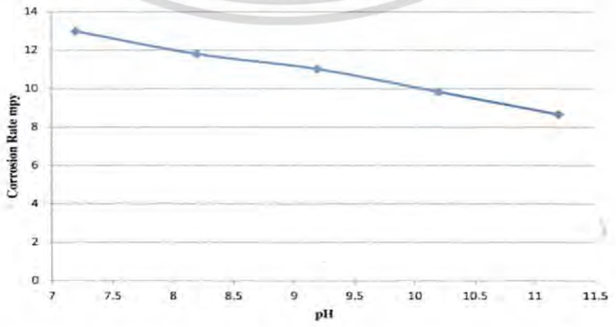


Fig. 2.3 Corrosion rate against pH of mild steel in bore-hole water at room temperature using 1M NaOH solution [14].

2.1.5.2 Oxidizing agent

Oxidizing agents may accelerate the corrosion of one class of materials and retard the corrosion of another class. In the latter case, the behavior of the material usually represents the surface formation of oxides or layers of absorbed oxygen which make the material more resistant to further chemical attacks. This property of chromium is responsible for the principle corrosion resisting characteristics of stainless steels.

2.1.5.3 Fluid velocity

This effect is the relative between the velocity of corrosive fluid which flow through a metallic surface. The corrosion rate is accelerated due to the higher rate at which corrosive chemicals, including oxidizing substances such as water, are brought to the corroding surface. If the metal is readily passivated, the effect of high velocity may be either to prevent passivated layer, or to remove them after they are formed. Whereas, easily passivated materials such as stainless steel and titanium frequently are more corrosion resistant when the velocity of the corrosion medium is high. Corrosion rate influenced by fluid velocity occurs frequently in small-diameter tubes or pipes at high velocity such as in condenser tubes and evaporation tubes.

2.1.5.4 Temperature

Rate of corrosion tends to increase with rising temperature. Higher temperature can increase the diffusion of oxygen through protective film, passivated layer. Temperature also enhance solubility of air, especially oxygen, in solution.

Recent experimental results that the passivation current density increased with increasing the solution temperature observed in Fig. **2.4**. This tendency is due to the reason that most of the electrochemical and chemical reactions proceed more rapidly at higher temperature [19].

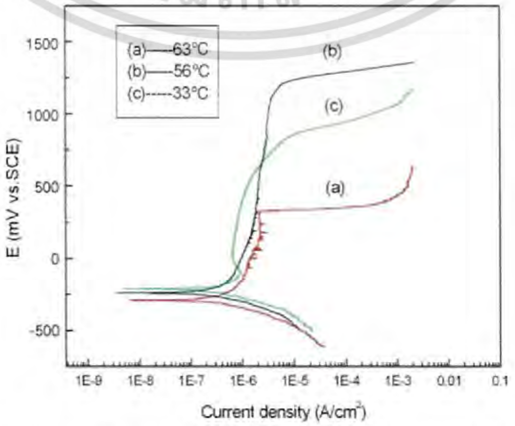


Fig. 2.4 Anodic polarization curves for UNS S31803 in 1 M NaCl with potential scan rate 1 mV/s at different temperatures [14].

2.1.5.5 Corrosive concentration

An increase in the corrosive concentration can change the stability of steel due to metal will exhibit passivity effects by wide changes in corrosive concentration. Initially, as the concentration of corrosive is increased, the corrosion rate is likewise increased. Because, the amount of hydrogen ions, which are the active species, are increased as acid concentration is increase.

2.2 Inhibitor

In general, any corrosion retardation process can be considered corrosion inhibition. Corrosion inhibition has been achieved by the addition of a chemical compound that inhibits the oxidation of the metal. The chemical inhibitor added to the system may be in the form of a liquid or vapor or both.

2.2.1 Inhibitor classification

Inhibitors are classified according to their inhibition mechanism, application or chemical nature. The following classes of inhibitors are discussed in this part: (i) Inorganic inhibitors; (ii) Organic inhibitors; (iii) Surfactant inhibitors; (iv) Mixed material inhibitors.

2.2.1.1 Inorganic inhibitors

2.2.1.1.1 Anodic inhibitors

Anodic inhibitors (also called passivation inhibitors) act by a reducing anodic reaction that blocks the anode reaction and supports the natural reaction of passivation metal surface, also, due to the forming a film adsorbed on the metal. In general, the inhibitors react with the corrosion product, initially formed, resulting in a cohesive and insoluble film on the metal surface [20].

The anodic inhibitors reacts with metallic ions which is produced on the anode, forming generally, insoluble hydroxides which are deposited on the metal surface as insoluble film and impermeable to metallic ion. From the hydrolysis of inhibitors results in OH^- ions.

When the concentrations of inhibitor become high enough, the cathodic current density at the primary passivation potential becomes higher than the critical anodic current density, that is, shift the potential for a noble sense, and, consequently, the metal is passivated [21, 22]. Some examples of anodic inorganic inhibitors are nitrates, molybdates, sodium chromates, phosphates, hydroxides and silicates.

2.2.1.1.2 Cathodic inhibitors

During the corrosion process, the cathodic corrosion inhibitors prevent the occurrence of the cathodic reaction of the metal. These inhibitors have metal ions able to produce a cathodic reaction due to alkalinity, thus producing insoluble compounds that precipitate selectively on cathodic sites. Deposit over the metal a compact and adherent film, restricting the diffusion of reducible species in these areas. Thus, increasing the impedance of the surface and the diffusion restriction of the reducible species, that is, the oxygen diffusion and electrons conductive in these areas. These inhibitors cause high cathodic inhibition.

The cathodic inhibitors form a barrier of insoluble precipitates over the metal, covering it. Thus, restricts the metal contact with the environment, even if it is completely immersed, preventing the occurrence of the corrosion reaction. Due to this, the cathodic inhibitor is independent of concentration, thus, they are considerably more secure than anodic inhibitor.

Some examples of inorganic cathodic inhibitors are the ions of the magnesium, zinc, and nickel that react with the hydroxyl $(OH)^-$ of the water forming the insoluble hydroxides as $Mg(OH)_2$, $Zn(OH)_2$, $Ni(OH)_2$, which are deposited on the cathodic site of the metal surface, protecting it. Also, can be cited polyphosphates, phosphonates, tannins, lignins and calcium salts as examples that presents the same reaction mechanism.

2.2.1.2 Organic inhibitors [20]

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

These materials build up a protective film of adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. Because the metal surface covered is proportional to the inhibitor concentrates, the concentration of the inhibitor in the medium is critical. For example, a concentration of 0.05% sodium benzoate or 0.2% sodium cinnamate is effective in water with a pH of 7.5 and containing either 17 ppm sodium chloride or 0.5% by weight of ethyl octanol. The corrosion due to ethylene glycol cooling water systems can be controlled by the use of ethanolamine as an inhibitor.

2.2.1.3 Surfactant 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'', as shown in Fig. 2.5. 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.

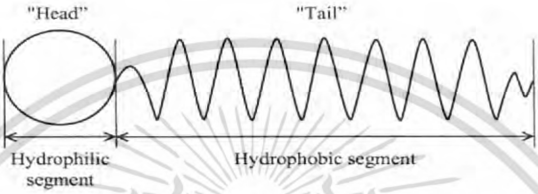


Fig. 2.5 The basic molecular structure of a surfactant molecule [18].

Surfactant inhibitors have many advantages, for example, high inhibition efficiency, low price, low toxicity, and easy production. 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.

2.2.1.4 Mixed material inhibitors

Mixed material inhibitors affect both anodic and cathodic branches of a polarization curve. Organic compounds function as mixed-type inhibitors. The organic inhibitors adsorbed on the metal surface provide a barrier to dissolution at the anode and a barrier to oxygen reduction at the cathodic sites. The protective functional groups in the organic mixed-type inhibitors can be amino, carboxyl, or phosphonate.

2.2.2 Influence of enviromental factors

A change in temperature can affect (i) kinetics and mechanism of metal dissolution and oxide formation and (ii) adsorption and desorption. Thus, change in temperature can increase or decrease or have no effect on corrosion inhibition. Changes in temperature can cause decomposition of the inhibitor or changes in the metal dissolution process. The data on the effective activation energy for the corrosion of iron in 1 N HCl solution as a function of inhibitor concentration have been attributed to the nature of adsorption, changes in the metal dissolution mechanism, and the thermal stability of the inhibitor [23].

The pH of the solution can influence the effectiveness of the inhibitor. In neutral solutions containing dissolved oxygen, there is a critical pH value above which passivation is favored. Some pitting corrosion inhibitors are effective in neutral solutions and ineffective in acid solutions. Other inhibitors effective in acid solutions can be ineffective in neutral solutions. The surface coverage of an inhibitor and, in some instances, even monolayer coverage has proven to give adequate protection.

The extent of inhibition usually increases with an increase in concentration of the inhibitor. In some cases, the corrosion may decrease with increase in inhibitor concentration, which may be attributed to the formation of soluble metal complexes, change in the mode of adsorption or the inhibitor may act as a cathodic depolarizer at higher inhibitor concentrations. In the case of some inhibitors used in small concentrations, the inhibitors can act as cathodic depolarizers and increase the corrosion rate. For example, in a solution containing 30 mg/L of NaCl and 70 mg/L of Na_2SO_4, chromate inhibitor at less than 50 mg/L increased the pitting rate of steel.

2.3 Surfactants

Surfactants, also called surface active agents, mean that when the compound is added to a liquid at low concentration, it should be able to adsorb on the surface or interface of the system and reduce the surface or interfacial excess free energy. The surface is a boundary between air and liquid and the interface is a boundary between two immiscible phases (liquid–liquid, liquid–solid and solid–solid) [24]. Surfactants are common know as cleaning agents in soaps and detergents [25]. Surfactants can act as detergents, wetting agents, emulsifiers, foaming agents and dispersants [26].

2.3.1 Composition of surfactants [27, 28]

The chemical structures having suitable solubility properties for surfactant activity vary with the nature of the solvent system to be employed and the conditions of use. In ''standard'' surfactant terminology, the ''head'' refers to the solubilizing group—the lyophilic or hydrophilic group, in aqueous systems—and the ''tail'' refers to the lyophobic or hydrophobic group in water as shown in Fig. 2.6.

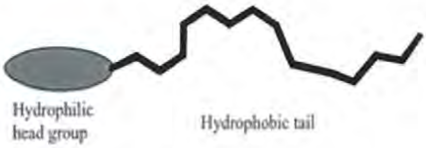


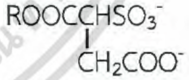
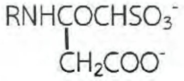
Fig. 2.6 Simplified surfactant structure [23].

2.3.2 Type of surfactants [25-28]

The surfactant is classified by their hydrophilic groups into four classes as anionic or negative charged, cationic or positive changed, and nonionic or no apparent ionic charged.

