Influence of cetyl trimethylammonium bromide on corrosion behavior of copper in sulfuric acid

Miss Nawarat Wong-inta
Mr.Pisit Akarapatanakul
Mr.Romchat Promchotichai

A Special Project submitted in Partial Fulfillment of the Requirements for
Petrochemical Technology
The Degree of Bachelor of Science
International Programs, Faculty of Science
King Mongkut's Institute of Technology Ladkrabang

Special Project Title	Influence of cetyl trimethylammonium bromide on corrosion behavior of copper in sulfuric acid
Workers	Miss Nawarat Wong-inta Mr. Pisit Akarapatanakul Mr. Romchat Promchotichai
Major	Petrochemical Technology
Special Project Advisor	Dr. Sutha Sutthiruangwong

ABSTRACT

This special project emphasized on corrosion behavior of the copper in difference concentrations of sulfuric acid and cetyl trimethylammonium bromide. The experiments were carried out using potentiodynamic polarization technique. Saturated calomel electrode was used as a reference electrode and the platinum was a counter electrode. Air pump was applied for maintaining oxygen concentration and media circulation. The critical micelle concentration (CMC) of CTAB has been determined by conductivity measurement. According to the results, polarization curves showed that the cetyl trimethylammonium bromide (CTAB) was an effective corrosion inhibitor in 0.01 N and 1 N H_2SO_4. But in a neutral environment, it promoted corrosion on copper.

Acknowledgements

This project would never been accomplished without the supporting, hard working and endless efforts of a large numbers of individuals and institution. We would like to express our gratitude to all those who gave us the opportunity to complete this special project.

First of all, we would like to express our deepest sincere gratitude to our advisor, Dr. Sutha Sutthiruangwong, for his assistance, encouragement and valuable suggestion throughout this special project. Our deep appreciations are also expressed to Asst.Prof.Dr. Phacernchai Chaiyasit, for kindly guidance about CMC.

We appreciatively thank to Assoc.Prof. Dr. Tawan Sooknoi and Asst. Prof. Dr. Suparat Rukchonlatee for all the questions and recommendation.

We wish to thank our lovely family and friends for their understanding, helping and encouragement.

Lastly, we would like to acknowledge the contribution of King Mongkut's Institute of Technology Ladkrabang for the financial support and the laboratory facilities for this project.

Miss Nawarat Wong-inta
Mr. Pisit Akarapatanakul
Mr. Romchat Promchotichai

Table of Contents

Table of Contents

Table of Contents

Page

Table of Contents

List of Tables

List of Figures

List of Figures

List of Figures

Chapter 1

Introduction

1.1 Motivation

In the past, studying about corrosion behavior and protection have not been received a good enough attention. But as the time passed, human tried to understand and control corrosion in an attempt to minimize the damage. Now a day, many of the researches and experiments have been done in order to conquer the corrosion problems.

Copper and its alloys are one amongst the materials that receive a great attention in prohibiting from corrosion. Copper are extensively used in many industries and agriculture according to their good properties e.g. excellent electrical conductivity, high thermal conductivity and moderate corrosion resistance.

In this work, the aim is to study an influence of cationic surfactant named cetyl trimethylammonium bromide (CTAB) on inhibition behavior of corrosion on copper (99.99%) in an absence and presence of sulfuric acid. CTAB is selected as corrosion inhibitor for this study as it is one of the well known, cationic surfactant. These studies provide more understanding and information about using CTAB as a corrosion inhibitor on copper in neutral and various acidic environment.

1.2 Objective

This project intended to study the influence of cetyl trimethylammonium bromide (CTAB) on corrosion behavior of copper in an absence and presence of various concentrations of sulfuric acid.

1.3 Scope of Study

1.3.1 Study the inhibition effect of cetyl trimethylammonium bromide .

1.3.2 Determine corrosion rate of copper by using poteniodynamic polarization technique.

Chapter 2

Literature review

2.1 Copper

Copper is a chemical element with the symbol Cu. Copper and its alloys are the earliest metals which the human have known and used from prehistoric times. At present it very important than ever before and widespread use depends on a combination of corrosion resistance in a variety of environment, excellent work ability, high thermal and electrical conductivities, and attractive mechanical properties at low, normal and moderately elevated temperatures.

Pure copper is very soft and malleable. To improve the properties for particular application, it is alloyed with small quantities of metal such as beryllium, tellurium, silver, cadmium, arsenic and chromium. Larger alloying additions of zinc, tin and nickel are made to improve the mechanical properties of metal, and to retain its excellent corrosion resistance under more arduous service condition. [1,2]

2.1.1 History

Copper Age

Copper was used long before the Roman Empire. It is one of the earliest metals known to humans. One reason for this is that copper occurs not only as ores (compounds that must be converted to metal), but occasionally as native copper. A history of the using of a native copper has at least 10,000 years old and was mined and used in the Tigris-Euphrates valley (modern Iraq) as long as 7,000 years ago. Copper ores have been mined for at least 5000 years because it is fairly easy to get the copper out of them. In prehistoric times an early human could simply find a chunk of copper and hammer it into a tool with a rock. (Copper is very malleable, meaning that it can be hammered easily into various shapes, even without heating) [3,4]

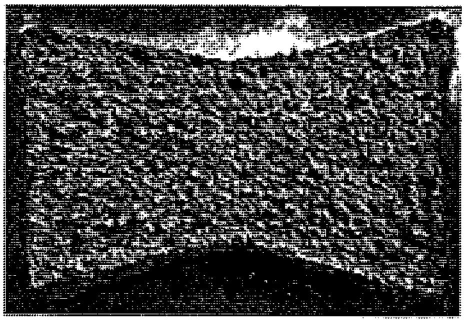


Figure2.1 Verdigris [3]

Bronze Age

Brass or bronze was the alloyed of copper,tin and a bit of lead or other metal which realized soon after discovery. It had generally been accepted that bronze casting began in Greece, Egypt and China. Recently, however, archaeologists discovered evidence of bronze making near Ban Chiang, Thailand, as far back as 4500 B.C. Interestingly, this site lacked evidence of the production of any kind of bronze weapons – an artifact hugely popular with other Bronze Age civilizations. Instead, the culture forged bronze for special religious and funerary objects. This anachronism is one of many in the history of bronze casting. [5]

Copper was a very important resource for the Romans, Greeks and other ancient peoples .Copper metallurgy was flourishing in South America, particularly in Peru around the beginning of the first millennium AD. Copper technology proceeded at a much slower rate on other continents. Africa's major location for copper reserves is Zambia. Copper burial ornamentals dated from the 15th century have been uncovered, but the metal's commercial production did not start until the early 1900s. Australian copper artifacts exist, but they appear only after the arrival of the Europeans; the aboriginal culture apparently did not develop their own metallurgical abilities. [3]

2.1.2Classification of coppers and copper alloys

Copper and copper alloys can be classified according to a designation system administered by the Copper Development Association (CDA). In this system, number of copper from C100 through C799 designate wrought alloys and numbers from C800 to C999. [2]

2.1.3Characteristics and properties

2.1.3.1 Color

Copper has a reddish, orangish, or brownish color because a thin layer of tarnish (including oxides) gradually forms on its surface when gases (especially oxygen) in the air react with it. Pure copper, when fresh, is actually a pinkish or peachy metal. Copper, caesium and gold are the only three elemental metals with a natural color other than gray or silver. The usual gray color of metals depends on their "electron sea" that is capable of absorbing and re-emitting photons over a wide range of frequencies.

Copper has its characteristic color because of its unique band structure. By Madelung's rule the 4s subshell should be filled before electrons are placed in the 3d subshell but copper is an exception to the rule with only one electron in the 4s subshell instead of two. The energy of a photon of blue or violet light is sufficient for a *d* band electron to absorb it and transition to the half-full *s* band. Thus the light reflected by copper is missing some blue/violet components and appears red. This phenomenon is shared with gold which has a corresponding 5s/4d structure. In its liquefied state, a pure copper surface without ambient light appears somewhat greenish, a characteristic shared with gold. When liquid copper is in bright ambient light, it retains some of its pinkish luster. [3]

2.1.3.2 Mechanical properties

Copper is easily to ductile and malleable. The ease with which it can be drawn into wire makes it useful for electrical work in addition to its excellent electrical properties. Copper can be machined, although it is usually necessary to use an alloy for intricate parts, such as threaded components, to get really good machinability characteristics for good thermal conduction make it useful for heatsinks and in heat exchangers. Copper has good corrosion resistance, but not as well as gold. It has excellent brazing and soldering properties and can also be welded, although best results are obtained with gas metal arc welding.

2.2.3.3 Electrical properties

Copper has the second highest electrical conductivity of any element after silver. This is due to virtually all the valence electrons (one per atom) taking part in conduction. The resulting free electrons in the copper amounting to a huge charge density of $13.6x10^9$ C/m .Which responsible for the rather slow drift velocity of currents in copper cable. [3,6]

2.1.4 Applications

Copper is malleable and ductile and is a good conductor of both heat and electricity. The purity of copper is expressed as 4N for 99.99% pure or 7N for 99.99999% pure. The numeral gives the number of nines after the decimal point when expressed as a decimal (e.g. 4N means 0.9999, or 99.99%). Copper is often too soft for its applications, so it is incorporated in numerous alloys. For example, brass is a copper-zinc alloy, and bronze is a copper-tin alloy. It is used extensively, in products such as:

2.1.4.1 Piping

Including water supply, or used extensively in refrigeration and air conditioning equipment because of its ease of fabrication and soldering.

2.1.4.2 Electronics

copper wire, oxygen-free copper, electromagnets, printed circuit board, lead free solder(or alloyed with tin) , electrical machines (especially electromagnetic motors, generator and transformers), electrical relays , electrical bus bars and electrical switches, vacuum tubes, cathode ray tubes, and the magnetrons in microwave ovens, wave guides for microwave radiation, integrated circuits(increasingly replacing aluminium because of its superior electrical conductivity) , as a material in the manufacture of computer heat sinks, as a result of its superior heat dissipation capacity to aluminium. [3]

2.1.4.3 Architecture / Industry

Copper has been used as water-proof roofing material since ancient times, giving many old buildings their greenish roofs and domes. Initially copper oxide forms, replaced by cuprous and cupric sulfide, and finally by copper carbonate. The final carbonate patina is highly resistant to corrosion, Statuary: The Statue of Liberty, for example, contains 179,220 pounds (81.3 tonnes)of copper., Alloyed with nickel, e.g. cupronickel and Monel, used as corrosive resistant materials in ship building, Watt's steam engine firebox due to superior heat dissipation, Copper nails were used in making oast cowls ,copper compounds are used as wood preservatives ,copper compounds in liquid form are used as a wood preservative, particularly in treating original portion of structures during restoration of damage due to dry rot ,copper wires may be placed over non-conductive roofing materials to discourage the growth of moss (Zinc may also be used for this purpose) ,copper has been used as water-proof roofing material since ancient times, giving many old buildings their greenish roofs and domes. Initially copper oxide forms, replaced by cuprous and cupric sulfide, and finally by copper carbonate. The final carbonate patina is highly resistant to corrosion. [3]

2.1.4.4 Household products

Copper plumbing fittings and compression tubes, Doorknobs and other fixtures in houses, Roofing, guttering, and rainspouts on buildings, In cookware (such as frying pans), Most flatware (knives, forks, spoons) contains some copper (nickel silver), Sterling silver (if it is to be used in dinnerware must contain a few percent copper), copper water heating cylinders, copper range hoods, copper bath tubs, copper counters, copper sinks, copper slug tape.

2.1.4.5 Chemical applications

Compounds, such as Fehling's solution, have applications in chemistry, as a component in ceramic glazes, and to color glass. [3,6]

2.1.5 Copper Alloys

The small quantities of metal used to add in copper to modify the properties. Numerous copper alloys exist, many with important historical and contemporary uses. Speculum metal and bronze are alloys of copper and tin. Brass is an alloy of copper and zinc. Monel metal, also called cupronickel, is an alloy of copper and nickel. While the metal "bronze" usually refers to copper-tin alloys, it also is a generic term for any alloy of copper, such as aluminium bronze, silicon bronze, and manganese bronze and we used it in different application upon the suitability. [6,7]

2.1.6 Copper Compounds

Native Copper

Common oxidation states of copper include the less stable copper (I) state, Cu^{+}; and the more stable copper (II) state, Cu^{2+}, which forms blue or blue-green salts and solutions. Under unusual conditions, a 3+ state and even an extremely rare 4+ state can be obtained. Using old nomenclature for the naming of salts, copper (I) is called *cuprous*, and copper (II) is *cupric*. In oxidation copper is mildly basic.

Copper (II) carbonate is green from which arises the unique appearance of copper-clad roofs or domes on some buildings. Copper (II) sulfate forms a blue crystalline pentahydrate which is perhaps the most familiar copper compound in the laboratory. It is used as a fungicide, known as Bordeaux mixture.

There are two stable copper oxides, copper (II) oxide (CuO) and copper(I) oxide (Cu_2O). Copper oxides are used to make yttrium barium copper oxide ($YBa_2Cu_3O_{7-\delta}$) or YBCO which forms the basis of many unconventional superconductors. [8]

2.2 Corrosion

Most people have seen the end results of corrosion on a number of appliances, vehicles, and other items that included metal components. Corrosion, the deterioration caused by chemical reaction with the environment, affects materials as different as structural metals, ceramics, and wood. Corrosion technology is a field of study that focuses on the mechanisms of corrosion and on the design of protective schemes to prevent it or limit its extent.

Corrosion is the deterioration of a material as a result of reaction with its environment, especially with oxygen. Although the term is usually applied to metals, all materials, including ceramics, plastics, rubber, and wood, deteriorates at the surface to some extent when they are exposed to certain combinations of liquids and/or gases. Common examples of metal corrosion are the rusting of iron, the tarnishing of silver, the dissolution of metals in acid solutions, and the growth of patina on copper. Most research into the causes and prevention of corrosion involves metals, since the corrosion of metals occurs much faster under atmospheric conditions than does the corrosion of nonmetals. The cost of replacing equipment destroyed by corrosion in the United States alone is in the billion-dollar range annually.

Corrosion is usually an electrochemical process in which the corroding metal behaves like a small electrochemical cell. Since the corrosion of iron by dissolved oxygen is, from an economic standpoint, the most important redox reaction occurring in the atmosphere, it will be used here to illustrate the electrochemical nature of the process. A sheet of iron exposed to a water solution containing dissolved oxygen is the site of oxidation and reduction half-reactions, which occur at different locations on the surface. At anodic areas, iron is oxidized according to the reaction. At the same time, oxygen molecules in the solution are reduced at the cathodic areas. This two processes produce an insoluble iron hydroxide in the first step of the corrosion process.