2.3.2.1 Anionic surfactants

Anionic surfactants are the most commonly used class of surfactants in cleansing applications. The variety of anionic materials available arises primarily from the many types of hydrophobic groups that can be modified by the addition of the proper anionic species. Anionics can be classified according to the polar group and the following will be considered:

2.3.2.1.1 Sulfates	
-Alkyl sulfates	$ROSO_3^-$
-Alkyl ether sulfates	$R(OC_2H_4)_nOSO_3^-$
-Sulfated alkanolamides	$RCONHC_2H_4OSO_3^-$
-Monologycerride sulfates	$RCOOCH_2CHOHCH_2OSO_3^-$
2.3.2.1.2 Sulfonated hydrocarbons	
-Alkyl benzene sulfonates	$RC_6H_4SO_3^-$
-Alkane sulfonates	RSO_3^-
-Alpha-olefin sulfonateds	$RCH{=}CHR'SO_3^-$
2.3.2.1.3 Sulfonated esters	
-Acyl isothionates	$RCOOC_2H_5SO_3^-$
-Fatty ester sulfonates	 $R\underset{\overset{\vert}{SO_3^-}}{C}HCOOR'$
-Monoalkylsulfosuccinates	 $ROOC\underset{\overset{\vert}{CH_2COO^-}}{C}HSO_3^-$
2.3.2.1.4 Sulfonated amides	
-Acyl methyltaurateds	$RCON(CH_3)C_2H_4SO_3^-$
-Akyl sulfosuccinamates	 $RNHCOC\underset{\overset{\vert}{CH_2COO^-}}{}HSO_3^-$
2.3.2.1.5 Carboxylate	
-Soaps	$RCOO^-$
-Alkyl ethoxy carboxylates	$R(OC_2H_4)_nOCH_2COO^-$
-Acyl sarcosinates	$RCON(CH_3)CH_2COO^-$

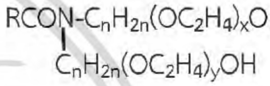
2.3.2.2 Cationic surfactants

Cationic surfactants are those surfactants where the ionic group on the hydrophobic group would go to the cathode and hence have a positive charge. 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. Cationic surfactants can be separated:

2.3.2.2.1 Non-nitrogenous

-Fatty alcohols	ROH
-Fatty alcohol exthoxylates	$R(OC_2H_4)_nOH$
-Aklphenol ethoxylates	$RC_6H_4(OC_2H_4)_nOH$
-Polyethylene glycol esters	$RCO(OC_2H_4)_nOH$

2.3.2.2.2 Alkarolamides

-Monoalkanolamides	$RCONHC_nH_{2n}OH$
-Diakanolamides	$RCON(C_nH_{2n}OH)_x$
_Ethoxalated monoalkanolamides	$RCONHC_nH_{2n}(OC_2H_4)_xOH$
-Ethoxaltaed diakanolamides	 $RCON(C_nH_{2n}(OC_2H_4)_yOH)\text{-}C_nH_{2n}(OC_2H_4)_xOH$

2.3.2.3 Nonionic surfactants

The term non-ionic surfactant usually refers to derivatives of ethylene oxide and/or propylene oxide with an alcohol containing an active hydrogen atom. However other types such as alkyl phenols, sugar esters, alkanolamides, amine oxides, fatty acids, fatty amines and polyols are all produced and used widely throughout the world in a multitude of industries.

-Monoalkyltrimethyllammonium salts	$RN^+(CH_3)_3$
-Dialkyldimethylammonium salts	$R_2N^+(CH_3)_2$

2.3.2.4 Amphoteric surfactant

The family of surfactants commonly referred to as amphoterics are surfaceactive materials that contain, or have the potential to form, both positive and negative functional groups under specified conditions.

-Trialkylaminoacetate	$R_3N^+CH_2COO^-$

2.3.3 Micelle formation [28-31]

The concentration of surfactant monomer may increase or decrease slightly at higher concentrations, but micelles will be the predominant form of surfactant present above a critical surfactant concentration, the critical micelle concentration (CMC) as illustrated in Fig. 2.7. The apparent solubility of the surfactant, then, will depend on not only the solubility of the monomeric material but also the solubility of the micelles or other aggregate structures

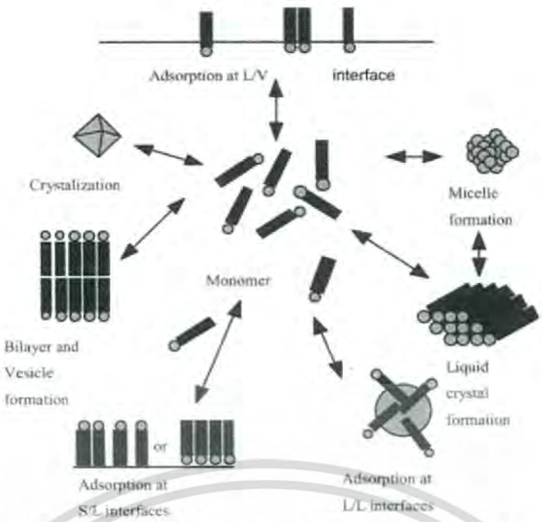


Fig. 2.7 Modes of surfactant action for the reduction of surface and interfacial energies [26].

The properties of surfactant at low concentration in water are similar to those of simple electrolytes except that the surface tension decreases sharply with increase in concentration. At a certain concentration, they can form spherical assemblies known as micelles where the interior of the micelle resembles a hydrocarbon separate phase in which the hydrophobic tails are shielded from water while the hydrophilic heads face water.

2.3.4 Critical micelle concentration (CMC) [24, 25]

The critical aggregation concentration is called the critical micelle concentration (CMC) when micelles form in an aqueous medium. The CMC is a property of the surfactant. It indicates the point at which monolayer adsorption is complete and the surface-active properties are at an optimum. Above the CMC, the concentrations of monomers are nearly constant. Hence, there are no significant changes in the surfactant properties of the solution since the monomers are the cause of the surface activity.

The CMC is a useful tool for the selection of surfactants for specific applications or properties. For example, surfactants with a low CMC are less of an irritant than those with high CMC. The CMC can be determined by measuring the changes in physical properties such as electrical conductivity, turbidity, surface tension, interfacial tension, solubilisation and auto diffusion.

For example, determination the Critical Micelle Concentration(CMC) of a surfactant by electrical conductivity measurement method.

A plot of the specific conductivity, k, of an ionic surfactant versus its concentration, C, in the aqueous phase is linear, with a break at the CMC, above which the (decreased) slope of the plot again becomes linear (Fig. 2.8). The break in the plot is due to the binding of some of the counterions of the ionic surfactant to the micelle [25].

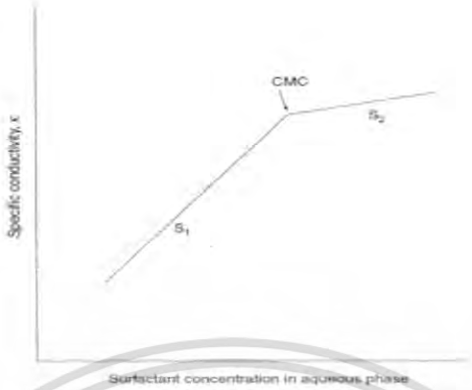


Fig. 2.8 Plot of specific conductivity, k, versus surfactant concentration in the aqueous phase, showing change in slopes before (S1) and after (S2) the CMC [25].

2.3.5 Application of surfactants

Surfactants are widely used and find a very large number of applications in several industries. Surfactants are the important components of laundry detergents, household, and personal care products. There is over half of all use of surfactants.

They are basic cleaning agents in soaps and detergents. The agents are added to lower surface tension of water, thereby to increase the wetting and dispersion properties of water.

Olefin sulfonates (AOS) are a mixture of alkene sulfonates and hydroxy alkane sulfonates AOS have been used successfully for many years in laundry powders and personal care products such as shampoos and liquid hand soaps. These surfactants have good cleaning and foaming properties [32].

Moreover, in paint and coatings Industry, wetting of the pigment particles and stabilization of the pigment dispersion are important to control quality of the interface. Thus, surfactants which have surface active properties such as wetting agents, foaming and dispersion are used in process.

In addition, Corrosion inhibition by surfactant molecules are related to the surfactant's ability to aggregate at interfaces and in solution. For example, sodium dodecyl sulfate (SDS) and polyoxyethylene nonylphenyl ether (PNE) are used as corrosion inhibitor [28, 29, 32].

2.4 Stainless steel

The family of austenitic stainless steel has a wide variety of grades precisely tailored for specific applications such as household and community equipment, transportation and food industry. The optimum choice of grades would depend in service needs and this would require a clear understanding of the metallurgical parameters, which control the microstructure and thus the mechanical properties, formability and corrosion resistance.

2.4.1 Austennitic stainless steel [33]

Austennitic stainless steel are the most common and familiar types of stainless steel. They are most easily recognized as non- magnetic. They are extremely formable and weldable, and they can be successfully used from cryogenic temperatures to the red-hot temperatures of furnaces and jet engines. They contain between about 16 and 25% chromium, and they can also contain nitrogen in solution, both of which contribute to their high corrosion resistance. Were it not for the cost of the nickel that helps stabilize their austenitic structure, these alloys would be used even more widely.

Austenitic stainless steels have many advantages from a metallurgical point of view. They can be made soft enough (i.e., with a yield strength about 200 MPa) to be easily formed by the same tools that work with carbon steel, but they can also be made incredibly strong by cold work, up to yield strengths of over 2000 MPa (290 ksi). Their austenitic (fcc, face-centered cubic) structure is very tough and ductile down to absolute zero. They also do not lose their strength at elevated temperatures as rapidly as ferritic (bcc, body-centered cubic) iron base alloys. The least corrosion-resistant versions can withstand the normal corrosive attack of the everyday environment that people experience, while the most corrosion-resistant grades can even withstand boiling seawater.

The austenitic alloys can have compositions anywhere in the portion of the Delong diagram labeled austenite shown in Fig. 2.9. This diagram was designed to show which phases are present in alloys in the as-solidified condition, such as found in welds.

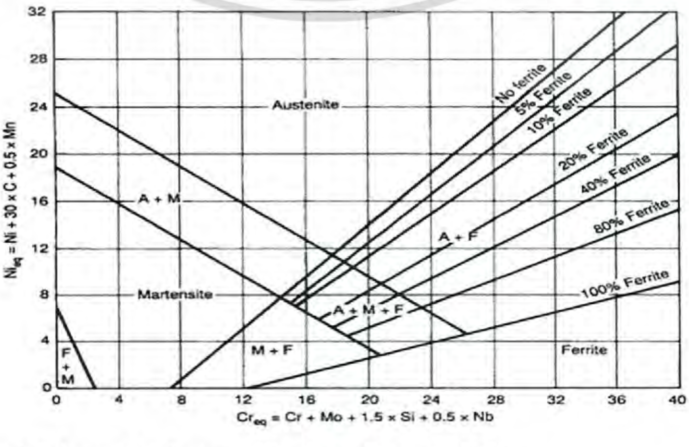


Fig. 2.9 Delong stainless steels constitution diagram [30].

The mechanical properties, like tensile strength, fatigue and creep strengths of austenitic stainless steels vary with temperature, composition and microstructure. Austenitic stainless steels have particularly low yield strengths, and several processes are used to improve them: appropriate thermomechanical treatments, hardening with nitrogen, precipitation hardening. Their creep strength is excellent up to 973 K, and can be further improved by alloying with N, Mo, Nb, Ti, W, V or B. In austenitic steels, at temperatures as low as -73 K, toughness is relatively unaffected, whereas their strength increases. They lend themselves remarkably to deep drawing and cold rolling, where their work-hardening characteristics enable high strength levels to be attained. Weldability is excellent, and welds, which do not transform to martensite during air-cooling, have mechanical properties similar to base metal.

2.4.2 Stainless Steel - Grade 304 (UNS S30400)

Grade 304 is the standard "18/8" stainless; it is the most versatile and most widely used stainless steel, available in a wider range of products, forms and finishes than any other. It has excellent forming and welding characteristics. The balanced austenitic structure of Grade 304 enables it to be severely deep drawn without intermediate annealing, which has made this grade dominant in the manufacture of drawn stainless parts such as sinks, hollow-ware and saucepans. For these applications it is common to use special "304DDQ" (Deep Drawing Quality) variants. Grade 304 is readily brake or roll formed into a variety of components for applications in the industrial, architectural, and transportation fields. Grade 304 also has outstanding welding characteristics. Post-weld annealing is not required when welding thin sections.

2.5 Related research

2.5.1 Corrosion Inhibition of Mild Steel in Hydrochloric Acid by Sodium Lauryl Sulfate (SLS) [34]

Effect of Sodium Lauryl Sulfate (SLS), a surfactant on corrosion of mild steel in 1 M hydrochloric acid was studied using three techniques namely: weight loss, electrochemical polarization and metallurgical research microscopy. Results, as shown in Fig. 2.10, obtained reveal that SLS is good inhibitor and shows very good corrosion inhibition efficiency (IE). The IE was found to vary with concentration of inhibitor and temperature. The electrochemical polarization result revealed that SLS is anodic in nature.

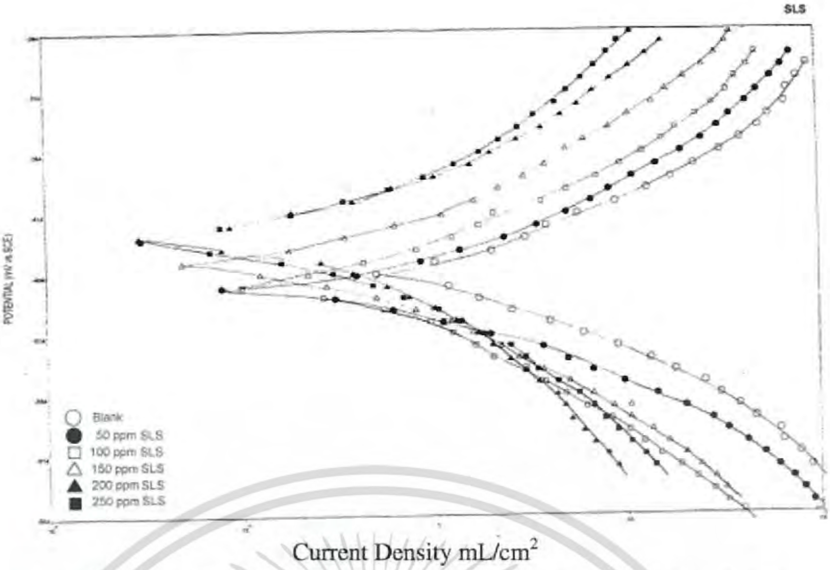


Fig. 2.10 Polarization curves of mild steel in 1M HCl in absence and presence of various concentrations of SLS [3].

As a result, shown in table 2.1, the addition of SLS also leads to change in cathodic and anodic Tafel slopes. The corrosion potential is found to shift to more positive potential with increase in inhibitor concentration in presence of both the inhibitors.

Table 2.1 Electrochemical parameters of mild steel corrosion in 1 M HCl solution contain various concentrations of Sodium Lauryl Sulfate (SLS) at 35 °C.

Concentration ppm	E corr mV	βamv/ decades	βcmv/ decades	I.corr. $\mu A/cm^2$	Corrosion Rate, mpy	IE, %
Blank	-464	1.95	2.48	1300	600.51	Blank
50	-475	11.11	2.89	0.560	258.68	56.92
100	-475	4.75	7.84	0.500	235.58	60.77
150	-455	11.76	5.56	0.140	189.39	68.46
200	-439	9.52	20.00	0.350	161.68	73.08
250	-436	19.05	11.63	0.340	157.06	73.85

2.5.2 *Silybum marianum* extract as a natural source inhibitor for 304 stainless steel corrosion in 1.0 M HCl [35]

The use of *Silybum marianum* leaves extract as a 304 stainless steel corrosion inhibitor in 1.0 M HCl solution was investigated by weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. Potentiodynamic polarization curves indicated that S. marianum extract behaves as mixed-type inhibitor. The adsorption of the extract constituents was further discussed in view of Langmuir adsorption isotherm. The effect of temperature on the inhibition efficiency was studied. Quantum chemical parameters were also calculated, which provided reasonable theoretical explanation for the adsorption and inhibition behavior of S. marianum extract on the 304 stainless steel.

The S. marianum extract acts as a good inhibitor for corrosion of 304 SS in 1.0 M HCl solution as shown in table 2.2. At the highest extract concentration of 1.0 g/L, the inhibition efficiency is increased markedly and reached 96%. The inhibition action is performed via adsorption of the extract constituents on 304 SS surface. The adsorption process is spontaneous and follows Langmuir adsorption isotherm. The inhibition efficiency increases with increasing extract concentration. Even at higher temperature also S. marianum extract is an effective corrosion inhibitor. Activation energy decreases with addition of inhibitor.

Table 2.2 Polarization parameters for 304 SS in 1M HCl in the presence and absence of S. marianum extract.

Concentration (g/L)	$-E_{corr}$ (mV, vs. Ag/AgCl)	$-b_c$ (mV dec^{-1})	b_a (mV dec^{-1})	I_{corr} (μA cm^{-2})	η_p (%)
Blank	439	88	111	342.0	–
0.2	434	90	58	73.2	78.6
0.4	425	94	59	42.1	87.6
0.6	419	86	64	26.4	92.2
0.8	417	85	59	19.7	94.2
1.0	414	86	84	12.1	96.4

2.5.3 Synthesis and corrosion inhibition study of benzodiazepines on mild steel in sulphuric acid medium [19]

2,4-diphenyl-2,3-dihydro-1H-1,5-benzodiazepine (DPBD) and 4-phenyl-2-(2-ethoxy-3-hydroxyphenyl)-2,3-dihydro-1H-1,5-benzodiazepine (EPBD) were synthesized by the condensation of o-phenylenediamine and chalcone catalyzed by sulphated zirconia and characterized by FTIR spectra. Corrosion inhibition property of the benzodiazepines on mild steel in sulphuric acid medium was investigated by mass loss and electrochemical methods. The Compound EPBD showed better corrosion protection properties than DPBD both at room temperature and at higher temperatures. The results showed that the compounds act as good inhibitor and the efficiency increased with increase in their concentration. The adsorption of the inhibitors on the surface of mild steel was found to obey Langmuir adsorption isotherm. SEM study showed the formation of a protective adsorptive film of the inhibitor on mild steel surface.

The synthesized benzodiazepine derivatives act as good corrosion inhibitor for mild steel in sulphuric acid medium with EPBD displaying 98% efficiency as shown in table 2.3. he Predominance of physical adsorption was proposed on the basis of thermodynamic parameters with slight deviation from Langmuir adsorption isotherm.

Table 2.3 Polarization parameters for mild steel in 1 M H_2SO_4 with and without selected concentration of benzodiazepines.

Name of the inhibitor	Concentration (ppm)	Tafel slopes (mV/dec)		E_{corr} (mV)	I_{corr} (μAmp/cm^2)	Inhibition efficiency (%)
		b_a	b_c			
BLANK	-	61	137	−480.0	414	-
DPBD	10	60	173	−480.2	272.0	34.29
	100	58	134	−480.6	198.0	52.17
	200	52	167	−500.0	156.0	62.31
EPBD	10	62	159	−476.8	163.0	60.62
	100	56	157	−471.1	23.0	94.44
	200	48	163	−445.4	20.0	95.16

2.5.4 The corrosion behaviour of AISI 304 stainless steel in methanol-H_2SO_4 mixtures [36]

The electrochemical behaviour of AISI 304 stainless steel has been studied in de-aerated methanolic solutions containing different concentrations of H_2SO_4 (0.001-1M). During cathodic polarization diffusion controlled behavior is observed which is prominent, particularly in mixtures containing low concentrations of acid in methanol solutions. With anodic polarization the critical current for passivity increases as the concentration of sulphuric acid is increased in methanol. In anodic studies in 1 and 0.1 M H_2SO_4 methanol solutions, cathodic loops are observed. Transpassivity is observed at above1.l Vinhigh concentrations of H_2SO_4. After anodic polarization the electrode surface was examined by SEM which showed numerous pits in each concentration of acid in methanol. The pitting potential is found to be nobler with higher acid concentrations.

Table 2.4 Corrosion parameters for AISI 304 in different concentrations of H_2SO_4 in methanol from anodic and cathodic polarization curves.

Molar concentration of H_2SO_4 in methanol	E_{corr} [ZmV (SCE)]	I_c [(μA)/cm^3]	I_p [(μA)/Cm^2]	I_{corr} [(μA)/cm^2]	b_a (mV/decade i)	b_c (mV/decade i)
1 M H_2SO_4	−215	50	1.0	8.5	70	110
0.1 M H_2SO_4	−190	20	1.8	1.4	50	135
0.01 M H_2SO_4	−140	10	2.5	Negligible	45	140
0.001 M H_2SO_4	−110	5	3.0	Negligible	35	140

2.5.5 Pitting corrosion behaviour of austenitic stainless steels combining effects of Mn and Mo additions [37]

Mn and Mo were introduced in AISI 304 and 316 stainless steel composition to modify their pitting corrosion resistance in chloride-containing media. Corrosion behaviour was investigated using gravimetric tests in 6 wt.% $FeCl_3$, as well as potentiodynamic and potentiostatic polarization measurements in 3.5 wt.% NaCl. Additionally, the mechanism of the corrosion attack developed on the material surface was analysed by scanning electron microscopy (SEM), X-ray mapping and energy dispersive X-ray (EDX) analysis. The beneficial effect of Mo additions was assigned to Mo^{6+} presence within the passive film, rendering it more stable against breakdown caused by attack of aggressive Cl ions, and to the formation of Mo insoluble compounds in the aggressive pit environment facilitating the pit repassivation. Conversely, Mn additions exerted an opposite effect, mainly due to the presence of MnS inclusions which acted as pitting initiators.

The results of this research suggest the following conclusions: (i) Mn additions (from 0.3 to 1.7 wt.%) have a detrimental effect on the pitting corrosion resistance of stainless steels studied in 3.5 wt.% NaCl. Its presence drastically reduces CPT values, dis- placing E_{corr} and E_{pit} toward less noble potential and increasing the corrosion current density of both AISI 304 and 316 austenitic stainless steels. On the other hand, Mo (from 0.3 to 2.7 wt.%) enhances their pitting corrosion resistance, reducing progressively the corrosion rate, increasing CPT values and ennobling both potentials. (ii) Mn presence favours the formation of MnS inclusions with low electrochemical stability, which tend to dissolve, initiating an attack at the inclusion/matrix interfaces and being the initial step before a further pit propagation. (iii) Mo has effect on more than one step in a pitting event. In first instance, Mo modifies the passive film rendering it more stable against breakdown caused by the attack of aggressive Cl ions. However, during MnS dissolution and the pitting stages, Mo may act by formation of oxidised insoluble species, which cover the pit walls, allowing the repassivation and the deactivation of growing pits.

2.5.6 The corrosion inhibition study of sodium dodecyl benzene sulphonate to aluminium and its alloys in 1.0 M HCl solution [38]

The corrosion inhibition of Al and its alloys are the subject of tremendous technological importance due to the increased industrial applications of these materials. This paper reports the results of weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) measurements on the corrosion inhibition of Al, (Al + 6%Cu) and (Al + 6%Si) alloys in 1.0 M HCl in the temperature range 10–60°C using dodecyl benzene sulphonate as an anionic surfactant (AS) inhibitor. The results showed that the addition of the surfactant inhibits the hydrochloric acid corrosion of the three Al samples. The inhibition occurs through adsorption of the surfactant on the metal surface without modifying the mechanism of corrosion process. The surfactant acts predominately as cathodic inhibitor. The inhibition efficiency increases with an increase in the surfactant concentration, but decreases with an increase in temperature. Maximum inhibition is observed around its critical micelle concentration (CMC). The inhibition efficiency for the three Al samples decreases in the order: (Al + 6%Si) > (Al + 6%Cu) > Al. Frumkin adsorption isotherm fits well with the experimental data. Thermodynamic functions for both dissolution and adsorption processes were determined. Results obtained from the three methods are in good agreement.

Table 2.5 The electrochemical parameters ($i_{corr.}$, $E_{corr.}$, b_c and b_a) associated with polarization measurements for the three samples in 1.0 M HCl solution in the absence and presence of different concentrations of the AS at 30 °C.