Generally, this iron hydroxide is further oxidized in a second step to produce $Fe(OH)_3$, the flaky, reddish-brown substance that is known as rust. Unfortunately, this new compound is permeable to oxygen and water, so it does not form a protective coating on the iron surface and the corrosion process continues. [9]

The existence of anodic and cathodic sites on the surface of a piece of metal implies that differences in electrical potential are found on the surface. These potential differences have a number of causes. One important mechanism is oxygen concentration cell corrosion, in which the oxygen concentration in the electrolyte varies from place to place. An underground pipe that passes from clay to gravel will have a high oxygen concentration in the gravel region and almost no oxygen in the impermeable clay. The part of the pipe in contact with the clay becomes anodic and suffers damage.

A similar situation is found where a pipe passes under a road. The section under the road (which is the more difficult to get at for repair) is oxygen deprived and will suffer the greatest damage. The cure for this is cathodic protection, which involves the use of a sacrificial anode such as zinc or aluminum. In this situation, the metal to be protected is connected electrically to a piece of scrap metal that will take its place as the anode. The anode is destroyed by the corrosion reaction, leaving the cathode intact. This technique is still used extensively to protect underground gas and water pipelines.

Concentration cells may also be formed where there are differences in metal ion concentration. A copper pipe in contact with copper ion solutions of different concentrations will corrode at the part in contact with the more dilute solution. This is an obvious problem when copper pipes are used to carry flowing water. Parts of the copper surface in contact with the more quickly moving fluid will be more negative and therefore anodic. This phenomenon plays an important part in the erosion corrosion of copper and its alloys.

Although most metals are crystalline in form, they generally are not continuous single crystals, but rather are collections of small grains or domains of localized order. Metal objects are formed from melts in which microcrystals form as the liquid cools and solidifies. In the final state, these microcrystals have different orientations with respect to one another. The edges of the domains form grain boundaries, which are an example of planar defects in metals. These defects are usually sites of chemical reactivity. The boundaries become anodic, while the grains themselves are the cathodes. The boundaries are also weaknesses, the places where stress cracking begins.

The best known of all corrosion types is galvanic corrosion, which occurs at the contact point of two metals or alloys with different electrode potentials. An example of this might be brass detail in contact with copper hot-water pipes. The brass becomes anodic and suffers the loss of its zinc atoms. Brass in contact with galvanized steel is protected, while the zinc coating on the steel is first dissolved, leaving the steel open to attack for the same reason.

An obvious area of concern is the use of one type of metal as bolts, screws, and welds to fuse together pieces of another metal. The combination to be desired is the large anode-small cathode combination. Bolts, screws, and so on should be made of the metal less likely to be oxidized so that the bolt or weld is cathodically protected.

The great importance is the conductivity of the corroding solution. When large areas of the surface are in contact with a water solution of high conductivity, such as seawater, the attack on the anodic metal may spread far from its contact point with the cathodic metal. This is a less severe situation than that which occurs in soft water or under atmospheric conditions in which the attack is localized in the vicinity of the contact. In the absence of dissolved oxygen or hydrogen ions to maintain the cathode process, galvanic corrosion does not occur. It is possible to combine different metals such as copper and steel in closed hot-water systems with little corrosion.

The first step in preventing material corrosion understands its specific mechanism. The second and often more difficult step are designing a type of prevention. Some metals produce corrosion products that are insoluble, about the same size molecularly as the parent metal, and that crystallize in the same type of lattice structure. These are often able to become attached to the metal surface and form a protective coat against further corrosion. The patina that forms on copper is an example of this type of coating.

Other preventive measures involve the use of protective coatings and modification of the environment. Some trace impurities can significantly reduce the rate of corrosion and can be added in low concentration to the surrounding medium. Paint is the most common coating used to slow the rate of atmospheric corrosion. Many other materials, such as plastics, ceramics, rubbers, and even electroplated metals, can be used as protective coatings. The corrosion resistance of a metal can be greatly increased by the proper choice of alloys. For example, aluminum added to brass will increase its corrosion resistance.

2.2.1 Forms of Corrosion

2.2.1.1 Uniform Corrosion

A uniform, regular removal of metal from the surface is the expected mode of corrosion. For uniform corrosion, the corrosive environment must have the same access to all parts of the metal surface, and the metal itself must be metallurgically and compositionally uniform. [9]

Figure 2.2 Uniform Corrosion

2.2.1.2 Galvanic Corrosion

When two dissimilar alloys are coupled in the presence of a corrosive electrolyte one of them is preferentially corroded while the other is protected from corrosion. [9]

Figure 2.3 Galvanic Corrosion

2.2.1.3 Crevice Corrosion

Corrosion of an alloy is often greater in the small sheltered volume of the crevice created by contact with another material. The second material may be part of a fastener (bolt, rivet, washer) of the same or a different alloy, a deposit of mud, sand, or other insoluble solid, or a nonmetallic gasket or packing. Crevice corrosion seems to be the preferred title for metal-metal crevices. Deposit corrosion and gasket corrosion are terms sometimes used when a nonmetallic material foams a crevice on the metal surface. [9]

Figure 2.4 Crevice Corrosion

2.2.1.4 Pitting Corrosion

Localized attack in an otherwise resistant surface products pitting corrosion. The pits may be deep, shallow, or undercut. The stainless steels and nickel alloys with chromium depend on a passive film for corrosion resistance and are especially susceptible to pitting by local breakdown of the film at isolated sites. A deep pit caused wall penetration and leaking. [9]

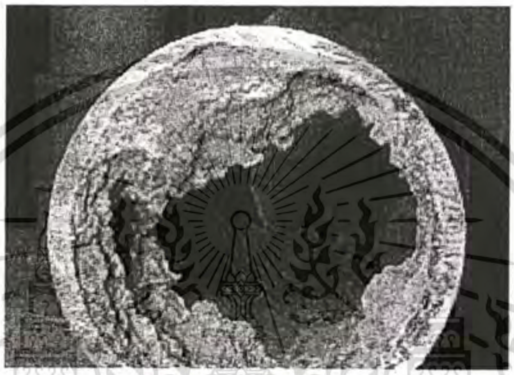


Figure 2.5 Pitting Corrosion

2.2.1.5 Hydrogen Damage

Hydrogen attack is the reaction of hydrogen with carbides in steel to form methane, resulting in decarburization, voids, and surface blisters. [9]

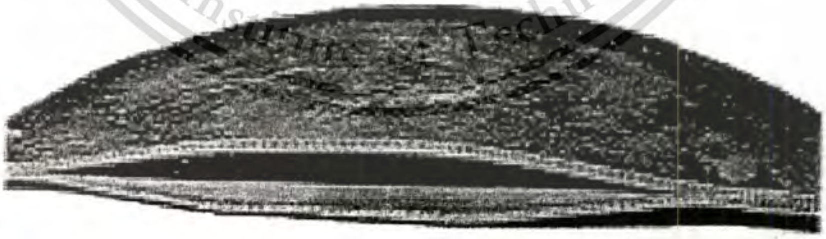


Figure 2.6 Hydrogen Damage

2.2.1.6 Intergranular Corrosion

This type of corrosion is due either to the presence of impurities in the boundaries, or to local enrichment or depletion of one or more alloying elements. Numerous alloy types can undergo intergranular attack, but the most important practical example is the intergranular corrosion of austenitic stainless steels, related to chromium depletion in the vicinity of the boundaries, due to the intergranular precipitation of chromium carbides ($Cr_{23}C_6$), during a "sensitizing" heat treatment or thermal cycle. [9]

Figure 2.7 Intergranular Corrosion

2.2.1.7 Dealloying

Dealloying is a common corrosion process during which an alloy is 'parted' by the selective dissolution of the most electrochemically active of its elements. This process results in the formation of a nanoporous sponge composed almost entirely of the more noble alloy constituents. Although considerable attention has been devoted to the morphological aspects of the dealloying process, its underlying physical mechanism has remained unclear. [9]

Figure 2.8 Dealloying

2.2.1.8 Erosion Corrosion

Erosion-corrosion is caused by the relative movement between a corrosive fluid and a metal surface. The mechanical aspect of the movement is important and friction and wear phenomena can be involved. This process leads to the formation of grooves, valleys, wavy surfaces, holes, etc., with a characteristic directional appearance (comet tails, horseshoe marks, etc. [9]

Figure 2.9 Erosion Corrosion

2.2.2 Thermodynamics

Thermodynamics is the study of the energy changes involved in the electrochemical reactions of corrosion. The thermodynamic of corrosion tells if there is a strong tendency of metal recombines with components of the environment that leads to the phenomenon known as corrosion. The energy changes provide the driving force of the spontaneous chemical reaction. However, the thermodynamic can not predict how fast of the corrosion rate. The rate of corrosion is explained by kinetic laws. [11]

2.2.2.1 Free energy

The change in free energy (ΔG) is a direct measurement of the work capacity or maximum electric energy available from a system. If the change in free energy accompanying the transition of system from one state to another in negative, it indicates loss in free energy and the spontaneous reaction direction of the system.

If the change of free energy is positive, It indicates that the reaction requires energy be added to the system. For the metal is corroded, ΔG must be negative.

The free energy change can be calculated by the following equation:

$$\Delta G = -nFE$$

Where: ΔG is the free energy change

n is the number of electrons involved in reaction

F is the Faraday's constant

E is equal the cell potential

2.2.2.2 Electrode Potential

The electric cell is consist of two differ type of electrode are dip into the electrolyte solution. Normally can write in this form

$$Zn/Zn^{2+}//Cu^{2+}/Cu$$

The zinc anode (oxidation) reaction is

$$Zn \longrightarrow Zn^{2+}+2e^{-}$$

And the copper cathode (reduction) reaction is

$$Cu^{2+}+2e^{-} \longrightarrow Cu$$

From these reactions, the theoretical potential obtainable from the cell can be calculated. The general form of electro potential equation is

$$E = E^0 + (RT/nF)\ (\ln [Ox]/[Red])$$

Where R = gas constant (8.314 J/mol.K)

T = temperature (K)

F = Faraday's constant (96,500 C/mol)

n = number of ion

E^0 = standard electropotential

[Ox] = concentration of oxidation

[Red] = concentration of reduction

The electropotential measurement can be done by using one electrode as the standard potential electrode compared with other electrodes. The most common reference electrode in the laboratory is the saturated calomel electrode (SCE). For the SCE, a combination of Hg_2Cl_2, mercury and a solution of chloride ions provide the very stable and reproducible potential.

2.2.3 Kinetics

Chemical kinetic is a study of the rate of such relation. Corrosion in aqueous systems is governed primarily by electrochemical reaction. The consideration of thermodynamics implicates corrosion reaction as evidenced by electrochemical potential. When the current flows, the corrosion change is occurred. Corrosion reaction which is not in equilibrium causes current to flow, so investigation of the relationship between potential and current is for the kinetics of corrosion.

Faraday's Law

The rate of electron flow during the reaction is the reaction rate. The measurement of corrosion rate is the measurement of current by using electrochemical method. Electrochemical reactions either produce or consume electrons. Therefore, the rate of electron flow to or from a reacting interface is a measure of reaction rate. Electron flow is conveniently measured as current (I) , in amperes, where I amperes is equal to 1 coulomb of charge (6.2×10^{18} electrons) per second. The proportionality between I and mass reacted, m, in an electrochemical reaction is given by Faraday's law:

$$m = Ita/nF$$

Where: F = Faraday's constant (96,500 coulombs/equivalent)

n = the number of equivalents exchanged

a = atomic weight

t = time

A divide of this equation through by time, t and the surface area, A, yields the corrosion rate, r:

$$r = m/tA = ia/nF$$

Where: i = current density (i = I/A)

2.3 Surfactant

The materials that preferentially adsorb at interfaces as a result of the presence of lyophilic and lyophobic structural units the adsorption generally result in the modification of the surface or interfacial properties of the system. Uniquely, if the concentration of surfactant reached at some specific point, it can assemble together in the bulk solution forming an aggregate which called as micelle.

Various types of surfactant compounds, organic inhibitors, have been use as inhibiting agent for corrosion control in many different environments. In general, surfactants are considered to be amphiphilic compound which composed of 2 parts, meaning they contain both hydrophobic and hydrophilic group. This made surfactants soluble in both water and organic solvents. [12]

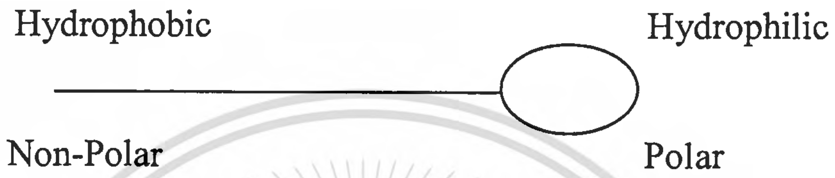


Figure 2.10 Amphiphilic molecule

2.3.1Classification of surfactant

Categorization of surfactants has been done according to the charge on its head. In case of no charge presented on its head it is called as non-ionic surfactant. If the hydrophilic head carry a negative charge so it is called an-ionic; if the charge is positive, it is called as cat-ionic and if the surfactant can be both positive and negative charged its termed Amphoteric. [12]

2.3.1.1 Anionic Surfactant

Anionic Surfactants, The largest class of surface active agent being use today, constituting up to 70-75% of the total worldwide surfactant consumption. The variety of anionic materials arises primarily from the many types of hydrophobic groups that can be modified by the addition of the proper anionic species. Some examples of well known anionic surfactant are shown in Figure 2.11. [12,13]

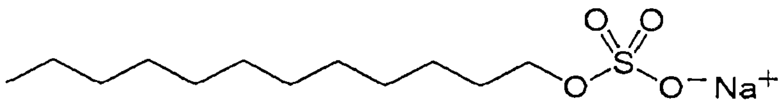


Figure 2.11 Sodium dodecyl sulfate (SDS or NaDS) ($C_{12}H_{25}SO_4Na$) [13]

2.3.1.2 Cationic Surfactant

Surfactants which carrying positive charge on its head, first became important when the commercial potential of their bacteriostatic properties in 1938. Many applications of cationic surfactants have been developed since world war two. Currently this type of surfactant plays an important role as an antiseptic agent in cosmetic, as general fungicides and germicides, as fabric softeners and hair conditioner. [12,13]

Figure 2.12 Cetylpyridinium chloride (CPC) [13]

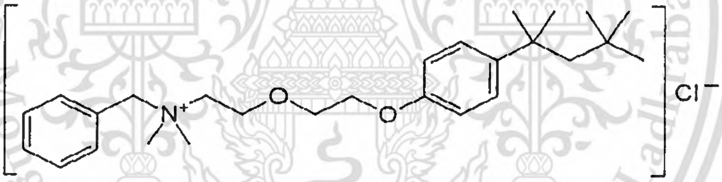


Figure 2.13 Benzethonium chloride [13]

2.3.1.3 Nonionic Surfactants

The term nonionic refer to surfactant that carry no electrical charged on its head, their solubility in water derived from the polar functionality capable of hydrogen bonding interaction with water. Some advantages of nonionic surfactant came from their charge less head, including lower sensitivity to the presences of electrolytes in the system, a reduced effect of solution pH, and the synthetic flexibility of the ability to design the required degree of solubility in to the molecule by the careful control of the size of the hydrophilic group.