C (M)	E_{corr}, SCE (mV)			j_{corr} (μA cm^{-2})			b_a (mV dec^{-1})			$-b_c$ (mV dec^{-1})		
	Al	(Al + 6%Cu)	(Al + 6%Si)	Al	(Al + 6%Cu)	(Al + 6%Si)	Al	(Al + 6%Cu)	(Al + 6%Si)	Al	(Al + 6%Cu)	(Al + 6%Si)
0.00	−1109	−1075	−1053	4.5000	3.8100	3.3600	191	185	183	433	418	416
2×10^{-4}	−1065	−1033	−1012	4.2210	3.4671	2.9820	188	184	180	428	413	416
4×10^{-4}	−1033	−1000	−981	3.9500	3.1242	2.6000	187	184	179	427	411	414
6×10^{-4}	−997	−967	−847	3.6000	2.7540	2.1373	185	184	178	426	410	414
2×10^{-3}	−967	−938	−919	1.7760	1.2000	0.8000	185	183	178	425	412	413
4×10^{-3}	−929	−900	−883	0.9180	0.5715	0.3800	184	182	180	425	411	412
6×10^{-3}	−902	−875	−858	0.5850	0.3620	0.2352	182	181	183	420	411	414
10×10^{-3}	−867	−842	−825	0.3263	0.2200	0.1428	183	179	182	418	409	412

The corrosion inhibition studies of pure Al, (Al + 6%Cu) and (Al + 6%Si) alloys in 1.0 M HCl solution using sodium dodecyl benzene sulphonate as an AS inhibitor showed that the corrosion resistance of the three samples in 0.10 M HCl solution increases in the order: Al > (Al + 6%Cu) > (Al + 6%Si). The presence of sodium dodecyl benzene sulphonate inhibits the corrosion of the three Al samples in 1.0 M HCl solution. Potentiodynamic polarization measurements showed that this surfactant behaves as a cathodic inhibitor. The inhibition is due to the adsorption of the surfactant on the surface of the three Al samples and blocking their active sites.

The inhibition efficiency increases with the increase of inhibitor concentration but decreases with the increase of temperature. The inhibition efficiency for the three Al samples decreases in the order: (Al + 6%Si) > (Al + 6%Cu) > Al. The results obtained fit well with the Frumkin adsorption isotherm. The data obtained from three different methods, namely weight loss, potentiodynamic polarisation and EIS are in good agreement.

2.5.7 Pitting inhibition of stainless steel by surfactants: an electrochemical and surface chemical approach [39]

Pitting corrosion of stainless steels causes tremendous damage in terms of material loss and resulting accidents. Organic surfactants have been tried as pitting inhibitors but the understanding of the inhibition mechanisms is mainly speculative. In the present study the inhibition of the pitting corrosion of 304 stainless steel by N-lauroylsarcosine sodium salt (NLS) in 0.1 M NaCl solutions at neutral pH was studied using an approach that combines surface chemical techniques with electrochemical ones. It was found that NLS increases the pitting resistance of 304 stainless steel, with possible complete inhibition at high NLS concentration (30 mM).

Adsorption of NLS on 304 stainless steel particles was directly measured. NLS adsorbs significantly on 304 stainless steel with maximum adsorption density close to bilayer coverage. Electrophoretic mobility data for 304 stainless steel particles show that the surface of 304 stainless steel is negative in NaCl solution at neutral pH. The adsorption of NLS makes the interfacial charge even more negative. The relationship between pitting inhibition and adsorption density of NLS suggests that NLS does not adsorb preferentially on the pit nucleation sites and complete inhibition requires that the whole surface be covered completely by NLS. The inhibition mechanism of NLS is proposed to be due mainly to the blocking effect of a negatively charged NLS adsorption layer. This study shows that in addition to the adsorption amount of surfactant, interfacial charge also plays an important role in pitting inhibition.

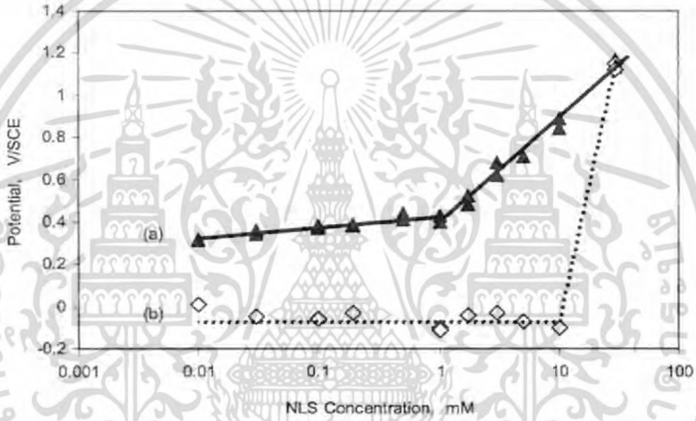


Fig. 2.11 (a) Pitting potential and (b) protection potential of 304 stainless steel in 0.1 M NaCl with NLS at pH 6 and 25 °C [35].

N-lauroylsarcosine is able to inhibit pitting corrosion of 304 stainless steel in NaCl solutions as indicated by the increase in pitting potential. Inhibition efficiency is a function of NLS concentration with complete pitting inhibition at high NLS concentration of 30 mM. NLS adsorbs on 304 stainless steel with a maximum adsorption density corresponding to bilayer adsorption. The surface of 304 stainless steel is negatively charged in NaCl solutions, and the adsorption of NLS makes it even more negative. The correlation between inhibition and adsorption suggests that NLS does not adsorb preferentially on the nucleation sites. The inhibition by NLS is proposed to be due to a combination of complete surface coverage by NLS and the electrostatic repulsion between adsorbed NLS layer and chloride ions.

2.5.8 Inhibition of stainless steel pitting corrosion in acidic medium by 2-mercaptobenzoxazole [40]

The corrosion behavior of stainless steel samples (304L and 316L) in HCl and H_2SO_4 solution has been studied using potentiodynamic, cyclic voltammogram, EDX and scanning electron microscope (SEM) techniques. The inhibition characteristics of 2-mercaptobenzoxazole (MBO) on 316L stainless steel (316L SS) in HCl solutions were investigated at different temperatures (25, 40, 50 and 60 °C). MBO compound has proven to be efficient inhibitors for general and pitting corrosion of 316L SS in HCl solution. The inhibitive property of MBO may be argued to the formation of very low soluble bis-benzoxazolyl disulfide (BBOD) layer and a compact Fe–MBO complex film on the electrode surface. Some samples were examined by scanning electron microscope. The inhibition efficiencies increased with the increasing of MBO concentration but decreased with increasing temperature. The activation energy and thermodynamic parameters were calculated.

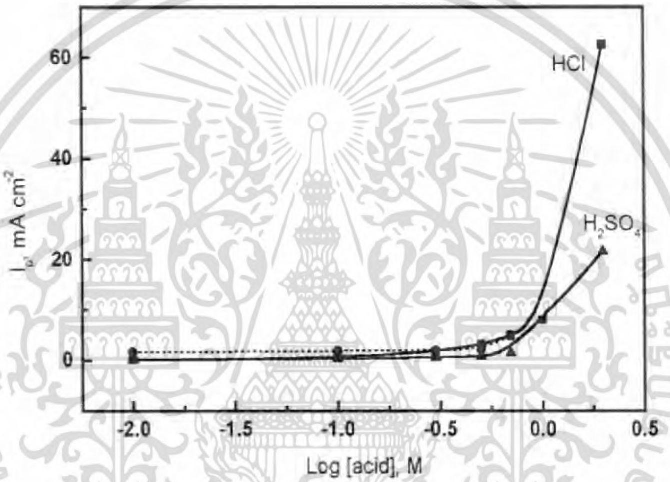


Fig. 2.12 Current peak density (Ip) as a function of acids concentrations for 316L SS [36].

MBO compound has proven to be efficient inhibitor for general and pitting corrosion of 316L SS in HCl solution. The MBO inhibition efficiency increases by increasing of the inhibitor concentration, but decreases with the increasing of temperature. The inhibitive property of MBO may be argued to the formation of very low soluble bis-benzoxazolyl disulfide layer and a compact Fe–MBO complex film on the electrode surface. The inhibition of 316L SS in HCl solution at different temperatures was found to obey the Langmuir adsorption isotherm. The thermodynamic values obtained from this study (Ea, DH, DG and DS) indicate that the presence of MBO inhibitor increase the activation energies and the negative values of DG indicate the spontaneous adsorption of MBO on the surface of stainless steel.

2.5.9 Effects of applied potential on stable pitting of 304 stainless steel [41]

Effects of applied potential on stable pitting corrosion of 304 stainless steel were studied by potentiostatic polarization and three-dimensional video microscope.

The results showed that pit mouth morphologies and three-dimensional structures were dependent on potential. Higher potentials resulted in more open pits. Pit volume, depth, and width increased with potential. The ratio of pit depth to width continuously changed with time and potential. The pitting current density of a single pit increased with potential, indicating that an ohmic potential drop presented between the pit internal surface and the bulk solution, but stable propagation was still controlled by corrosion products diffusion.

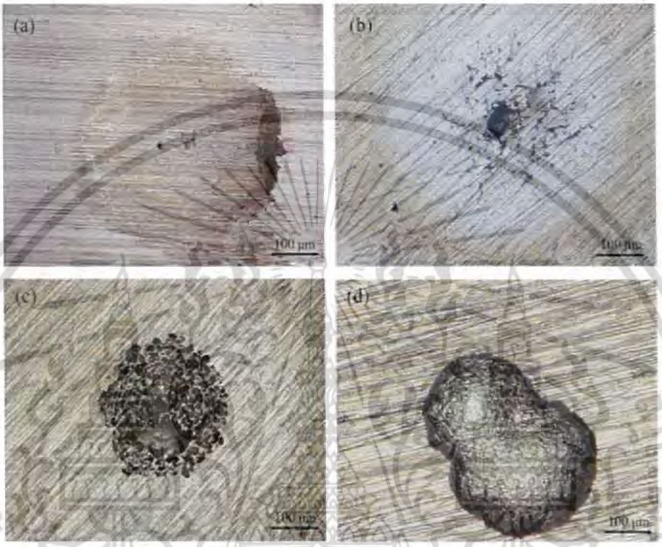


Fig. 2.13 Typical features of pit mouth for stable pits formed at different applied potentials of (a) 0.05 V (SCE), (b) 0.15 V (SCE), (c) 0.25 V (SCE) and (d) 0.35 V (SCE) on 304 stainless steel in 3.5% (mass fraction) sodium chloride solution [37].

2.5.10 Metastable pitting corrosion of 304 stainless steel in 3.5% NaCl solution [42]

Metastable pitting corrosion of 304 stainless steel was studied by potentiostatic polarization and three- dimensional video microscope. The results showed that the dissolution rate of metastable pits increased with time, and peaked before repassivation. The average lifetime of metastable pits decayed with potential. Whereas maximum pit lifetime, average peak value of current transients and pitting nucleation numbers increased with potential. Metastable pits were transformed from cone-shaped to dish-shaped during metastable growth. The ohmic potential drop presented between the pit interior and bulk solution, but the growth controlling factor was metal cations diffusion.

2.5.11 Pitting corrosion resistance of cast duplex stainless steels in 3.5% NaCl solution [43]

The pitting corrosion resistance of cast duplex stainless steels ASTM A890 grades 1A and 3A were evaluated at different temperatures in order to determine critical pitting temperatures (CPT) in 3.5% NaCl solution. Microstructures were changed by aging treatments at 850 °C for 15 min and 475 °C for 100 h. The CPT obtained values were compared and results were discussed taking into account microstructures and chemical compositions of the two materials.

2.5.12 Pitting corrosion mechanism of Type 304 stainless steel under a droplet of chloride solutions [44]

Pitting corrosion of Type 304 stainless steel under drops of $MgCl_2$ solution has been investigated to clarify the rusting mechanism in marine atmospheres. A pitting corrosion test was performed under the droplets with various combinations of the diameter and thickness (height) by exposure to a constant relative humidity. Probability of occurrence of pitting corrosion decreased with decreasing the diameter and thickness. Pitting corrosion progressed only when the [Cl^-] exceeded 6 M (RH < 65%). In almost cases, there was a small hole (10 lm diameter) in the center of a single pit, which may be the trace of an inclusion particle like MnS dissolved out. The pitting corrosion mechanism of Type 304 under droplets containing chloride ions has been proposed.

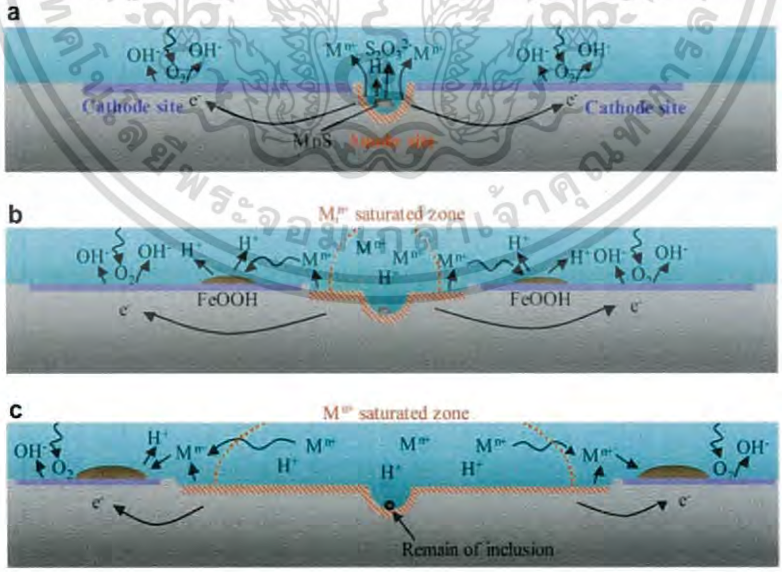


Fig. 2.14 Schematic of pitting corrosion mechanism under thin electrolyte solution layer [40].

2.5.13 Influence of chloride concentration and pre-passivation on the pitting corrosion resistance of low-alloy reinforcing steel in simulated concrete pore solution [45]

The effect of chloride concentration and pre-passivation on the pitting corrosion resistance of low-alloy steel and conventional low-carbon steel in simulated concrete pore solution was investigated using electrochemical techniques and surface analysis measurements. The results show that the passive film could enhance the pitting corrosion resistance for both investigated steels. Low-alloy steel exhibits slightly lower pitting corrosion resistance at low chloride concentration compared to low-carbon steel, regardless of the passivation condition. However, at high chloride concentration, low-alloy steel shows higher pitting corrosion resistance due to the formation of Cr-enriched protective rust layer.

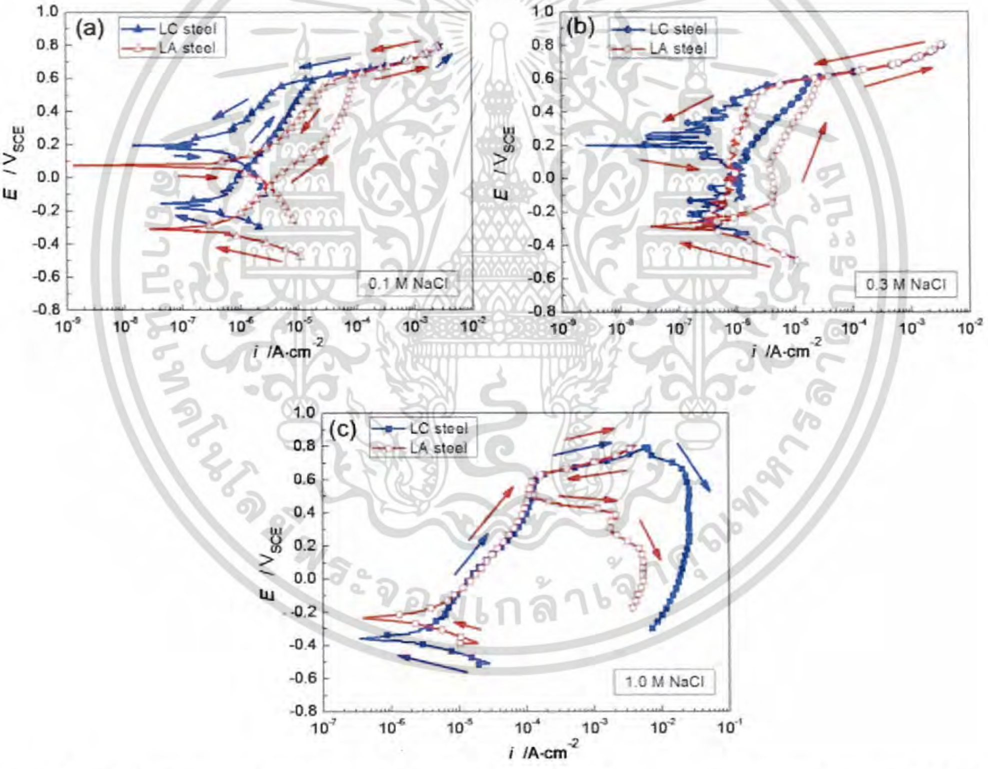


Fig. 2.15 CPP curves for LC and LA steels after 10 days of passivation in SCPS with various chloride concentrations [41].

2.5.14 Effect of pH and chloride on the micro-mechanism of pitting corrosion for high strength pipeline steel in aerated NaCl solutions [46]

The pitting corrosion mechanism of high strength pipeline steel in aerated NaCl solutions with different pH and chloride content was investigated, using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM). The pitting behavior in alkaline solutions was found to be significantly different from that in neutral and acidic solutions. Electrochemical results and SEM images indicate that the product film formed on the steel surface results in different corrosion behavior in an alkaline solution. SEM images show that pH and chloride concentration in the bulk solution have a great influence on the pitting morphology. Unique large pit morphology due to corrosion in neutral/acidic solutions with 0.05 mol/L NaCl was observed. The relationship between solution pH and the effect of chloride concentration is also discussed.

2.5.15 Initiation and propagation steps in pitting corrosion of austenitic stainless steels: monitoring by acoustic emission [47]

Acoustic emission (AE) technique was used to study the development of pitting corrosion on AISI 316L austenitic stainless steel, in a 3% NaCl solution acidified to pH 2. The initiation and the propagation steps of the pits were separately studied owning to a specific polarization procedure. It appears that the initiation step of pitting corrosion is not significantly emissive, whereas the propagation step is characterized by the emission of resonant signals. This kind of AE signals is representative of the development of the pits in the form of occluded cells, in which the evolution of hydrogen bubbles appears to be the emissive phenomenon. A subsequent change in the mode of corrosion, i.e. the transfer to uniform corrosion, can be detected by the AE technique.

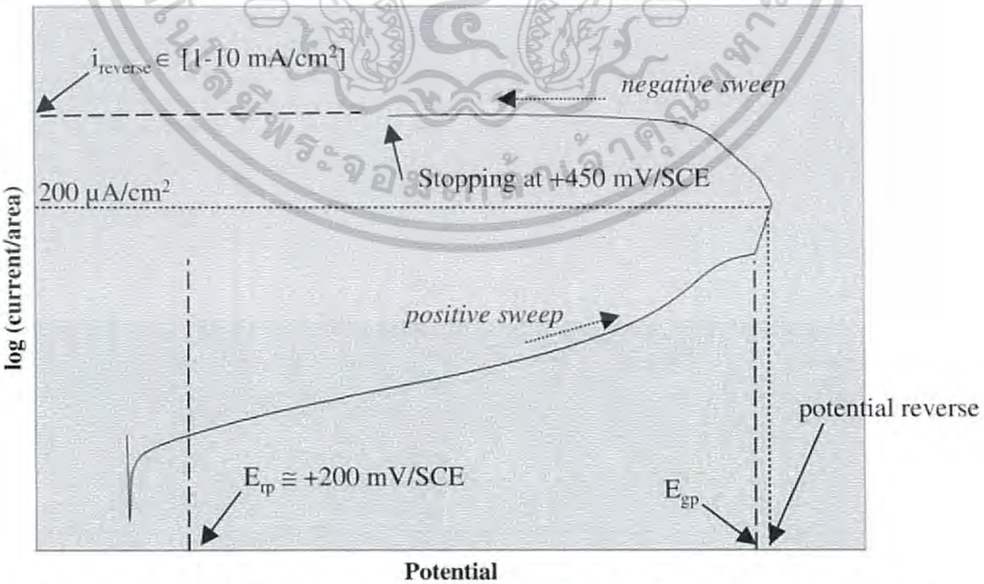


Fig. 2.16 Evolution of the current density with the potential during the cyclic polarization step [43].

CHAPTER 3

EXPERIMENTAL

3.1 Chemical reagents

1. Nitric acid 65% (analytical reagent grade, CAROL EBRA)
2. Sodium 2-ethylhexyl 50% in water (commercial grade, SIGMA-ALDISH)
3. Sodium chloride 99% (analytical reagent grade, Fisher Chemical)
4. Nitrogen gas 99.99% (PRAXIAR)

3.2 Apparatus and instruments

1. AISI 304 Stainless steel plates with diameter of 10 mm
2. pH meter (SevenEasy S20 from Mettler-Toledo Inc.)
3. AUTOLAB PGSTAT12 Potentiostat–Galvanostat
4. Conductometer (COND 51+ with 2301 T)
5. Inverted Trinocular Metallurgical Microscope (Reich)
6. A three-electrode cell system
7. Saturated calomel electrode (SCE)
8. Abrasive paper with 80, 220, 600, 800, 1500, and 2000 grit (TOA Paint (Thailand) Co., Ltd.)
9. Laboratory glassware (DURAN by Otto Schott)
10. Gas flow controller (Cole-Parmer Instrument Company)

3.3 Preparation of samples

The AISI 304 stainless steel plate was cut to obtain a circular shape with a diameter of 15 mm and 3 mm thick plate. The outer surface, which exposed to the aggressive solutions, was prepared wet polished using emery paper grade 80, 220, 600, 800, 1500 and 2000 respectively, and was rinsed with distilled water.

For passivation according to ASTM A967–05 [48], these specimens were immersed in 30% nitric acid for 30 minutes at room temperature, immediately rinsed with distilled water and dried with hot air.

3.4 Critical micelle concentration measurement

The critical micelle concentration (CMC) of SEHS in 0.9 wt.% NaCl solution was determined by measuring the conductivity of solution at room temperature. The obtained data were plotted (conductivity (μS/cm) versus surfactant concentration (M)). The slope changes when the critical micelle concentration (CMC) is observed.

The CMC value was used to adjust the concentration of SEHS in 0.9 wt.% NaCl solution in order to obtain chloride solutions with different concentrations of SEHS below and above CMC for further electrochemical measurements as can be seen in Table 3.1.

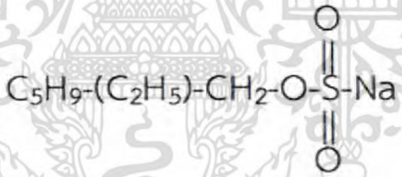
Table 3.1 The various concentrations of SEHS in 0.9 wt.% NaCl

[SEHS] related to CMC	[SEHS] in 0.9 wt.% NaCl (mM)
0	0
0.25×CMC	0.890
0.50×CMC	1.780
0.75×CMC	2.660
1×CMC	3.550

3.5 Electrochemical techniques

3.5.1 Potentiodynamic polarization

The test media was 0.9 wt.% NaCl solutions and the tested surfactant was sodium 2-ethylhexyl sulfate as show in Fig. 3.1



$$C_5H_9\text{-}(C_2H_5)\text{-}CH_2\text{-}O\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}Na$$

Fig. 3.1 Sodium 2-ethylhexyl sulfate (SEHS).

The electrochemical measurement was performed in 1 L glass cell with a three-electrode assembly. The working electrode was a sample with crevice-free sealing, platinum plate counter-electrode and reference electrode (saturated calomel electrode, SCE) which pointing to the sample via Luggin probe were used in this study. The tip of Luggin probe was placed at the distance of about 2 mm from the surface of sample during measurement. These experiments were carried out with a AUTOLAB PGSTAT12 Potentiostat–Galvanostat.

The measurements were carried out in 0.9 wt.% NaCl solution without and with the presence of SEHS. The working electrode was set in a sample holder exposing only a 1 cm^2 of area to the solution. All potentials were measured against reference electrode. The working electrode was immersed in test solution until the pitting potential (E_{pit}) was observed.