Figure 2.14, 2.15, 2.16 shows some of the nonionic surfactant containing different size of hydrophilic group. [12]

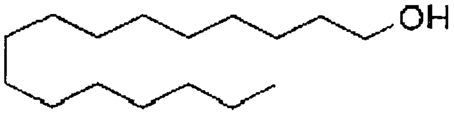


Figure 2.14 Cetyl alcohol [13]

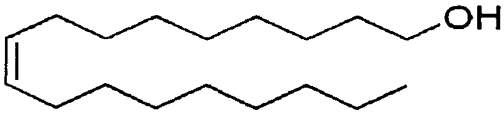


Figure 2.15 Oleyl alcohol [13]

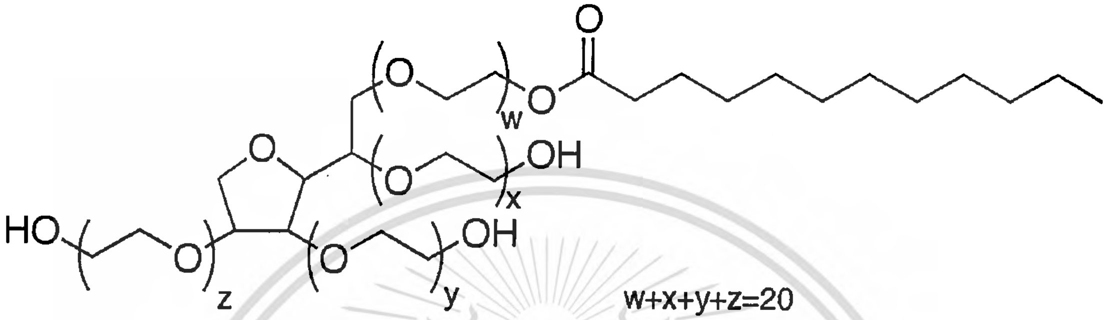


Figure2.16 Polysorbate 20 (Tween 20) [13]

2.3.1.4 Amphoteric Surfactants

These types of surfactant can be both cationic and anionic depending on the pH or other solution conditions, including those that are zwitterionic which contain permanently charged of each type. Although amphoteric materials represent only small portion of total worldwide surfactant production, their market position still increasing significantly due to their unique characteristic that such materials can impart to a formulation.

Utilization of their uniqueness can be seen in some biological contact such as "no tear" baby shampoo. In general, these types of surfactant are categorized in to four main groups which are imidazoline, betaines and sufobetaines, amino acid derivatives, and lecithin and related phosphatides. [14]

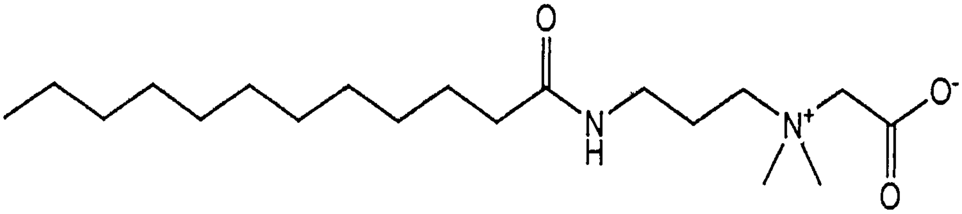
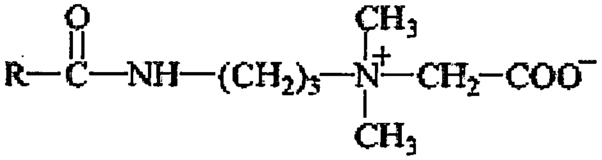


Figure 2.17 Cocamidopropyl betaine (CAPB) [13]



$$R-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{N^+}}}}-CH_2-COO^-$$

Figure 2.18 Alkylamidopropyl betaine [13]

2.3.2 Micelle [14]

The word micelle refers to an aggregation of surfactant into cluster or micelle in dilute solutions. Typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, the hydrophobic tail regions in the micelle centre(oil-in-water micelle). [13]

Another type which the head group agglomerate at the center and their tails point out called as inverse micelle (water-in-oil micelle).The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micelle is known as micellisation and forms part of the phase behavior of many lipids according to their polymorphism.

Micelle start to form when a sufficient concentration is reached (the CMC), and the temperature of the system is greater than the critical micelle temperature, or Krafft temperature. Many form of micelle are observed, some of them are shown in Figure 2.19

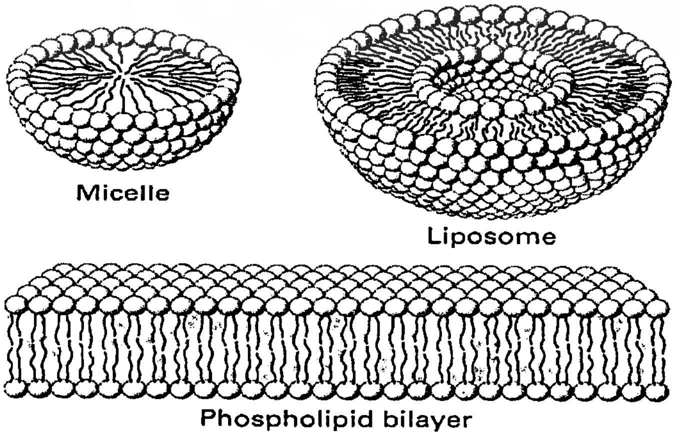


Figure 2.19 Basic forms of micelle [13]

2.3.2.1 Citical Micelle Concentration

Critical micelle concentration (CMC) is defined as the concentration of surfactants above which micelles are spontaneously formed. When the surface coverage by the surfactants increases and the surface free energy (surface tension) has decreased, the surfactants start aggregating into micelles, thus again decreasing the system free energy by decreasing the contact area of hydrophobic parts of the surfactant with water. Upon reaching CMC, any further addition of surfactants will just increase the number of micelles (in the ideal case).

In determining CMC, some experimental procedure may be employed e.g. conductivity measurement, surface tension technique and viscosity measurement.

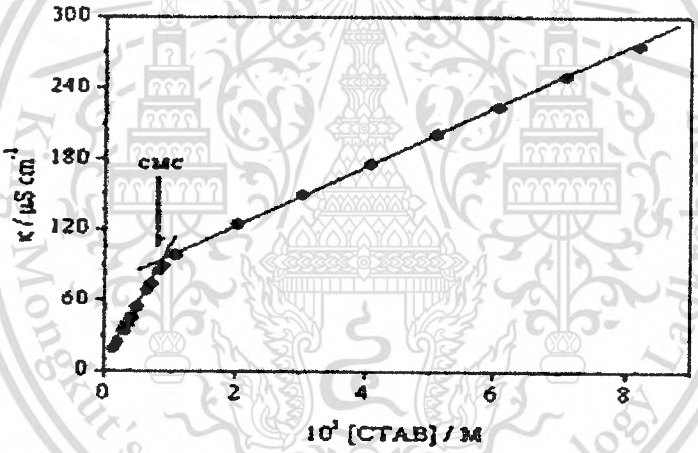


Figure 2.20 CMC measurements by using Conductivity measurement [13]

2.4 Inhibition

From an ancient time, many phenomena has been notify human to realize the significance of corrosion, as corrosion is death, an irreversible reaction that need to supply large amount of energy to forge, there is no cure, prevention is the only solution. Humans try to develop their new innovation in order to slow down the damage or get rid of them if possible.

Now a day, materials such as metals and alloys are extensively use in manufacturing and processing of many industry as they can with stand high temperature and pressure. More over, another specialty that can be enhanced by an addition of additives or further strengthens techniques makes metals and alloys be the first choice in consideration while materials selection are introduced. However, there is no materials that can last for centuries or perfectly immune in all kind of environments, so as metals and alloys, even though they can satisfy the need of strength and durability, but still can being degraded by the corrosion effects, accordingly, corrosion control of metals and alloys against the corrosive environments are being investigated. [12]

2.4.1 Types of protection

Many solutions of corrosion control and protection are either obtained from researching in laboratory or developed by practical experiences

2.4.1.1 Coating

Coating is a common method use for inhibiting metals and alloys from corrosive environment using an inhibitive pigment or some types of polymer coating on the surface object. As coating is quite simple compared to another technique so we can see this kind of materials protection quite often for example in cars coating, house painting, metal pipe coated with some types of polymer and etc. This method is based on excluding the corrosive environment from the substrate that means the materials will not be exposed to the environment due to the prohibition of coating materials. In common painting materials, there are 3 parts that are necessary. [9,10]

First is binder, can be sub divided in to an oil based and latex based binder which oil base refer to the pigment that made from vegetable oil and alkyds, on the other hand latex based binder composed of solid plastic like materials dispersed in water come out like white liquid called latex or emulsion. Binder is a very important ingredient that affects major properties of the coating, especially: adhesion force, resistance to blistering, cracking and peeling, more over this part also take the responsibilities of leveling and film building as well. Binder it self usually present in form of clear and glossy film when dried.

Second part is pigments which normally indicate the color of the paint must be stable in solid form at ambient temperature, usually have special properties e.g.

anticorrosive properties. Now, many chemical substances have been used as pigment to obtain high degree of inhibition.

Third part is a solvent that help adjust the viscosity for easily processing and utilization. This part usually evaporate out when finished film formation step.

The film formation of paints started when the paint is being applied on to the surface and the water or solvent evaporate out, the particle of binder and pigment will come closer and closer as a result of solvent evaporation. At last, binder and pigment molecules will fuse together with great force forming a film on the substrate. This process is called coalescence.

2.4.1.2 Anodizing

Anodize method, the term anodize came from being treated at anode electrode in an electrical circuit, simply referred to the electrolytic passivation process that change the surface of metals in to metal oxide called anodic films. These oxide films not only enhance the corrosion resistance by turned into an oxide form but it also providing a better adhesion for coating materials as well. Now, many types of metals and alloys has been use this technique to increase corrosion resistance, the most popular are those Aluminums and their alloys. Some other metals such as Zinc, Magnesium and Niobium are also available for this kind of protection too. [9]

Although this technique is very effective but it still has a limitation, in some substrates the present or occurrence of an oxide film does not strongly adhere to the substrate but flakes off instead as rust e.g. Carbon steel or iron. The rust neither slows down the corrosion rate nor inhibits the substrate from the corrosive environment. Further technique that help anodizing method achieve higher inhibition efficiency is sealing as coating metal oxide it self occur in a porous film even if it is thick. There are two different ways of sealing, first is simply immerse anodized object in to hot boiling de-ionized water or steam. The oxide film will be converted in to hydrated form reduce the porosity of the surface. Second way is cold sealing which pores are closed by impregnation of sealant at room temperature. Cold sealing technique is more popular due to energy savings.

The anodic film is generated by passing a direct current through an electrolytic solution which the object stood at anode side. A current is releasing hydrogen at cathode together with oxygen at anode, creating an oxide film. Mostly the current applied is in range of 1-300V DC ,depends on the area of materials being anodized, higher voltage result in thicker coating formed in sulfuric and organic acid.

Anodizing is performed in an acid solution as acids can slowly dissolve oxide, this kind of action will balance the oxidation rate forming a microscopic pores 10-150 nm. These pores allow the electrolyte solution and current to reach the substrate and further growth the coating to greater thickness beyond auto passivation. Some conditions such as acidity, electrolyte concentration, temperature and current need to be in control in order to achieve a consistent oxide layer.

The film thickness and hardness can be obtained from low concentration solution, lower temperature together with higher voltages and currents. In anodizing oxide film layer can be ranged from thinner than 0.5 microns up to 150 microns according to the use of the substrates.

The advantages and disadvantages of this technique are

Advantage

Normally anodic films have more adherent and stronger than most types of paints so less cracking and peeling.

Disadvantage

As anodizing method has their limitation due to the characteristic of metal oxide film so only some type of metals and alloys can under goes this technique.

2.4.1.3 Cathodic protection

Cathodic protection, a name which is almost self-explanting, can be divided in to two types which are sacrificial anode and Impress current cathodic protection (ICCP). [10]

2.4.1.3.1 Sacrificial Anode

Cathodic protection has been in use since 1824, this technique is one of the well known methods for handling corrosion behavior by making it works as cathode in an electrochemical cell, achieved by placing the substrates to be protected with another metal which is more corrosive, sacrificial anodes. At present, galvanic or sacrificial anodes are produced in many shapes e.g. zinc, aluminium and magnesium, these kind of metals have more appropriate properties such as electrochemical potential ,current capacity and consumption rate compared to iron. In general, although the potential of sacrificial anodes have higher negative electrochemical potential than those substrates to be protected but they still need to be polarized (pushed) more negative until the surface has a uniform potential. At that stage, the driving force for the corrosion reaction is halted. [13,15]

2.4.1.3.2 Impress current cathodic protection (ICCP)

Impress current cathodic protection (ICCP) is designed for a large structure which sacrificial anode or galvanic anode can not deliver enough current to provide a complete protection. ICCP system is constructed by connect the anode to a DC power source. This technique always used in conjunction with protective coating, the latter being intended as primary protection with the use of cathodic protector as back up in those area where coating defects may be present. [13]

2.4.1.3.3 Galvanization

Another method that may refer to the cathodic protection is galvanization. This is done by passing iron or steel through molten zinc at a temperature around 860 °F. The coated zinc when exposed to the atmosphere, reacts with oxygen forming zinc oxide, then further reacts with carbon dioxide to form zinc carbonate. At this stage, the coated zinc carbonate can efficiently stop further corrosion in many circumstances, protecting the steel from corrosion damage. [10,13]

The reason why galvanizing is said to be one of cathodic protection because when the coated zinc is scratched or smashed out and the steel is exposed, the surrounding area of zinc acts as sacrificial anode forming a galvanic cell, provide a localized cathodic protection.

2.4.1.4 Corrosion inhibitors

Defending against corrosion by using a corrosion inhibitors have been used for long time in many industries especially in oil extraction processes. However, major parts of knowledge have grown from doing trial and error experiments due to the insufficient of theoretical information. Corrosion inhibitor is some what a chemical substance that can efficiently decrease the corrosion rate while using in only small concentrations. The corrosion efficiency can be expressed by the following formula. [16]

$$\text{Inhibition Efficiency (\%)} = 100 \times \frac{(\text{CR uninhibited} - \text{CR inhibited})}{\text{CR uninhibited}}$$

Where CR uninhibited = corrosion rate of the uninhibited system
CR inhibited = corrosion rate of the inhibited system

In common, corrosion efficiency is directly proportional to an inhibitor concentration in the system. Many relating article and scientific technical literature has reports and lists numerous chemical substances that exhibit the inhibition effect but there are only some that practically use. This because of the toxicity, environmental concern and cost of production or synthesize. Commercially corrosion inhibitor are trading under different unique name with few or none information about there composition. Practically, formulations of the inhibitor compose of one or more anticorrosive agent with an additional of additives that enhance the inhibition properties. [16]

In general, corrosion inhibitor operation is to react with the metals surface or its environments forming a protective film by adsorbing themselves on the metallic surface.