On separate specimens, after immersion, the sample was cathodically polarized to - 0.500 V with respect to open circuit potential. Then the potential was increased from - 0.500 to 1.500 V with respect to open circuit potential. The potentiodynamic scan rate during polarization was fixed at 2000 V h^{-1}. At the end of scanning, the potentiodynamic polarization curve was obtained. Afterward, this curve was arranged in a form of a Tafel plot, log current density (log i) versus potential (E). The Tafel extrapolation was applied to determine corrosion current density (i_{corr}) as well as corrosion potential (E_{corr}). The pitting potential (E_{pit}) was also determined from potentiodynamic polarization curve.

3.5.2 Chronoamperometry

Chronoamperomety was carried out using a two-step procedure. At first the working electrode was held at the open circuit potential for 60 s to attain steady state. Then the potential was forced to 0.400 V for 20 minutes. The current was then recorded as a function of time

3.6 Surface analysis

3.6.1 Inverted trinocular metallurgical microscope

Sample surfaces were examined by microscope at the end of the chronoamperometry experiment in order to evaluate the effects of SEHS on corrosion from the surface morphology. For this purpose, sample of stainless steel after chronoamperometry at 0.400 V for 20 minutes in 0.9 wt.% NaCl in absence of SEHS and presence of SEHS at 1xCMC were cleaned with distilled water to remove any deposited corrosion product.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Critical micelle concentration

Normally, the addition of surfactant to aqueous solution causes an increase in the number of ion such as Na^+ and consequently. An increase in the conductivity. Above the CMC, more addition of surfactant increases the micelle concentration while the monomer concentration remains constant at the CMC level. Since a micelle is much larger than monomer, it diffuses slower in the solution and it is also a less efficient charge carrier. A plot of conductivity against surfactant concentration, based on data in Table 4.1 shows a change in slope at the CMC as seen in Fig. 4.1. The obtained CMC of SEHS in 0.9 wt.% NaCl solution is equal to 3.55 mM.

Table 4.1 Conductivity of SEHS in 0.9 wt.% NaCl at various concentrations

Concentration (mM)	Conductivity (mS/cm)
0	14.9
1.0	15.1
1.5	15.2
2.0	15.3
3.0	15.5
3.5	15.6
4.5	15.7
5.5	15.8
6.5	15.9
7.5	16.0

In literature, CMC of SEHS in distilled water is about 13.00 mM [49]. The decrease of CMC of SEHS in NaCl solution is primarily due to the reduction of the electrostatic repulsion between anionic hydrophilic head group by Na^+ [50]. Consequently, micellization occurs easier and causes CMC of SEHS in 0.9 wt.% NaCl solution to be lower than the value reported in distilled water.

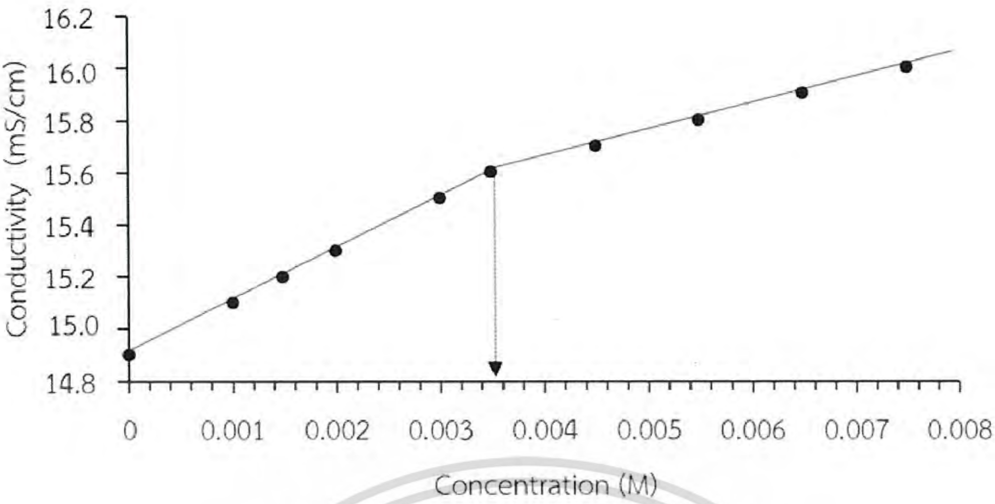


Fig. 4.1 Conductivity of 0.9 wt.% NaCl solution with the presence of SEHS at various concentrations.

As seen from Fig. 4.2, when the conductivity increases almost linearly with the increase in SEHS concentration, monomeric SEHS gradually adsorb on metal surface. With further increasing SEHS concentration, the slope changes steeply at certain concentration (3.55 mM), which indicates that the micelles are formed and entangled with each other in NaCl solution.

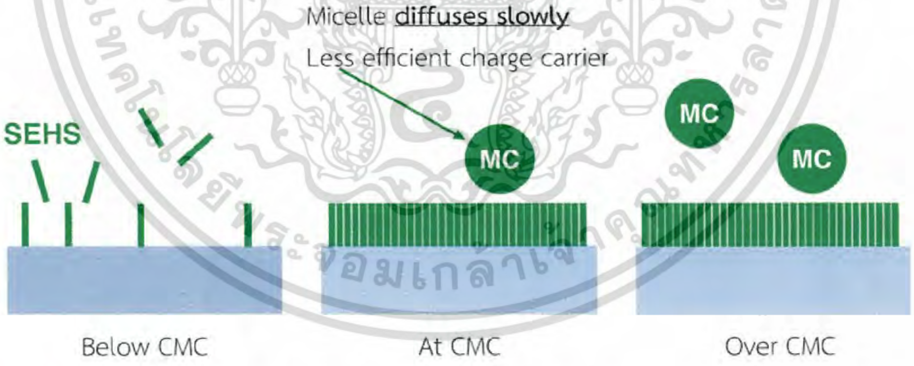


Fig. 4.2 The micelle formation of SEHS in 0.9 wt.% NaCl solution.

4.2 Corrosion behavior

4.2.1 Polarization measurements

Fig. 4.3 shows the potentiodynamic polarization curves at stainless steel in 0.9 wt.% NaCl solution in the absence and presence SEHS at different concentration. It is known that the electrochemical reaction of the stainless steel in corrosive medium is the anodic dissolution reaction of iron as shown in eq. 4.1 and cathodic reactions related to the oxygen and proton reduction as shown in eq. 4.2.

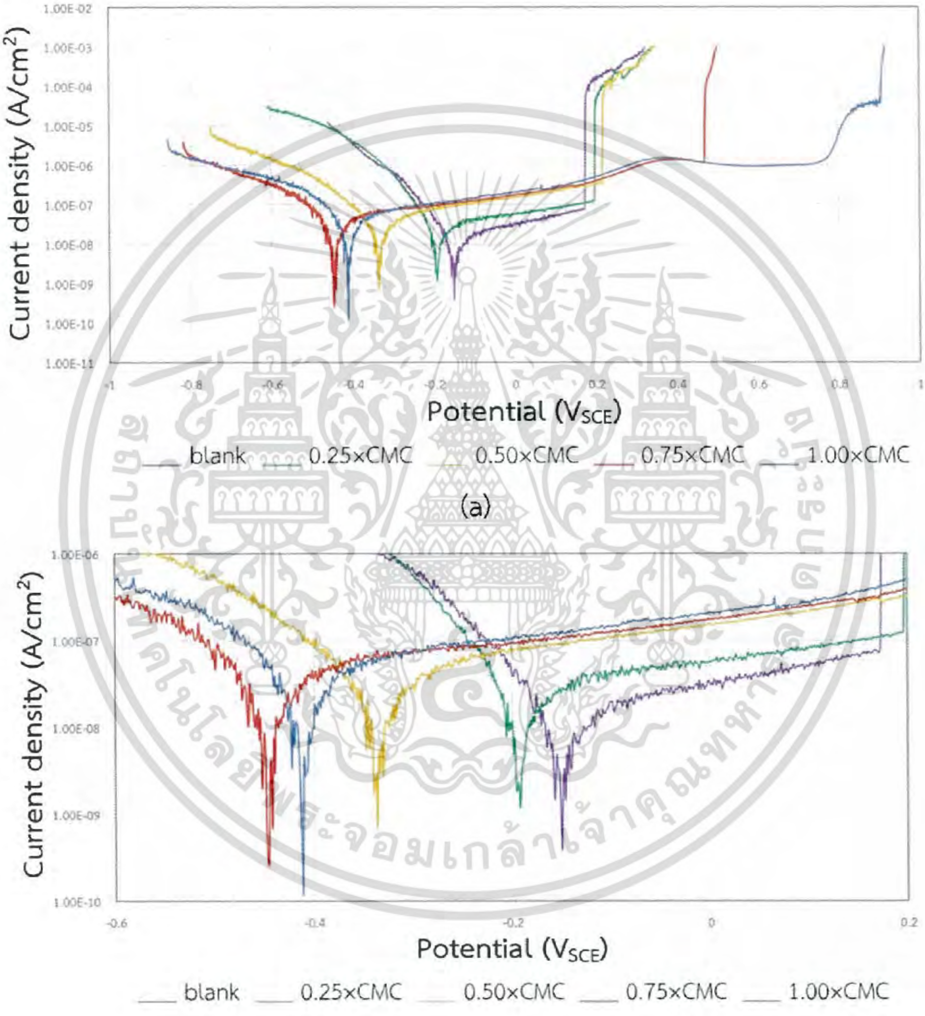
Anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^-$ (4.1)

Cathodic reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (4.2)

These reactions lead to hydrolysis and hydroxide precipitation of iron hydroxides:

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ (4.4)

$2Fe(OH)_2 + H_2O + 1/2O_2 \rightarrow 2Fe(OH)_3$ (4.5)



(b)

Fig. 4.3 Potentiodynamic polarization curves of 304 stainless steel in 0.9 wt.% NaCl solution at various concentrations of SEHS.

From Fig. 4.3 (b) the corrosion potential (E_{corr}) is slightly shifted to a more active value with increasing concentration of SEHS in 0.9 wt.% NaCl solution. The values of corrosion potential are summarized in Table 4.2. The corrosion potential of sample in test solution without addition of SEHS is -0.186 V whereas a potential of

-0.424 V is obtained from 1×CMC solution. The shift of corrosion potential to a more active value suggests lower oxidizing power of the solution due to SEHS addition. However, this effect seems to be insignificant on corrosion current density (i_{corr}) because it leads to all i_{corr} in about the same order of magnitude of 10^{-8} A/cm^2.

Table 4.2 Electrochemical parameters of 304 stainless steel in 0.9 wt.% NaCl solution in the absence and presence of SEHS.

[SEHS] (xCMC)	[SEHS] (mM)	i_{corr} (A/cm^2)	E_{corr} (V_{SCE})	E_{pit} (V_{SCE})
0	0.00	1.30E-08	-0.186	0.174
0.25	0.89	2.84E-08	-0.195	0.196
0.5	1.78	4.74E-08	-0.344	0.217
0.75	2.66	5.09E-08	-0.456	0.473
1	3.55	5.74E-08	-0.424	-

After the SEHS is added, the pitting potential (E_{pit}) is clearly shifted to more noble potential. This is good in corrosion viewpoint as the higher pitting potential means the higher pitting resistance. The lowest E_{pit} of 0.174 V can be obtained from solution without SEHS addition. The pitting potential is continuously shifted to more noble or more position value where the SEHS concentration is increased. However as observed from the sample in 1×CMC solution, no pit is formed after the end of the polarization. This means that the 1×CMC solution can completely inhibit the pitting on 304 stainless steel surface. The results are shown in Fig. 4.4.

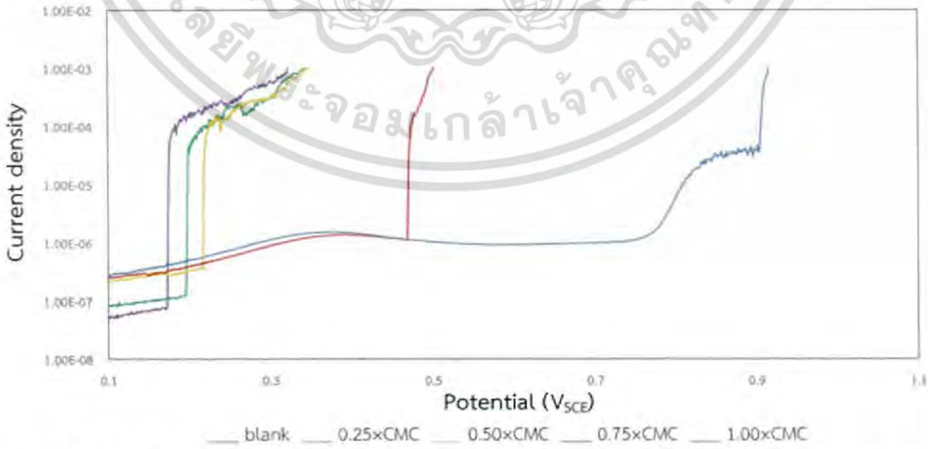


Fig. 4.4 Potentiodynamic anodic polarization curves of 304 stainless steel in 0.9 wt.% NaCl solution at various concentrations of SEHS.

From the Pourbaix diagram for iron in Fig. 4.5, at pH of about 10.1, it is found that the oxygen evolution starts at 0.75 VSHE. For this study, saturated caromel electrode is used as reference electrode. First convert the electrode potential to the saturated caromel scale.

E vs. SCE = E vs. SHE – 0.242 V

= 0.75 - 0.242 V

= 0.508 V

This potential is lower than the potential that the current is sharply increased in case of 1×CMC solution. Therefore the potential obtained from 1×CMC solution is not a pitting potential but an oxygen evolution potentials which confirmed by no pit is observed on the surface.

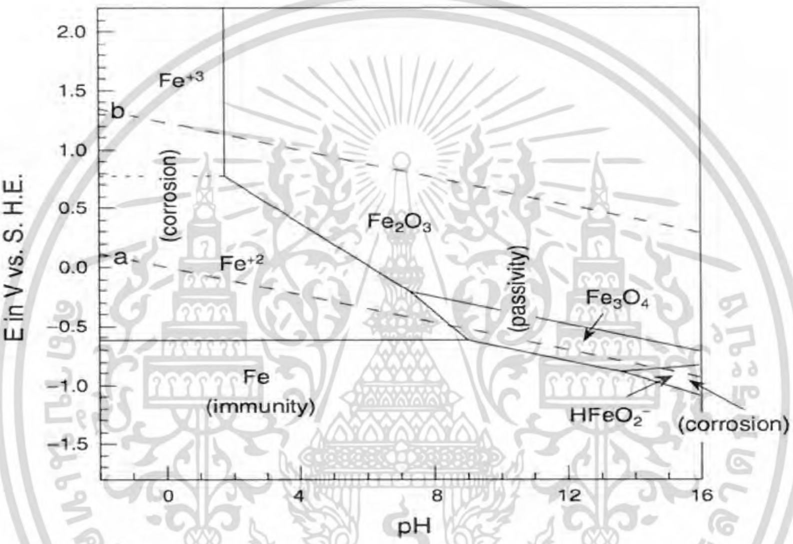


Fig. 4.5 Pourbaix diagram for iron.

4.2.2 Chronoamperometry

In order to compare the efficiencies of the SEHS in 0.9 wt.% NaCl the chronoamperometry was applied to the samples at one fixed potential in two different solutions (with and without SEHS addition). Fig. 4.6 shows the surface of stainless steel after chronoamperometry at 0.400 V for 20 minutes in 0.9 wt.% NaCl in absence of SEHS (Fig. 4.6 (a)) and presence of SEHS at 1xCMC (Fig. 4.6 (b)). According to Fig. 4.4, the potential of 0.400 V for the polarization curve obtained from the solution without SEHS is clearly higher than the pitting potential. And for the solution with SEHS at 1xCMC, a potential of 0.400 V is still in the passive region. Pitting can be observed all over the surface of stainless steel without SEHS addition after measurement. For the same potential, the stainless steel with addition of SEHS at CMC shows no sign of pitting corrosion. This also confirms the pitting inhibition performance of SEHS.

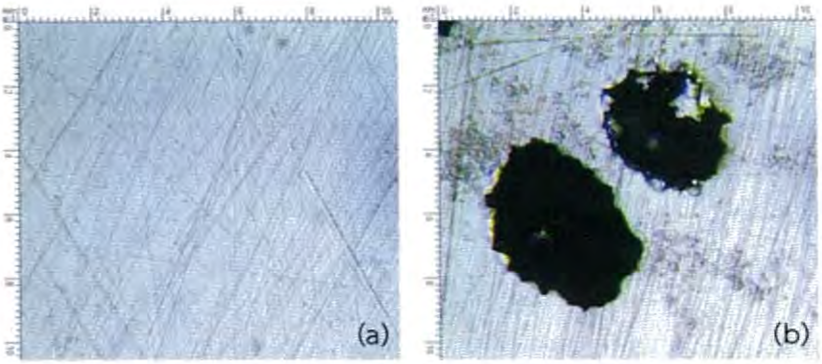


Fig. 4.6 Stainless steel after chronoamperometry at 0.400 V for 20 minutes in 0.9 wt.% NaCl; (a) without SEHS addition; (b) with SEHS at 1×CMC.

According to the penetration mechanism, chloride ions are transported through the oxide film to the underlying metal surface. The Cl^- migration through oxygen vacancies is a possible mechanism of chloride entry into the passive film [4]. Moreover, the chloride ions can adsorb on the oxide surface and then form surface complexes with the oxide film which lead to local dissolution and thinning of the passive film. Thus iron oxide dissolves to some extent in the presence of sodium chloride solutions, then the passive film is thinning [5]. However, as the SEHS is added into the solution with the presence of Cl^- ion, these surfactant molecules can adsorb on the oxide film and form additional protection organic layer. The Cl^- migration as mentioned before is therefore more difficult to occur. Eventually the pitting is completely inhibited at the maximum as the micelle is starting to form beyond this concentration. From this reason the Cl^- ions have almost no chance to attack the present oxide film. And no pit observed from 1×CMC solution, as seen in Fig. 4.7.

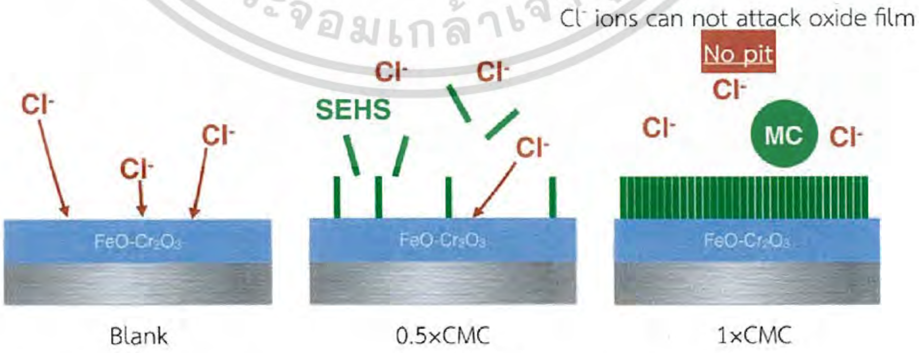


Fig. 4.7 Adsorption of SEHS on stainless steel in 0.9 wt.% NaCl.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

This study shows that the SEHS was able to inhibit pitting corrosion in NaCl solutions, as indicated by the increase in pitting potential after SEHS addition. The inhibition by SEHS was believed to be due to the formation of a SEHS adsorbed film on the 304 stainless steel surface.

The pitting of 304 stainless steel was completely inhibited with SEHS addition at the concentration of 1×CMC.

5.2 Suggestions for Future studies

5.2.1) To study the corrosion inhibition efficiency of sodium 2-ethylhexyl sulfate for other metals.

5.2.2) To study the influence of branched alkyl and straight alkyl chain on corrosion inhibition.

REFERENCES

[1] Rozenfel'd, I. L. 1981. **Corrosion Inhibitors.** New York : McGraw-Hill.

[2] Abbasov, V. M. El-Lateef, Hany M. Abd. Aliyeva, L. I. Ismayilov, T. A. Ismayilov, I. T. and Mamedxanova, S. A. 2013. "Evaluation of New Complex Surfactants Based on Vegetable Oils as Corrosion Inhibitors for Mild Steel in CO₂-Saturated 1.0% NaCl Solutions." *Journal of Materials Physics and Chemistry.* 1(2) : 19-26.

[3] Elachouri, M. Hajji, M. S. Salem, M. Kertit, S. Aride, J. Coudert, R. and Essassi, E. 1996. "Some Nonionic Surfactants as Inhibitors of the Corrosion of Iron in Acid Chloride Solutions." *CORROSION.* 52(2) : 103-108.

[4] Aparicio, M. Jitianu, A. Rodriguez, G. Al-Marzoki, K. Jitianu, M. Mosa, J. and Klein, L. C. 2017. "Thickness-properties synergy in organic–inorganic consolidated melting-gel coatings for protection of 304 stainless steel in NaCl solutions." *Surface and Coatings Technology.* 315 : 426-435.

[5] Zheng, Z. B. and Zheng, Y. G. 2016. "Effects of surface treatments on the corrosion and erosion-corrosion of 304 stainless steel in 3.5% NaCl solution." *Corrosion Science.* 112 : 657-668.

[6] Shabani-Nooshabadi, M. and Ghandchi, M. S. 2015. "Santolina chamaecyparissus extract as a natural source inhibitor for 304 stainless steel corrosion in 3.5% NaCl." *Journal of Industrial and Engineering Chemistry.* 31 : 231-237.

[7] Finšgar, M. Fassbender, S. Nicolini, F. and Milošev, I. 2009. "Polyethyleneimine as a corrosion inhibitor for ASTM 420 stainless steel in near-neutral saline media." *Corrosion Science.* 51(3) : 525-533.

[8] Heakal, F. E.-T. Hefny, M. M. and El-Tawab, A. M. A. 2010. "Electrochemical behavior of 304L stainless steel in high saline and sulphate solutions containing alga Dunaliella Salina and β-carotene." *Journal of Alloys and Compounds.* 491(1) : 636-642.

[9] Craye, G. Löbmann, K. Grohganz, H. Rades, T. and Laitinen, R. 2015. "Characterization of Amorphous and Co-Amorphous Simvastatin Formulations Prepared by Spray Drying." *Molecules.* 20(12) : 19784.

[10] Fontana, M. G. 1986. **Corrosion Engineering.** New York : McGraw-Hill.

[11] Popov, B. N. 2015. **Corrosion Engineering: Principles and Solved Problems.** Amsterdam : Elsevier Science.

[12] Palanna, O. G. 2009. **Engineering Chemistry.** India : McGraw-Hill Education (India) Pvt Limited.

[13] Administration, F. A. 2013. **Aviation Maintenance Technician Handbook.** Newcastle : Aviation Supplies & Academics, Incorporated.

[14] Wilson, R. E. 1923. "The Mechanism of the Corrosion of Iron and Steel in Natural Waters and the Calculation of Specific Rates of Corrosion." *Industrial & Engineering Chemistry.* 15(2) : 127-133.

[15] Bayliss, D.A. and Deacon, D.H. 2003. **Steelwork Corrosion Control.** Florida : CRC Press.

[16] Guo, R. Liu, T. and Wei, X. 2002. "Effects of SDS and some alcohols on the inhibition efficiency of corrosion for nickel." *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 209(1) : 37-45.

[17] Clugston, M. and Flemming, R. 2000. **Advanced Chemistry.** Oxford : Oxford University Press.

[18] Shreir, L. L. 2013. **Corrosion: Metal/Environment Reactions.** Amsterdam : Elsevier Science.