Other important roles of corrosion inhibitor are listed below.

-Increasing the anodic or cathodic polarization behavior

-reducing the movement of diffusion of ions to the metallic surface

-Increasing the electrical resistance of the metallic surface

Classification of inhibitor have been done differently by many author, the one shown below is grouped by their functionality.

- Inorganic Inhibitor, a kind of crystalline salts e.g. sodium phosphate, molybdate or chromate. This should be noted that only the negative anions are involved in corrosion inhibiting mechanism.

- Organic anionic, frequently use in cooling water and antifreeze solutions e.g. sodium sulfonates, phosphonates.
- Organic Cationic, generally be a large aliphatic or aromatic compound with positively charged amine group.

However, another most popular organization scheme has been regrouping corrosion inhibitor in a functionality scheme as follows.

2.4.1.4.1 Anodic Inhibitor (Passivating inhibitor)

This type of inhibitor affects a large anodic shift of corrosion potential by forcing the metallic surface in to the passivation range, can be further divided in to oxidizing anions and non oxidizing anions, which the first species can passivate the steel in an absence of oxygen but another require a present of oxygen. [15]

It should be noted that, these kind of inhibitor are the most effective and also most widely use compares to other.

2.4.1.4.2 Precipitation inhibitors

These kinds of inhibitors are compound that curse the formation of precipitates on the metallic surface, providing a protective film. For example hard water that high in magnesium and calcium is less corrosive than soft water soft water because of the higher tendency of salt in the hard water to precipitate and form a protective film. [16]

2.4.1.4.3 Organic Inhibitors

Normally, when we talk about organic inhibitor, it's implying the meaning of utilizing of surfactant in order to reduce the corrosion effect. [16,17]

Classification of surfactant has been done according to the charge on its head. In case of no charge presented on its head it is called as non-ionic surfactant. If the hydrophilic head carry negative charge so it is called an-ionic; if the charge is positive, it is called as cat-ionic and if the surfactant contain both positive and negative charge its termed zwitterionic. [13,17]

Protection mechanism of organic inhibitor usually designated as a hydrophobic protection film covered on a metallic surface. In order to fully cover the whole surface, sufficient concentration is required. As film forming is an adsorption process, chemical composition, molecular structure and their affinities are all affect the effectiveness of the protection layer. External variables such as temperature and pressure also deal large effect on efficiency by influence the adsorption mechanism. [16,17]

In this article, we are interested in using the surfactant named Cetyl trimethylammonium bromide (CTAB) which is one of the well known cationic surfactant. The information about chemical and physical properties is shown below.

Cetyl trimethylammonium bromide (CTAB) [13]

IUPAC Name: hexadecyl-trimethyl-ammonium bromide

Molecular Formular: $C_{19}H_{42}BrN$

Molar mass: 364.448

Melting point: 237-243

Micelle:

CTAB forms micelles in aqueous solutions. At 303 K (30 °C) it forms micelles with aggregation number 75-120 (depending on method of determination, usually avg. ~95) and degree of ionization α (fractional charge) 0.2 - 0.1 (from low to high concentration).

Application and uses:

Cetrimonium bromide ($(C_{16}H_{33})N(CH_3)_3Br$) is one of the components of the topical antiseptic cetrimide. The cetrimonium cation is an effective antiseptic agent against bacteria and fungi. It is a cationic surfactant. Its uses include providing a buffer solution for the extraction of DNA. It has been widely used in synthesis of gold nanoparticles (e.g., spheres, rods, bipyramids). It is also widely used in hair conditioning products.

Molecular structure:

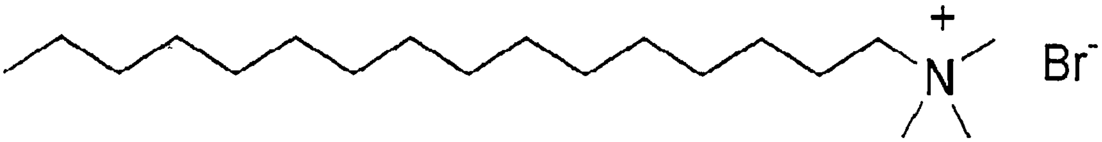


Figure 2.21 Molecular structure of CTAB

2.5 Review about related experiment

Caroline M. Murira, Christian Punckt, Hannes C. Schniepp, Boris Khusid, and Ilhan A. Aksay[18], has studied an inhibition and promotion of copper corrosion by CTAB in a microreactor system. They report on an optical microscopy technique for the analysis of corrosion kinetics of metal thin films in microreactor systems and use it to study the role of cetyltrimethylammonium bromide surfactant as a corrosion inhibitor in a copper-gold galvanic coplanar microsystem. A minimum in the dissolution rate of copper is observed when the concentration is ~ 0.8 mM. They complement their optical measurements with zero resistance ammetry (ZRA) and atomic force microscopy (AFM) and show that the role of CTAB as both a corrosion inhibitor and promoter relates to its different functions on the cathode and the anode, while the surfactant inhibits cathodic reaction on gold, it also promotes the corrosion of copper. For the result, the experiments with separated half cells show that CTAB promotes the corrosion of copper in copper-gold galvanic pair which is most likely due to the catalytic action of bromide counterions on the copper surface. These measurements also show that CTAB inhibits the reaction taking place on the gold electrode. These two competing processes lead to the minimum in dissolution rate as a function of CTAB concentration.

S. Ramesh, S. Rajeswari, S. Maruthamuthu[19], has studied corrosion inhibition of copper by new triazole phosphonate derivatives. Study of mechanistic action of corrosion inhibitors has relevance both from the point of view of a search for new inhibitors and also for their effective usage. New corrosion inhibitors, namely 3-vanilidene amino 1,2,4-triazole phosphonate (VATP) and 3-anisalidene amino 1,2,4-triazole phosphonate (AATP) were synthesized and their action along with biocide on corrosion control of copper in neutral aqueous environment has been studied. To analyse their inhibition behavior they employed the potentiodynamic polarization measurement and electrochemical impedance spectroscopy (EIS). Various corrosion parameters such as corrosion potential (E_{corr}),corrosion current density (i_{corr}) and the inhibition efficiency (IE) were determined by Tafel extrapolation method. From the result, VATP showed better protection over the other inhibitors used. The dissolution of copper in presence of VATP and AATP with biocide mixture is negligible compared to blank. A combination of electrochemical methods and surface examination techniques are used investigate the protective film and explain the mechanistic aspects of corrosion inhibition.

Howaida M. El-Kashlan [20], have studied in the kinetic study of the effect of selected surfactants on corrosion of copper. By determined the measuring of the limiting current of anodic dissolution of copper in phosphoric acid in presence and in absence of cetyl trimethyl ammonium bromide (CTAB) and cetyl pyridinium bromide (CPYB). The rate of corrosion is found to decrease by increasing the concentration of the surfactant. The percentage of inhibition ranged from 1.85 to 33.97% depending on the type of surfactant and its concentration. Increasing the copper electrode height, and concentration of H_3PO_4 decreases the rate of copper corrosion. The investigated adsorption isotherms indicate that the two surfactants fit Langmuir and Flory Huggins isotherm. The thermodynamic parameters show that corrosion is a diffusion controlled process.

Houyi Ma, Shenhao Chen, Bingsheng Yin, Shiyong Zhao, Xianqian Liu [21], has studied the impedance spectroscopic study of corrosion inhibition of copper by surfactants in the acidic solutions. This study aim to investigate how the surfactants of different types, including the cationic surfactant-cetyltrimethylammonium bromide (CTAB), the anodic surfactants-sodium dodecyl sulfate (SDS) and SO, and the nonionic surfactant-polyoxythylene sorbitan monooleate (TWEEN-80), inhibit the copper corrosion in aerated 0.5 $moldm^{-3}$ H_2SO_4 by using electrochemical impedance spectroscopy (EIS), together with other electrochemical techniques, and to propose the adsorption model of surfactants on the copper surface. These surfactants acted as the mixed-type inhibitors and lowered the corrosion reactions by blocking the copper surface through electrostatic adsorption or chemisorption. The inhibitor effectiveness increased with the exposure time to aggressive solutions, reached a maximum and then decreased, which implies the orientation change of absorbed surfactant molecules on the surface. CTAB inhibited most effectively the copper corrosion among the four surfactants. The copper surface was determined to be positively charged in sulfuric acid solutions at the corrosion potential, which is unfavourable for electrostatic adsorption of cationic surfactant,CTAB. The IE decreases with the immersion time despite the fact more the surfactant molecules adsorb at copper/solution interface.

Houyi Ma,Shenhao Chen, Shiyong Zhao, Xiagqian Liu, and Degang Li [22], has studied corrosion behavior of copper in acidic solutions containing cetyltrimethylammonium bromide. They investigated the inhibitive effect of CTAB on copper corrosion in aerated H_2SO_4 solution by using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. And they showed that CTAB inhibited copper corrosion more strongly than tetramethylammonium bromide (TMAB) under the same conditions due to the chemisorption of the n-cetyl group on the copper surface. The surface of the copper electrode was positive charged in sulfuric acid solution at the corrosion potential. The copper corrosion inhibition of CTAB and TMAB was attributed to the synergistic effect between bromide anions and positive quaternary ammonium ions. From the result can conclude that the inhibition efficiency of CTAB depended on the CTAB concentration and the immersion time for the copper electrode in corrosive solutions. Based upon the variation of impedance display of copper with the CTAB concentration and the immersion time, and adsorption model of CTAB on the copper surface was proposed. The $C_{16}H_{33}N(CH_3)^{3+}$ ions adsorbed on the copper surface by horizontal binding to hydrophobic hydrocarbon chains at the low CTAB concentrations, whereas a perpendicular adsorption dominated as a result of an interhydrophobic chain interaction when the CTAB concentration increased.

Chapter 3

Experimental

3.1 Chemicals

1. Sulfuric acid
2. Cetyl trimethylammonium bromide (CTAB)
3. Distilled water

3.2 Materials and apparatus

1. Copper sample (purity 99.99%)
2. Conductometer
3. Potentiostat
4. Ultrasonic bath
5. Corrosion cell
6. Platinum electrode
7. Saturated calomel electrode (SCE)
8. Magnetic Stirrer
9. Forceps
10. Dryer
11. Air pump

3.3 Procedure

In studying the influence of cetyl trimethylammonium bromide (CTAB) on corrosion behavior of copper consists of the following stages.

3.3.1 Critical Micelle Concentration measurement

The critical micelle concentration (CMC) of surfactant in distilled water, 0.01 and 1 N sulfuric acid has been done by using conductivity measurement, at approximately 25 degree Celsius. The CMC in acidic solution believes to be lower than in pure distilled water (9 mM) based on literatures. The measurement is described as following.

1. Preparation of 0.01M cetyl trimethylammonium bromide (CTAB) stock solution.
2. Fill in different portions of surfactant in 100ml volumetric flask.
3. Weight sulfuric acid that will give a desire acid concentration and put in to each flask.
4. Fill up the prepared 100ml volumetric flasks with distilled water until 100ml volumes are reached.
5. Measure the conductivity value of the prepared samples.
6. Plot the graph between conductivity and Surfactant concentration to find CMC.

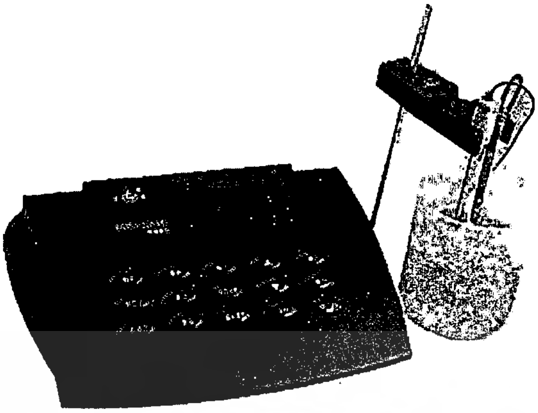


Figure 3.1 Conductometer

3.3.2 Sample preparation

First, copper rod was cut to obtain diameter of 0.625 inch. Before each experiment, copper sample was ground with #600 emery paper, followed by #1200 emery papers, to eliminate oxide and dirt on the copper surface. Second, oil and impurity that may originate by touching sample with bare hand are removed by using ultrasonic bath. The sample was installed in a sample holder and only its cross-sectional area was allowed to contact the solution.

3.3.3 Chemical preparation

1. Weigh 51g and 0.51g of 96% Sulfuric and put in to in 1000ml volumetric flask. (for distilled water skip this step).

2. Add desired amount of CTAB in to the prepared volumetric flasks.

3. Fill up the distilled water until 1000ml volume reached, and as a result, distilled water, 0.01N and 1N sulfuric acid solution with different concentrations of CTAB are obtained respectively.

3.4 Corrosion testing

Potentiodynamic polarization measurement consists of three electrodes.

- Working electrode (the sample, copper)
- Reference electrode (saturated calomel electrode)
- Counter electrode (platinum plate)

Aside from the three electrodes, air pump was installed in order to maintain saturation of oxygen level in the solution and also provide continuous circulation in the system. Potentiostat was connected through an adapter for determining the polarization curve. After the experiment has been finished, potentiodynamic polarization curve was obtained. The program will rearrange data in form of Tafel plot, log current (log I) versus potential (E). Finally, corrosion current density (i_{corr}) and corrosion potential (E_{corr}) are obtained.

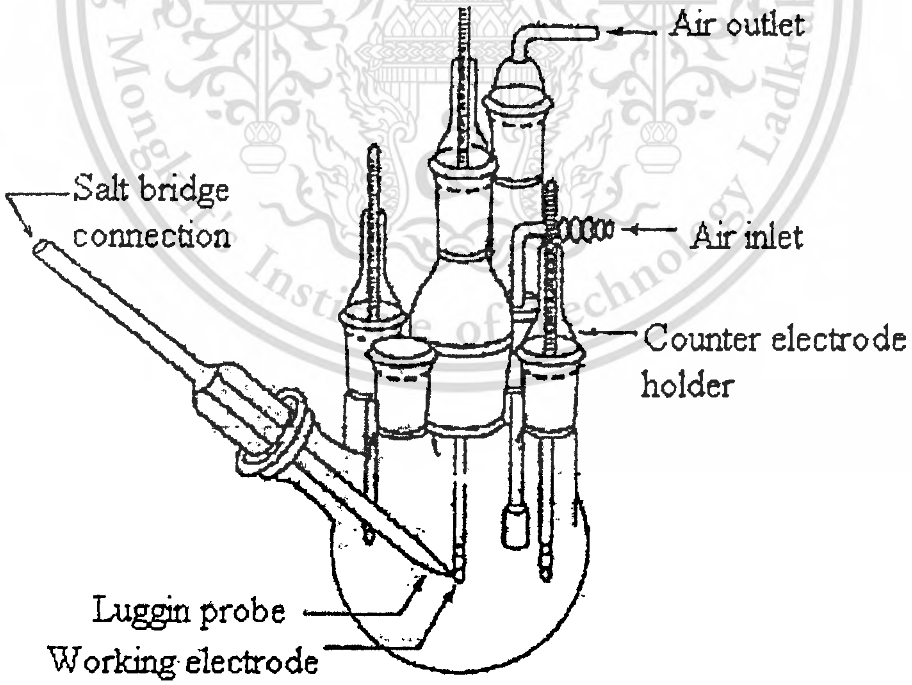


Figure 3.2 Corrosion cell [3]

3.5 Data analysis

3.5.1 Corrosion current density (i_{corr})

Corrosion current density (i_{corr}) indicates the corrosion rate according to Faraday's law.

$$W = iAtM/nF$$

Where; W = weight loss (g)/cm^2×year

M = atomic weight of metal (g/mol)

i = current density (A/cm^2)

n = number of electron moles during corrosion

F = Faraday's constant (96,500 C/mol)

A = surface area (cm^2)

t = time (s)

Chapter 4
Results and Discussion

4.1 Critical micelle concentration (CMC) of cetyl trimethylammonium bromide (CTAB) in sulfuric solution

4.1.1 CMC of CTAB in distilled water

Determination of critical micelle concentration of CTAB in distilled water was done by using conductivity measurement. The conductive property of sample solution is directly proportional to an amount of ion (carrier) and mobility of the carrier. However, when the CMC point is reached, surfactant monomers started to aggregate together forming micelle in the system which then decreases down their mobility. Therefore, the rate of increasing in conductivity becomes slower. The CMC point can be observed from the drastically change in conductivity slope. The conductivity data of CTAB in distilled water are shown in the Table 4.1.

Table 4.1 Conductivity of distilled water with various concentration of CTAB

Concentration of CTAB (mole/L)	Conductivity (µS/cm)
0.0004	43.3
0.0005	54.1
0.0006	58.8
0.0007	71.3
0.0008	81.0
0.0009	92.4
0.0010	96.5
0.0011	97.0
0.0012	95.6
0.0013	100.1

As we plotted the data of conductivity versus concentration of CTAB in distilled water, the CMC point is obtained. Figure 4.1 shows the CMC of CTAB in distilled water.

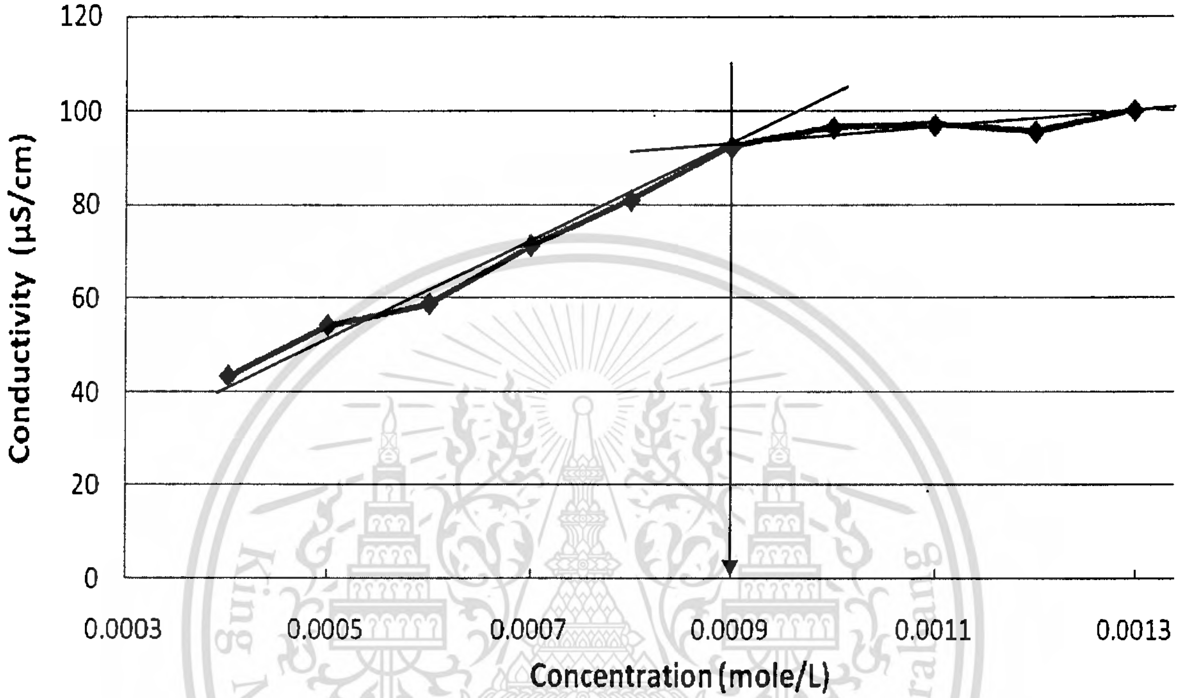


Figure 4.1 CMC of CTAB in distilled water

4.1.2 CMC of CTAB in 0.01N Sulfuric acid

Critical micelle concentration (CMC) in 0.01N sulfuric acid was carried out by using the same experiment. The result has shown the lower in CMC as compared to those in distilled water (0.9mM for distilled water and 0.7mM for 0.01N sulfuric). The explanation may be proposed by the postulation that the sulfate anions (SO_4^{2-}) (from sulfuric acid) which carrying negative charge acts as a binder to reduce the electrostatic repulsion force between the hydrophobic head groups (CTAB has positively charged on its head). This makes CTAB monomer in 0.01N sulfuric acid form micelle easier and deform harder than do in pure distilled water, hence the CMC point dropped down. The data of conductivity measurement in 0.01N sulfuric acid are shown in Table 4.2.

Table 4.2 Conductivity of 0.01N sulfuric acid in various concentration of CTAB

Concentration of CTAB (mole/L)	Conductivity (mS/cm)
0.00010	5.980
0.00020	6.000
0.00030	6.030
0.00040	6.040
0.00050	6.050
0.00060	6.060
0.00070	6.080
0.00080	6.070
0.00090	6.080
0.00100	6.085

As the conductivity data versus concentration of CTAB in 0.01N sulfuric acid is plotted, the slope showed a significant change at 0.7mM which indicated the CMC point. Figure 4.2 shows the CMC of CTAB in 0.01N sulfuric acid.

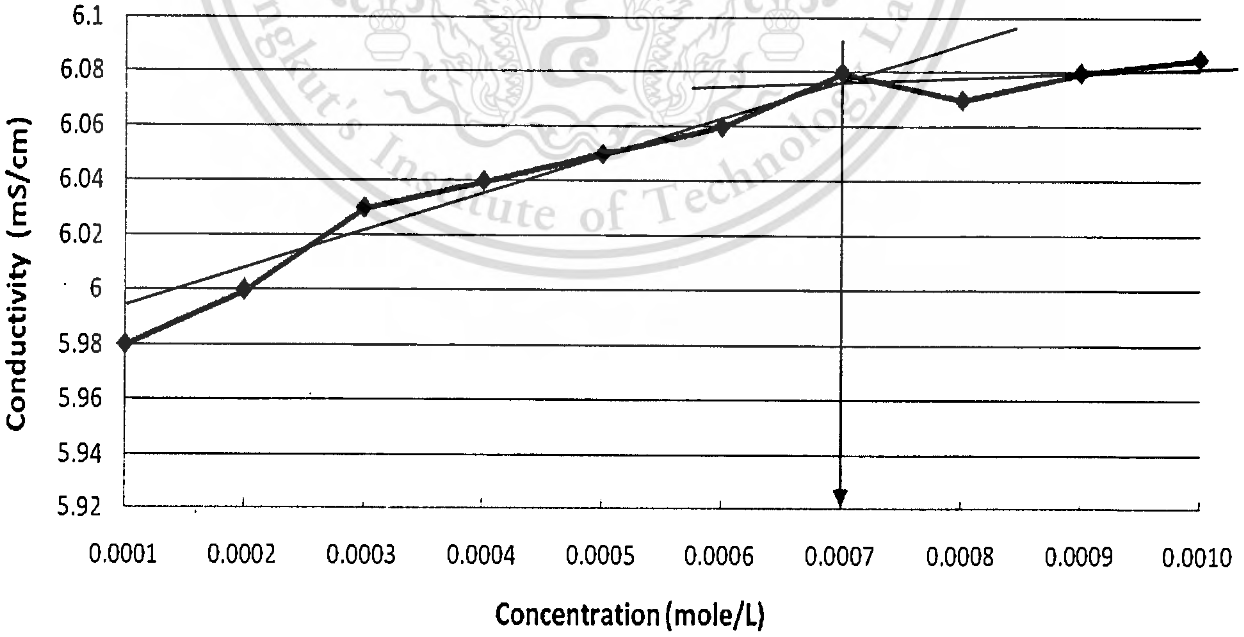


Figure 4.2 CMC of CTAB in 0.01N sulfuric acid

4.1.3 CMC of CTAB in 1N Sulfuric acid

Similarly to the previous experiments, the conductivity data of 1N sulfuric acid were determined by using conductivity measurement. The data showed the change in slope at 0.28mM which is lower than the result from 0.01N sulfuric acid (0.7mM). This experiment was carried out in a more acidic environment, so the lower in CMC is achieved and trend to be decreased even lower. The data of conductivity measurement in 1N sulfuric acid are shown in Table 4.3.

Table 4.3 Conductivity of 1N sulfuric in various concentration of CTAB

Concentration of CTAB (mole/L)	Conductivity (mS/cm)
0.00008	367.0
0.00012	368.0
0.00016	369.0
0.00020	369.0
0.00024	371.0
0.00028	372.0
0.00032	372.0
0.00036	372.5
0.00040	372.0
0.00044	372.5

As we plotted the data of conductivity versus concentration of CTAB in 1N sulfuric acid, the break point at 0.7mM which indicated the CMC point is obtained. Figure 4.3 shows the CMC point of CTAB in 1N sulfuric acid.

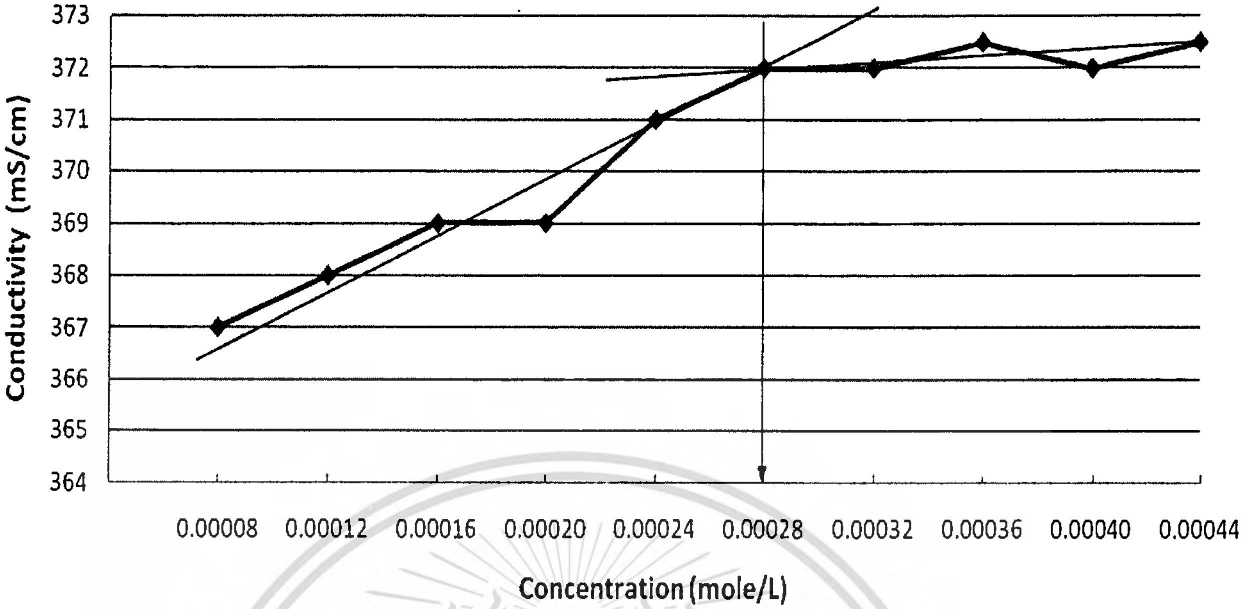


Figure 4.3 CMC of CTAB in 1N sulfuric acid

In comparing the three graphs with different acid concentration, we observed the drop of CMC due the amount of sulfuric acid added. These conclude that the drop in CMC of CTAB is affected by the addition of sulfate anions (SO_4^{2-}) in sulfuric acid.

4.2 Corrosion testing

4.2.1 Corrosion testing of copper in distilled water

By using potentiostat polarization technique, polarization curve of copper in pure distilled water is obtained. Figure 4.4 demonstrates the polarization curve of copper in distilled water without CTAB. The curve showed cathodic and anodic Tafel slope with no passivity, i_{corr} and E_{corr} values are at 2.47×10^{-4} mA/cm^2 and -7mV respectively.