[19] Deng, B. Jiang, Y. Gong, J. Zhong, C. Gao, J. and Li, J. 2008. "Critical pitting and repassivation temperatures for duplex stainless steel in chloride solutions." *Electrochimica Acta.* 53(16) : 5220-5225.

[20] Roberge, P. R. 2012. **Handbook of corrosion engineering, second edition.** New York : McGraw-Hill.

[21] DE PAULA NUNES, L. and DUTRA, A.C. 1994. **PROTEÇAO CATODICA - TECNICA DE COMBATE A CORROSAO.** Caracas : INTERCIENCIA.

[22] Bardal, E. 2007. **Corrosion and Protection.** London : Springer Science & Business Media.

[23] Kolotyrkin, Y.M. Akolzin, P.A. and Antropov, L.I. 1969. **Proceedings of the Third International Congress on Metallic Corrosion.** Moscow : Mir Publ.

[24] Farn, R. J. 2008. **Chemistry and Technology of Surfactants.** New York : Wiley.

[25] Rosen, M.J. and Kunjappu, J.T. 2012. **Surfactants and Interfacial Phenomena.** New York : Wiley.

[26] CTI Reviews. 2016. **A Conceptual Introduction to Chemistry.** Indiana : Cram101 Textbook Reviews.

[27] Myers, D. 2005. **Surfactant Science and Technology.** New York : Wiley.

[28] Jönsson, B. Lindman, B. Holmberg, K. and Kronberg, B. 2000. **Surfactants and Polymers in Aqueous Solution.** New York : Wiley.

[29] Holmberg, K. 2003. **Novel Surfactants: Preparation Applications And Biodegradability, Second Edition, Revised And Expanded.** Florida : CRC Press.

[30] Esumi, K. and Ueno, M. 2003. **Structure-Performance Relationships in Surfactants.** Florida : CRC Press.

[31] Cullum, D. C. 2012. **Introduction to Surfactant Analysis.** Netherlands : Springer Science & Business Media.

[32] Tai, L. H. T. and Nardello-Rataj, V. 2001. "Detergents-Detergents The main surfactants used in detergents and personal care products." *Oléagineux, Corps gras, Lipides.* 8(2) : 141-144.

[33] McGuire, M. F. 2008. **Stainless Steels for Design Engineers.** Ohio : ASM International.

[34] Kumar, A. 2008. "Corrosion inhibition of mild steel in hydrochloric acid by Sodium Lauryl Sulfate (SLS)." *Journal of Chemistry.* 5(2) : 275-280.

[35] Soltani, N. Tavakkoli, N. Khayat Kashani, M. Mosavizadeh, A. Oguzie, E. E. and Jalali, M. R. 2014. "Silybum marianum extract as a natural source inhibitor for 304 stainless steel corrosion in 1.0 M HCl." *Journal of Industrial and Engineering Chemistry.* 20(5) : 3217-3227.

[36] Singh, V. K. and Singh, V. B. 1988. "The corrosion behaviour of AISI 304 stainless steel in methanol-H2SO4 mixtures." *Corrosion science.* 28.4 : 385-395.

[37] Pardo, A. Merino, M. C. Coy, A. E. Viejo, F. Arrabal, R. and Matykina, E. 2008. "Pitting corrosion behaviour of austenitic stainless steels – combining effects of Mn and Mo additions." *Corrosion Science.* 50(6) : 1796-1806.

[38] Abd El Rehim, S. S. Hassan, H. H. and Amin, M. A. 2003. "The corrosion inhibition study of sodium dodecyl benzene sulphonate to aluminium and its alloys in 1.0 M HCl solution." *Materials Chemistry and Physics.* 78(2) : 337-348.

[39] Wei, Z. Duby, P. and Somasundaran, P. 2003. "Pitting inhibition of stainless steel by surfactants: an electrochemical and surface chemical approach." *Journal of colloid and interface science.* 259(1) : 97-102.

[40] Refaey, S. A. M. Taha, F. and Abd El-Malak, A. M. 2004. "Inhibition of stainless steel pitting corrosion in acidic medium by 2-mercaptobenzoxazole." *Applied Surface Science.* 236(1–4) : 175-185.

[41] Tian, W. Du, N. Li, S. Chen, S. and Wu, Q. 2015. "Effects of applied potential on stable pitting of 304 stainless steel." *Corrosion Science.* 93 : 242-255.

[42] Tian, W. Du, N. Li, S. Chen, S. and Wu, Q. 2014. "Metastable pitting corrosion of 304 stainless steel in 3.5% NaCl solution." *Corrosion Science.* 85 : 372-379.

[43] do Nascimento, A. M. Ierardi, M. C. F. Kina, A. Y. and Tavares, S. S. M. 2008. "Pitting corrosion resistance of cast duplex stainless steels in 3.5%NaCl solution." *Materials Characterization.* 59(12) : 1736-1740.

[44] Tsutsumi, Y. Nishikata, A. and Tsuru, T. 2007. "Pitting corrosion mechanism of Type 304 stainless steel under a droplet of chloride solutions." *Corrosion Science.* 49(3) : 1394-1407.

[45] Shi, J. Sun, W. Jiang, J. and Zhang, Y. 2016. "Influence of chloride concentration and pre-passivation on the pitting corrosion resistance of low-alloy reinforcing steel in simulated concrete pore solution." *Construction and Building Materials.* 111 : 805-813.

[46] Wang, Y. Cheng, G. Wu, W. Qiao, Q. Li, Y. and Li, X. 2015. "Effect of pH and chloride on the micro-mechanism of pitting corrosion for high strength pipeline steel in aerated NaCl solutions." *Applied Surface Science.* 349 : 746-756.

[47] Fregonese, M. Idrissi, H. Mazille, H. Renaud, L. and Cetre, Y. 2001. "Initiation and propagation steps in pitting corrosion of austenitic stainless steels: monitoring by acoustic emission." *Corrosion Science.* 43(4) : 627-641.

[48] ASTM International. 2013. **ASTM A967 / A967M-13, Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts.** [Online]. Available : https://www.astm.org/Standards/A967.htm.

[49] Saadi, S. A. Yi, Y. Cho, P. Jang, C. and Beeley, P. 2016. "Passivity breakdown of 316L stainless steel during potentiodynamic polarization in NaCl solution." *Corrosion Science.* 111 : 720-727.

[50] Guo, Q. Liu, J. Yu, M. and Li, S. 2015. "Effect of passive film on mechanical properties of martensitic stainless steel 15-5PH in a neutral NaCl solution." *Applied Surface Science.* 327 : 313-320.

APPENDICES

APPENDIX A

A1: Standard Specification for Chemical Passivation Treatments for Stainless Steel

This standard is issued under the fixed designation A 967, ASTM International.

Treatments in Nitric Acid Solutions

1. Passivation Treatment:

1.1. Stainless steel parts shall be treated in one of the following aqueous solutions and maintained within the specified temperature range for the specified time.

1.1.1 Nitric1—Thesolutionshallcontain20to25volume percent of nitric acid and 2.5 6 0.5 weight percent of sodium dichromate. The parts shall be immersed for a minimum of 20 min at a temperature in the range from 120 to 130°F (49 to 54°C).

1.1.2 Nitric2—Thesolutionshallcontain20to45volume percent of nitric acid. The parts shall be immersed for a minimum of 30 min at a temperature in the range from 70 to 90°F (21 to 32°C).

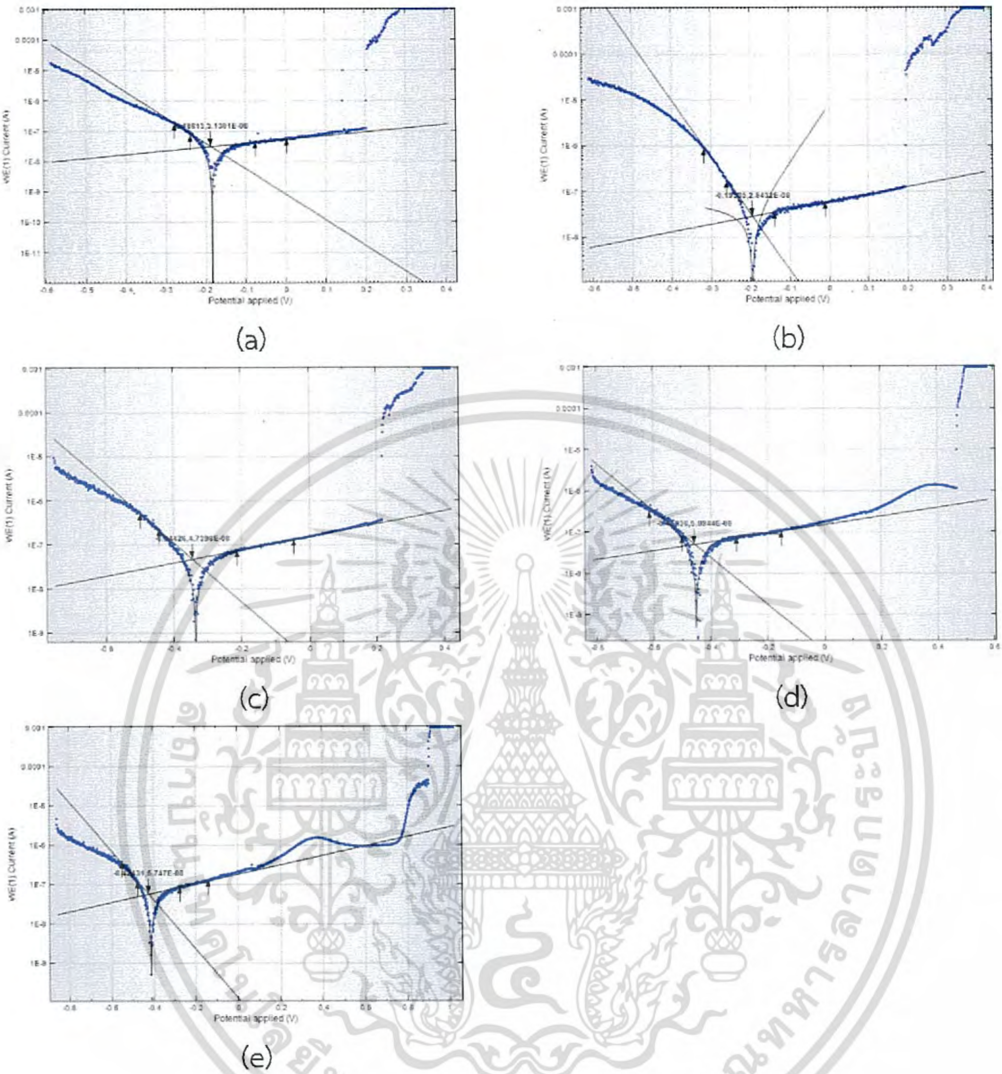
1.1.3 Nitric3—Thesolutionshallcontain20to25volume percent nitric acid. The parts shall be immersed for a minimum of 20 min at a temperature in the range from 120 to 140°F (49 to 60°C).

1.1.4 Nitric 4—The solution shall contain 45 to 55 volume percent of nitric acid. The parts shall be immersed for a minimum of 30 min at a temperature in the range from 120 to 130°F (49 to 54°C).

1.1.5 Nitric 5—Other combinations of temperature, time, and concentration of nitric acid, with or without other chemicals, including accelerants, inhibitors, or proprietary solutions, capable of producing parts that pass the specified test requirements.

1.2. Water Rinse—Immediately after removal from the passivating solution the parts shall be thoroughly rinsed, using stagnant, countercurrent, or spray washes singly or in combination, with or without a separate chemical treatment of the passivation media, with a final rinse being carried out using water with a maximum total solids content of 200 ppm.

A2: Polarization curves



(a)

(b)

(c)

(d)

(e)

Polarization curves recorded for AISI 304 stainless steel in 0.9 wt.% NaCl solutions without and with various concentrations (0.25-1xCMC) of SEHS (a) blank; (b) 0.25xCMC; (c) 0.5xCMC; (d) 0.75xCMC; (e) 1xCMC.

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