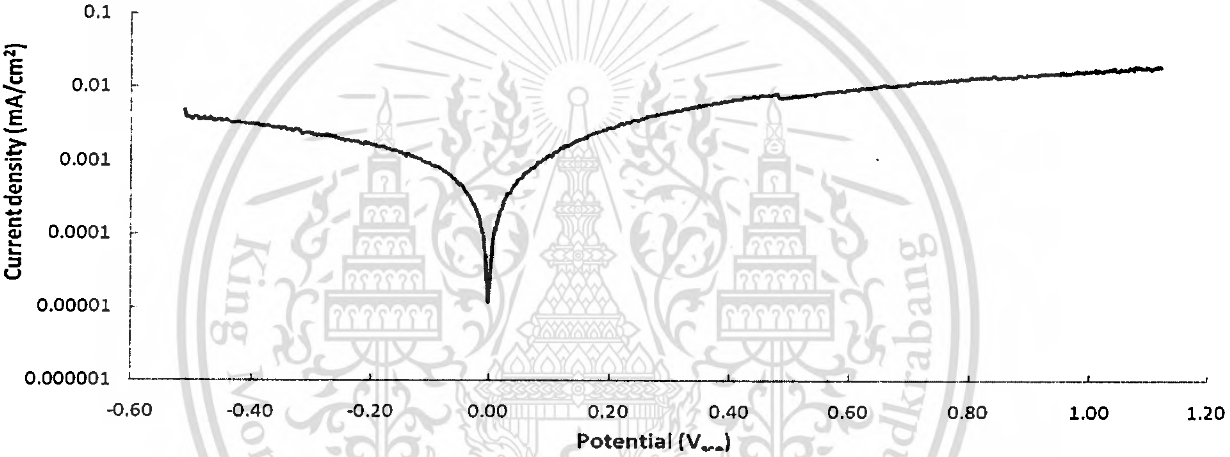


Figure 4.4 Polarization curve of copper without CTAB

Polarization technique is also employed in other experiments with an adding of CTAB. The results are plotted separately in low and high concentrations of CTAB, in order to make them easier to analyze. Polarization curves of Copper in various concentrations of CTAB are shown in Figures 4.5 and 4.6

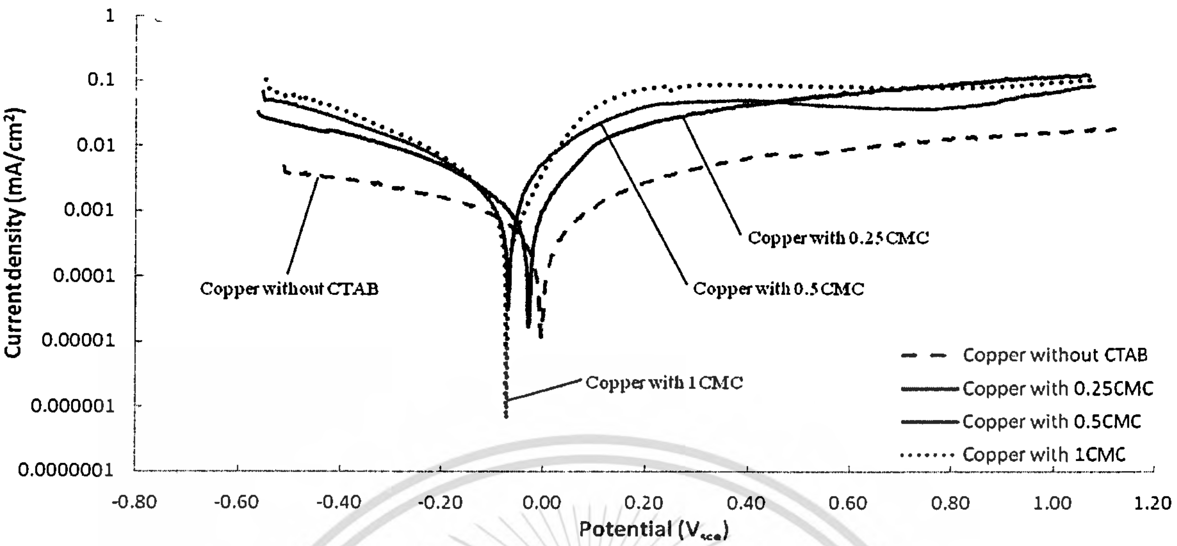


Figure 4.5 Polarization curves of copper in distilled water with low concentrations of CTAB

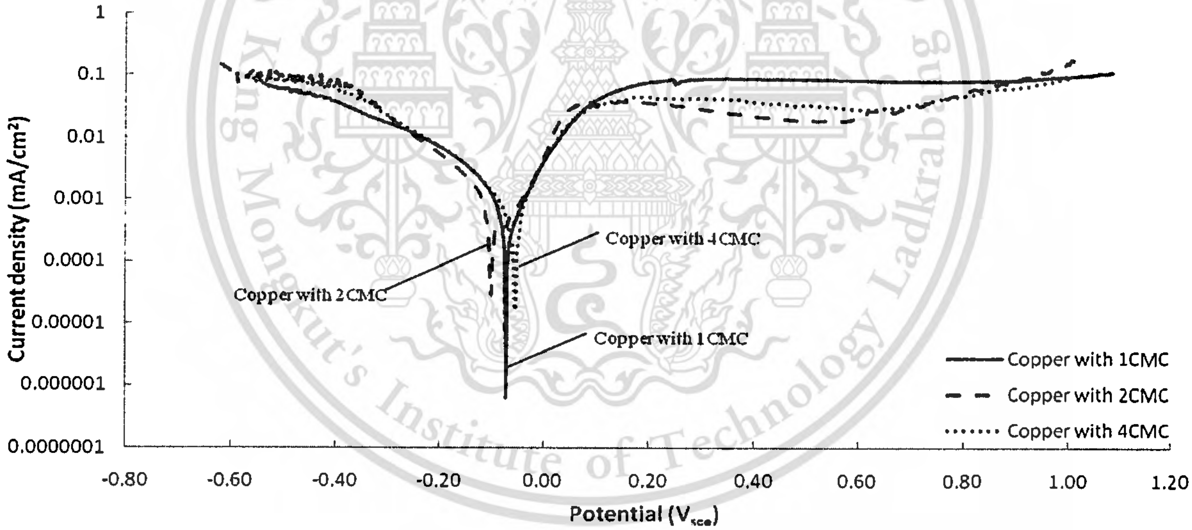


Figure 4.6 Polarization curves of copper in distilled water with high concentrations of CTAB

In comparing polarization curves of copper in distilled water with various concentration of CTAB, the results showed an increasing in current density when more CTAB is added, which led to a higher corrosion rate (i_{corr} shifted from 2.47×10^{-4} mA/cm^2 (distilled water) to 1.417×10^{-3} mA/cm^2 (4CMC)). These can be explained in to two ways, first is the aggressiveness of the electrolytes media that increase significantly while the CTAB is added (the conductivity is doubled). Another is while the surfactant forming a protective film which should help reduces the current density; it also promotes another counter reaction on copper.

According to the results, an exhibited higher in current density is most likely due to the more conductive electrolytes and the action of bromide counter-ions on the copper surface, which are corrosive. Since the experiments was carried out in only a neutral environment, it may be said that the affect of more conductive electrolyte media and bromide counter reaction are dominate in comparing to the protection from an adsorption of $C_{19}H_{42}N^+$.

Faraday's law has been used in calculating corrosion rate, the example of calculation part is shown in the Appendix B. By using the Faraday's Law, corrosion rate of copper in various concentrations of CTAB are obtained. The data of electrochemical parameters of copper which carried out in pure distilled water, in an absence and presence of CTAB are listed in the Table 4.4

Table 4.4 Electrochemical parameter of copper in pure distilled water with various concentrations of CTAB

[CTAB] (×CMC)	i_{corr} (mA/cm^2)	E_{corr} (V_{SCE})	Corrosion rate (g/cm^2.year)
0	2.47×10^{-4}	-0.007	2.564×10^{-3}
0.25	6.65×10^{-4}	-0.030	6.905×10^{-3}
0.5	8.73×10^{-4}	-0.067	9.065×10^{-3}
1	9.96×10^{-4}	-0.071	1.034×10^{-2}
2	1.09×10^{-3}	-0.102	1.132×10^{-2}
4	1.41×10^{-3}	-0.055	1.471×10^{-2}

4.2.2 Corrosion testing of copper in 0.01N sulfuric acid

By using potentiostat polarization technique, polarization curve of the surfactant-free 0.01N H_2SO_4 solution is obtained. Figure 4.7 show the polarization curve of copper in 0.01N sulfuric acid.

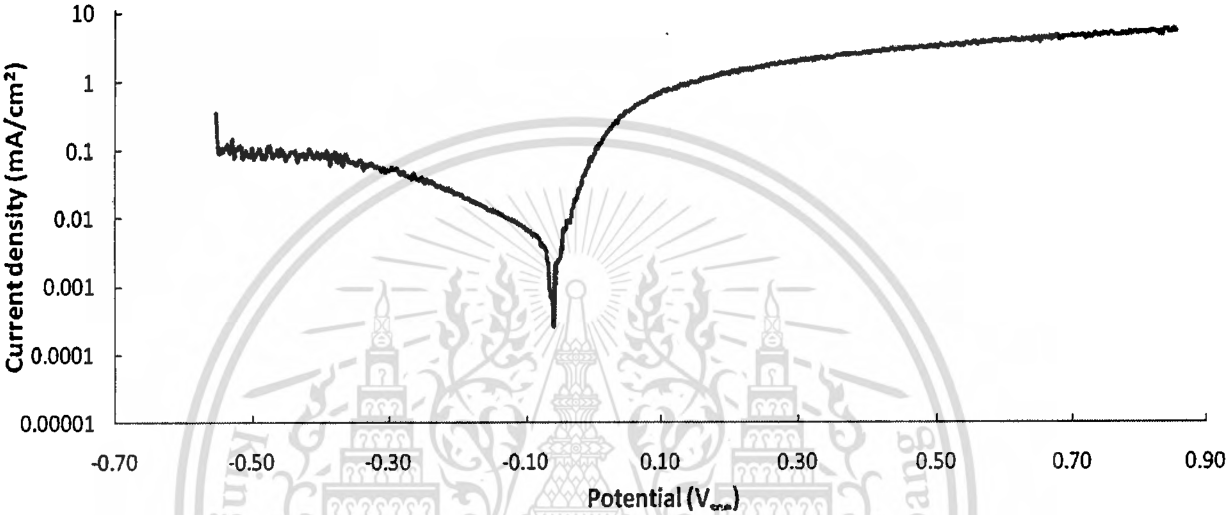


Figure 4.7 Polarization curve of copper in 0.01N sulfuric acid

The result in an absence of CTAB showed a very similar manner of curve in comparing to those in distilled water. It consists of, again, two main parts which are cathodic and anodic curves without any passivity, i_{corr} and E_{corr} value are shown at 3.757×10^{-3} mA/cm^2 and -60mV respectively. The value of i_{corr} has been increased from 2.47×10^{-3} mA/cm^2 in distilled water to 3.757×10^{-3} mA/cm^2 in 0.01N sulfuric, which can clearly be explained by the effect of sulfuric acid in the experimental environment.

After all the experiments have done, polarization curves of copper in 0.01N sulfuric acid in various concentrations of CTAB are shown in Figures 4.8 and 4.9

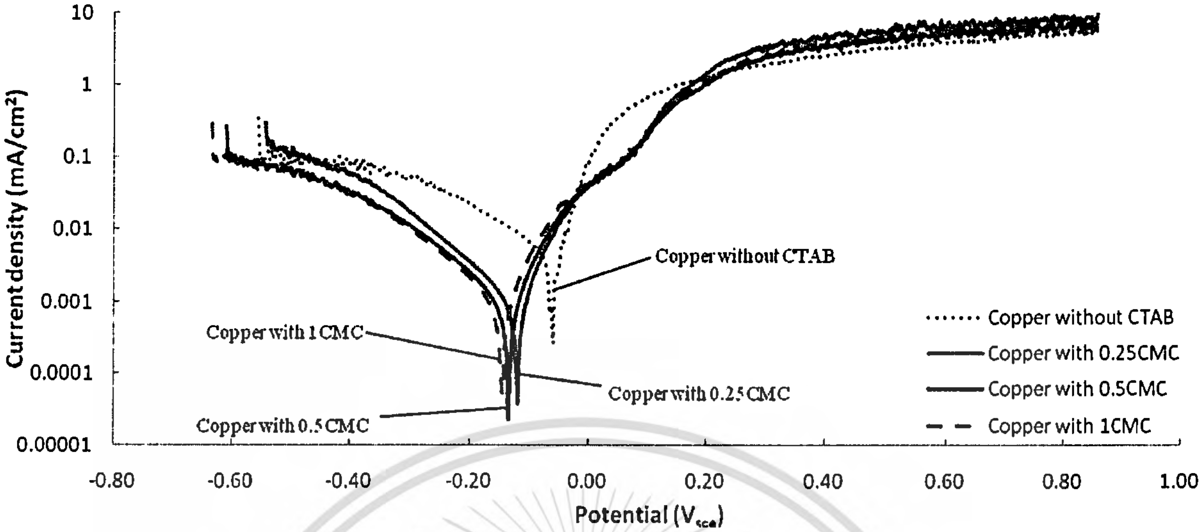


Figure 4.8 Polarization curves of copper in 0.01N sulfuric acid with low concentrations of CTAB

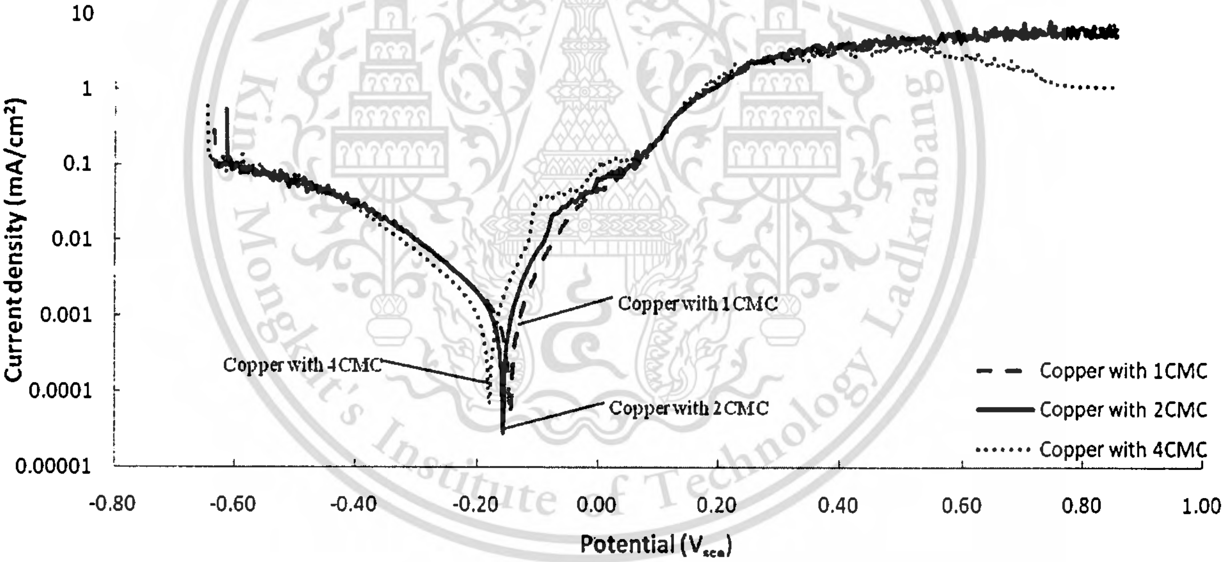


Figure 4.9 Polarization curves of copper in 0.01N sulfuric acid with high concentrations of CTAB

In the experiments, we observed the lowering of i_{corr} and E_{corr} with an increasing of CTAB concentration. The i_{corr} value shows a steady drop from 3.757×10^{-3} mA/cm^2 (no CTAB) to 9.361×10^{-4} mA/cm^2 (4CMC), E_{corr} shifted to more active value -60mV (no CTAB) to -179mV (4CMC). The CTAB monomers can adsorb on the copper surface and formed a protective layer, which help protect the copper from corrosive environment. Figure 4.10 illustrates the adsorption mechanism of CTAB on polarized copper surface.

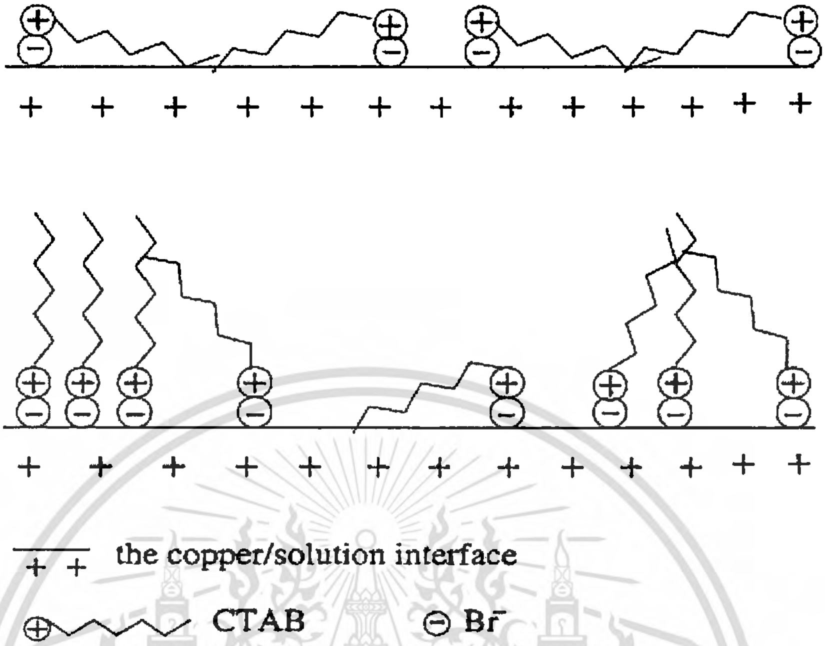


Figure 4.10 Adsorption of CTAB on polarized copper surface [21]

An adsorption mechanism of CTAB is proposed to be bilayer, where the surface of copper is first electrostatically adsorbed by the bromide ions which further attached to the $C_{19}H_{42}N+$. Adsorption of CTAB can possibly occur in perpendicular or in horizontal manner. The more detail on electrochemical parameters of copper which has been tested in 0.01N sulfuric acid in an absence and presence of CTAB are listed in the Table 4.5

Table 4.5 Electrochemical parameters of copper in 0.01N sulfuric acid with various concentrations of CTAB

[CTAB] (×CMC)	i_{corr} (mA/cm^2)	E_{corr} (V_{SCE})	Corrosion rate (g/cm^2.year)
0	3.757×10^{-3}	-0.060	3.901×10^{-2}
0.25	1.003×10^{-3}	-0.119	1.041×10^{-2}
0.5	9.228×10^{-4}	-0.132	9.582×10^{-3}
1	8.798×10^{-4}	-0.144	9.135×10^{-3}
2	9.224×10^{-4}	-0.156	9.578×10^{-3}
4	9.361×10^{-4}	-0.179	9.720×10^{-3}

4.2.3 Corrosion testing of copper in 1N sulfuric acid

From the result, i_{corr} and E_{corr} were at 1.926×10^{-2} mA/cm^2 and -5mV respectively. Figure 4.11 shows the polarization curve of copper in 1N sulfuric acid. The anodic part of the slope exhibit some drop in current density which may cause by the mass transport problem or the formation of copper oxide on the surface.

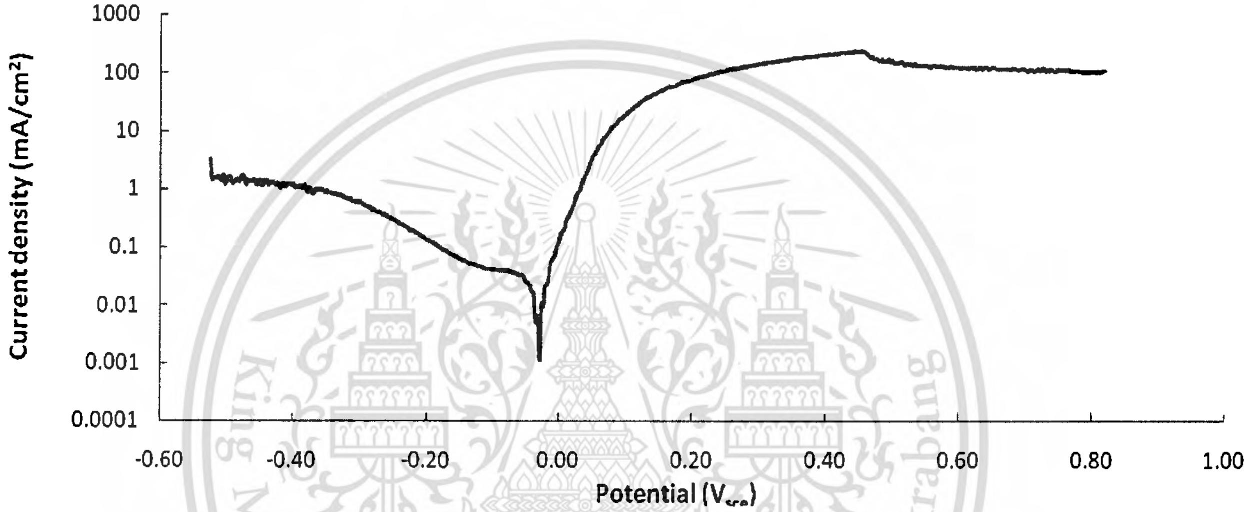


Figure 4.11 Polarization curve of copper in 1N sulfuric acid

The polarization curves of copper in 1N sulfuric with various concentrations of CTAB are shown in the Figure 4.12 and 4.13. The value of i_{corr} and E_{corr} showed a sharp decrease in a presence of low CTAB concentration, i_{corr} dropped from 1.926×10^{-2} mA/cm^2 (without CTAB) to 1.794×10^{-3} mA/cm^2 (0.25CMC) and E_{corr} shifted from -5mV to -106mV.

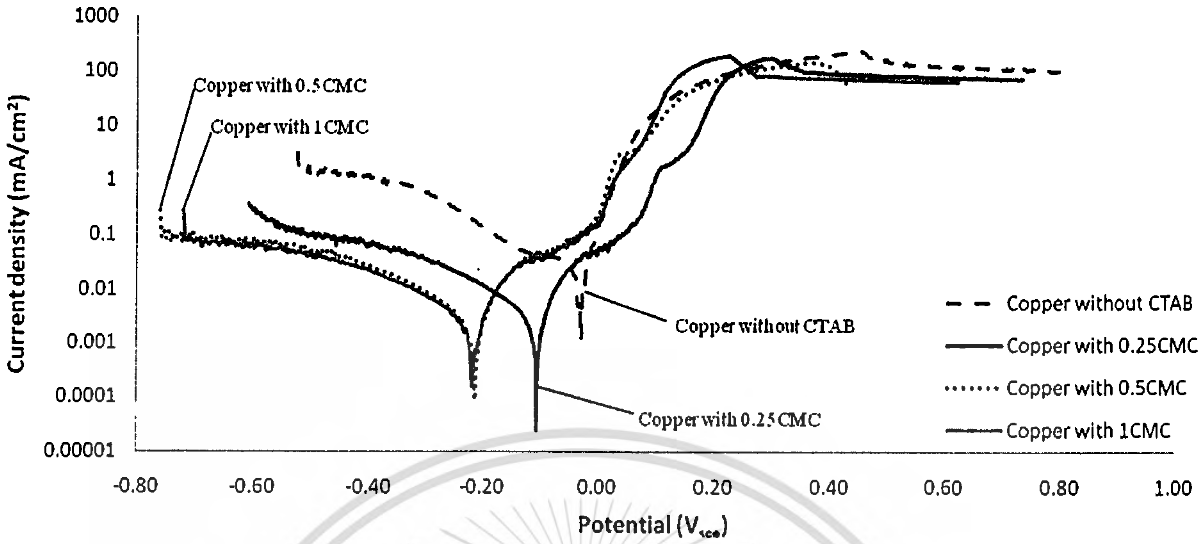


Figure 4.12 Polarization curves of copper in 1N sulfuric acid with low concentrations of CTAB

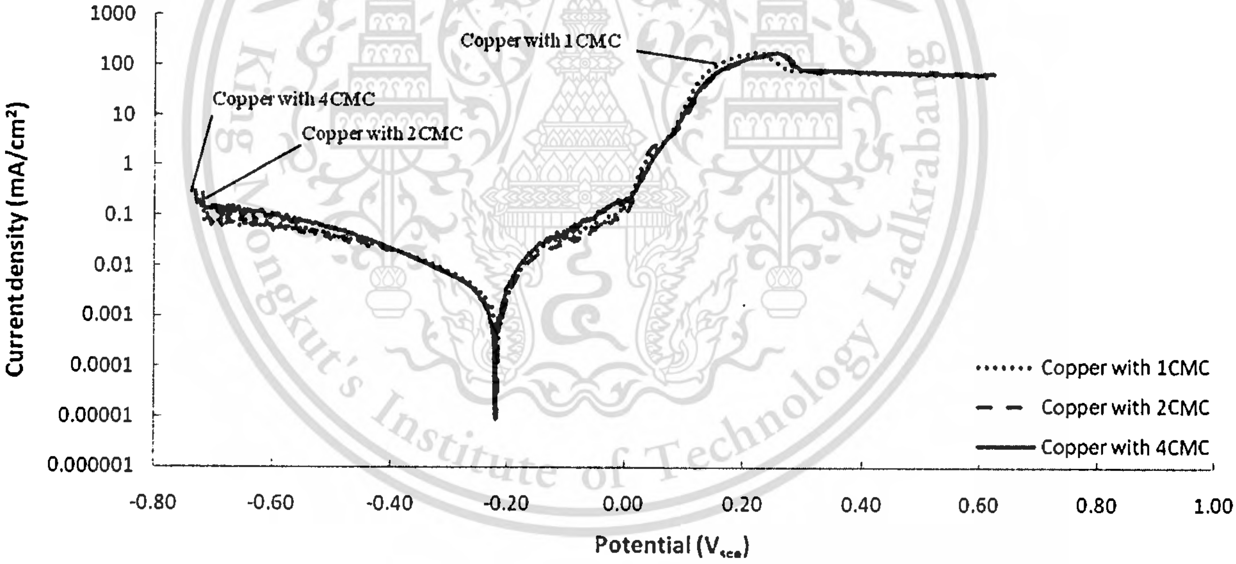


Figure 4.13 Polarization curves of copper in 1N sulfuric acid with high concentrations of CTAB

By discussing to the obtained results, it shows the drop of i_{corr} and E_{corr} as an increase in CTAB concentration. Higher CTAB concentration enhances the possibility of adsorption on the metallic surface which further acts as a protective layer. However, beyond the concentration of 0.5CMC, an additional of CTAB in to the system result in no affect on i_{corr} and E_{corr} values. This can be explained in the way that, when the concentration reached 0.5CMC the surface of copper is already covered by the perpendicular and horizontal adsorbed CTAB monomers (shown in Figure 4.10).

In an anodic slope, due to a very rapid corrosion rate, we observed a slightly fall in the current density which could be caused by the mass transport problem or an oxide formation. More detail on electrochemical parameters of copper which carried out in 1 N sulfuric acid, in an absence and presence of CTAB are listed in the Table 4.6

Table 4.6 Electrochemical parameters of copper in 1N sulfuric acid with various concentrations of CTAB

[CTAB] (×CMC)	i_{corr} (mA/cm^2)	E_{corr} (V_{SCE})	Corrosion rate (g/cm^2.year)
0	1.926×10^{-2}	-0.005	1.999×10^{-1}
0.25	1.794×10^{-3}	-0.106	1.862×10^{-2}
0.5	1.520×10^{-3}	-0.215	1.578×10^{-2}
1	1.097×10^{-3}	-0.185	1.139×10^{-2}
2	1.056×10^{-3}	-0.216	1.096×10^{-2}
4	1.102×10^{-3}	-0.221	1.144×10^{-2}

By analyzing corrosion effect in acid-free environment with the CTAB added, the results showed that CTAB itself promote corrosion rather than protect the copper, as corrosion rate increases with increased concentration of CTAB. On the other hand, in acidic solution, 0.01N and 1 N, the curves showed a sharp reduction in corrosion rate with low CTAB concentration; these showed that CTAB acted as a good corrosion inhibitor and can inhibit corrosion on copper in acidic solution. The curves that demonstrate the correlation between corrosion rate and CTAB concentration in distilled water 0.01N and 1N sulfuric acid are shown in the Figure 4.14

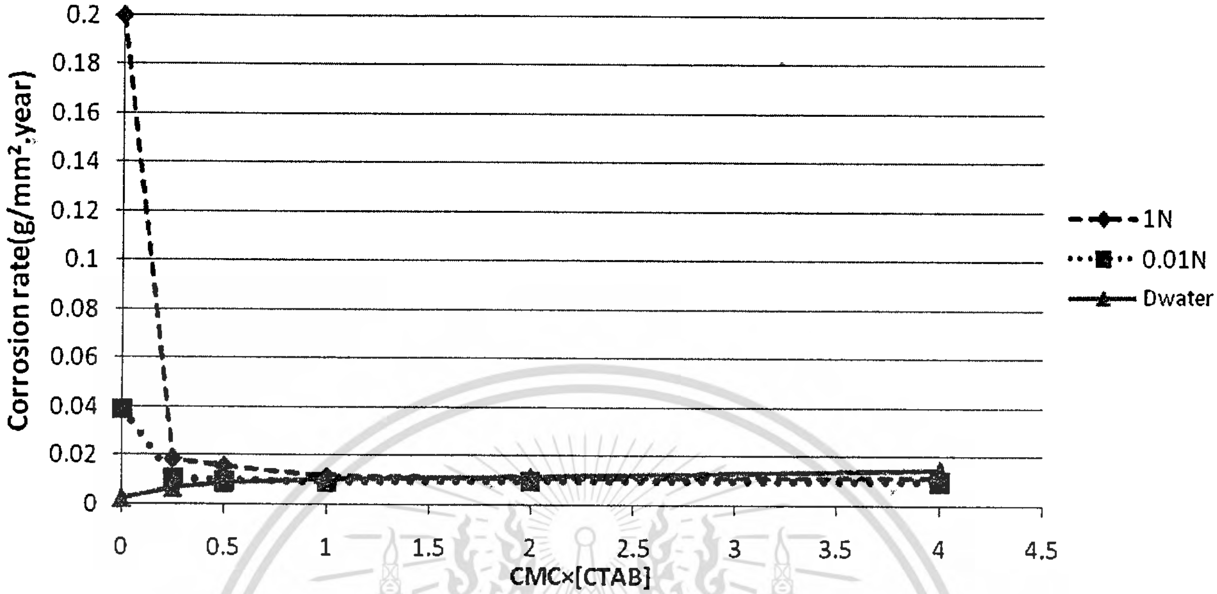


Figure 4.14 The plot between corrosion rates versus CTAB concentrations

Chapter 5

Conclusion

In this work, CMCs of CTAB in distilled water, 0.01N and 1N sulfuric acid have been determined by using conductivity measurement.

CMC of CTAB in distilled water was found to be at 0.9mM which agrees very well with the literatures.

In acidic environment, 0.01N sulfuric acid, CMC was dropped to 0.7mM which resulted from the binding effect of sulfate anions in sulfuric acid. As a consequence, due to more binding effect, CMC of CTAB in 1N sulfuric was noticed to be at 0.28mM.

Regarding to the potentiostat polarization technique, CTAB acted as a good corrosion inhibitor in protecting copper from acidic environment, 0.01N and 1N, by forming a protective layer on the copper surface. Conversely, in distilled water, CTAB seems to promote corrosion by significantly enhance an aggressiveness of the electrolytes media and causing the destructive action from the bromide counter ions of CTAB.

References

[1] Vin Calcutt, **"Introduction to Copper: Types of Copper"**, Copper Development Association Journal [online], 2001, http://www.copper.org/publications/newsletters/innovations/2001/08-intro/intro_toc.html#hcc [retrieved August 2001]

[2] Bannantine, Julie A, **"Fundamentals of metal fatique analysis"**, Englewood Cliffs,NJ: Prentice Hall, C1990 Imprinted

[3] Wikipedia, the free encyclopedia, **"Copper"**, Wikimedia Foundation, Inc., [online], http://en.wikipedia.org/wiki/Copper [retrieved 29 March 2009]

[4] Science Encyclopedia, **"History of Copper"**, Science Encyclopedia Vol.2 [online], http://science.jrank.org/pages/1780/Copper-History-copper.html

[5] Darby Patterson, **"The History of Bronze"**, Darby Associates [online], 2008 http://www.bronzeandglass.com/bronze-history.html

[6] ESPI, **"Copper rod (Cu)"**, ESPI [online database], http://www.espi-metals.com/metals/ [retrieved 8 June 2008] catcu_shot.htm

[7] Howard E. Boyer, Timothy L.Gall, **"Metals handbook"**, Metals Park, OH:American society for Metal,1992 Imprinted

[8] Wikipedia, the free encyclopedia, **"Copper"**, Wikimedia Foundation, Inc., [online], http://en.wikipedia.org/wiki/Thermodynamics [retrieved 7 April 2009]

[9] Denny A. Jones, **"Principles and prevention of corrosion"**, 2nd ed., Prentice-Hall, NJ, 1996

[10] Mars G. Fontana, **"Corrosion Engineering"**, 3rd ed., McGraw-Hill, Inc., Singapore, 1986

[11] Wikipedia, the free encyclopedia, **"Thermodynamics"**, Wikimedia Foundation, Inc., [online], http://en.wikipedia.org/wiki/Thermodynamics [retrieved 22 March 2009]

[12] Drew Myers, **"Surfactant Science and Technology"**, 3rd ed., John Wiley & Sons, Inc., Hoboken, NJ, 2006

[13] Wikipedia, the free encyclopedia, **"Surfactants"**, Wikimedia Foundation, Inc., [online], http://en.wikipedia.org/wiki/Surfactant [retrieved 24 March 2009]

[14] Krister Holmberg, **"Surfactants and Polymers in Aqueous Solution"**, England, 2001

[15] Zaki Ahmad, **"Principles of corrosion engineering and corrosion control"**

[16] R. Winston Rev, **"Uhlig's corrosion handbook second edition"**

[17] Kenneth R Trethewey and John Chamberlain, **"Corrosion for Science and Engineering"**, 2nd ed., Longman Singapore Publishers Ltd., 1995

[18] Caroline M. Murira, Christian Punckt, Hannes C. Schniepp, Boris Khusid, and Ilhan A. Aksay, **"Inhibition and Promotion of Copper Corrosion by CTAB in a Microreactor System."** Langmuir,2008,24 (24). pp. 14269-14275.

[19] S. Ramesh, S. Rajeswari, S. Maruthamuthu, **"Corrosion inhibition of copper by new triazole phosphonate derivatives."** J.Appl.Surf.Sci., vol.229,issue 1-4. pp. 214-225.

[20] Howaida M. EI-Kashlan, **"Kinetic study of the effect of selected surfactants on corrosion of copper."** Am.J.Appl.Sci., 5(4):2008, pp. 347-354.

[21] Houyi Ma,Shenhao Chen, Shiyong Zhao, Xiagqian Liu, and Degang Li , **"The impedance spectroscopic study of corrosion inhibition of copper by surfactants in the acidic solutions."** Corrosion Sci.,vol.45, issue 5,May 2003. pp. 867-882.

[22] Houyi Ma,Shenhao Chen, Shiyong Zhao, Xiagqian Liu, and Degang Li, **"A Study of corrosion behavior of copper in acidic solutions coantaining cetyltrimethylammonium bromide."** J.Electrochem. Soc., vol.148, issue 11,2001. pp. B482-B488.

Appendices

Appendix A

Anodic and cathodic Tafel slope extrapolation of copper in distilled water with different concentrations of CTAB

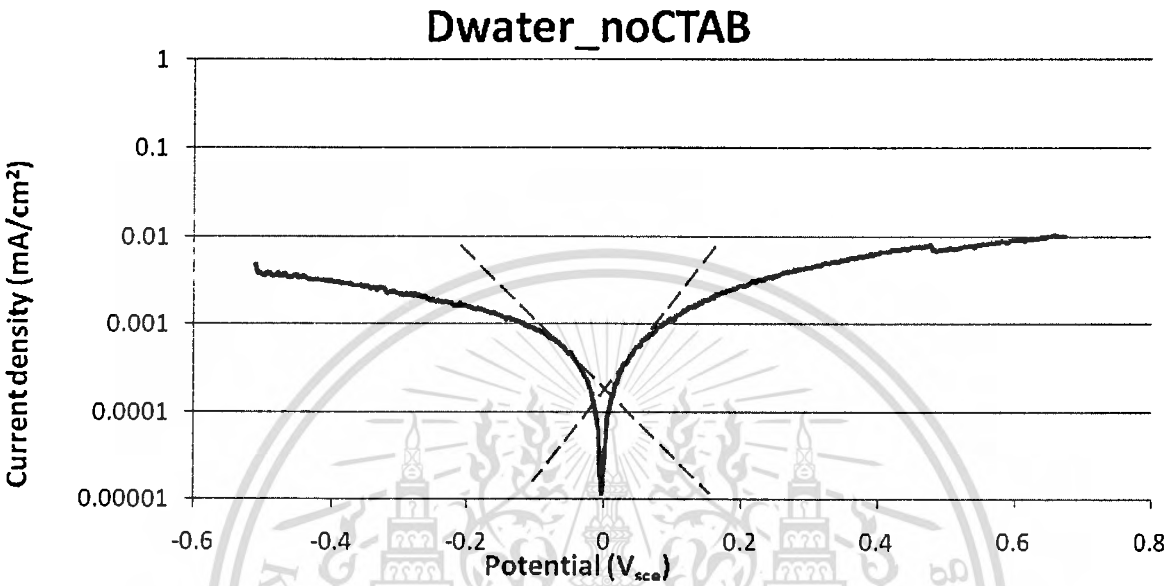


Figure A1 Anodic and cathodic Tafel slope extrapolation of copper in distilled water.

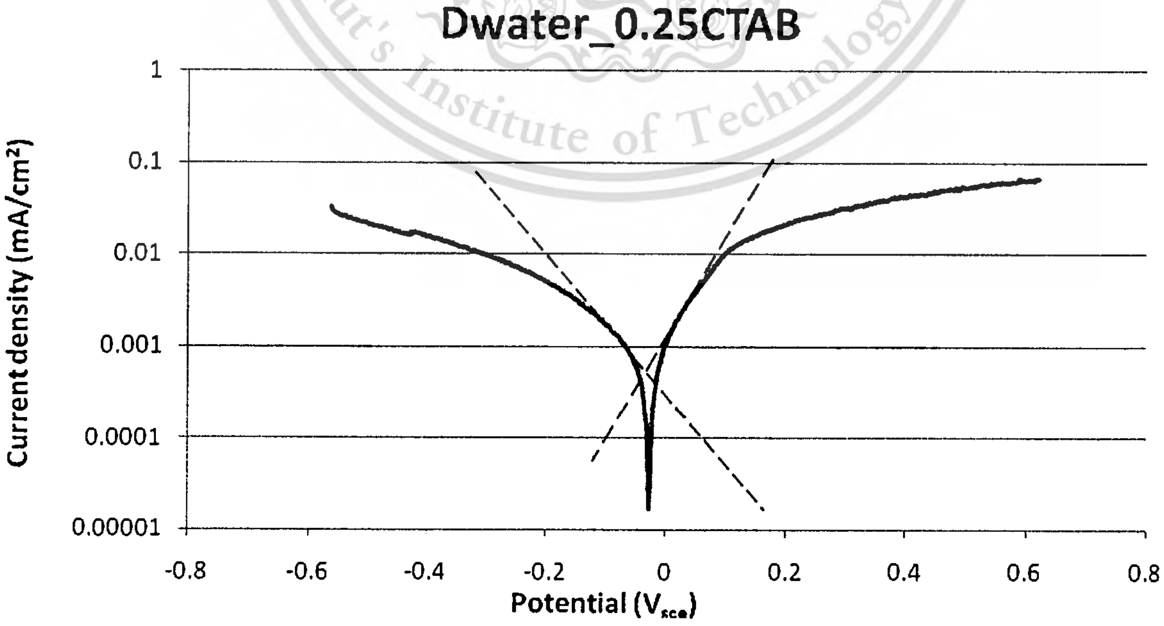


Figure A2 Anodic and cathodic Tafel slope extrapolation of copper in distilled water with 0.25 CMC of CTAB.

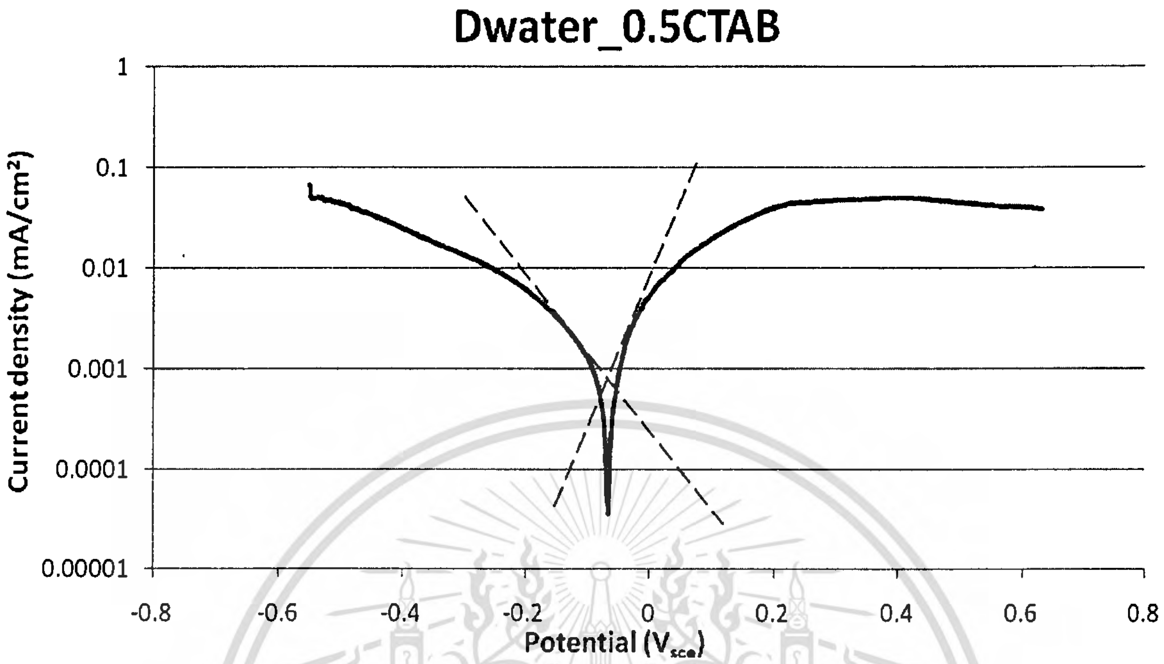


Figure A3 Anodic and cathodic Tafel slope extrapolation of copper in distilled water with 0.5 CMC of CTAB.

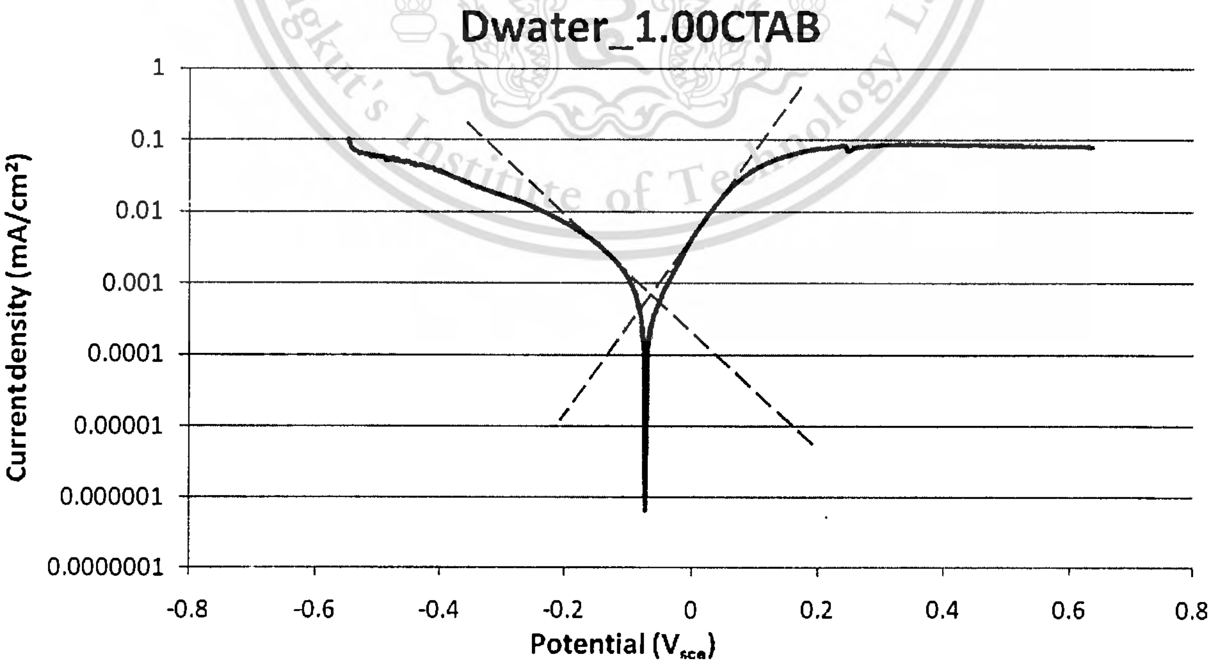


Figure A4 Anodic and cathodic Tafel slope extrapolation of copper in distilled water with 1.00 CMC of CTAB.

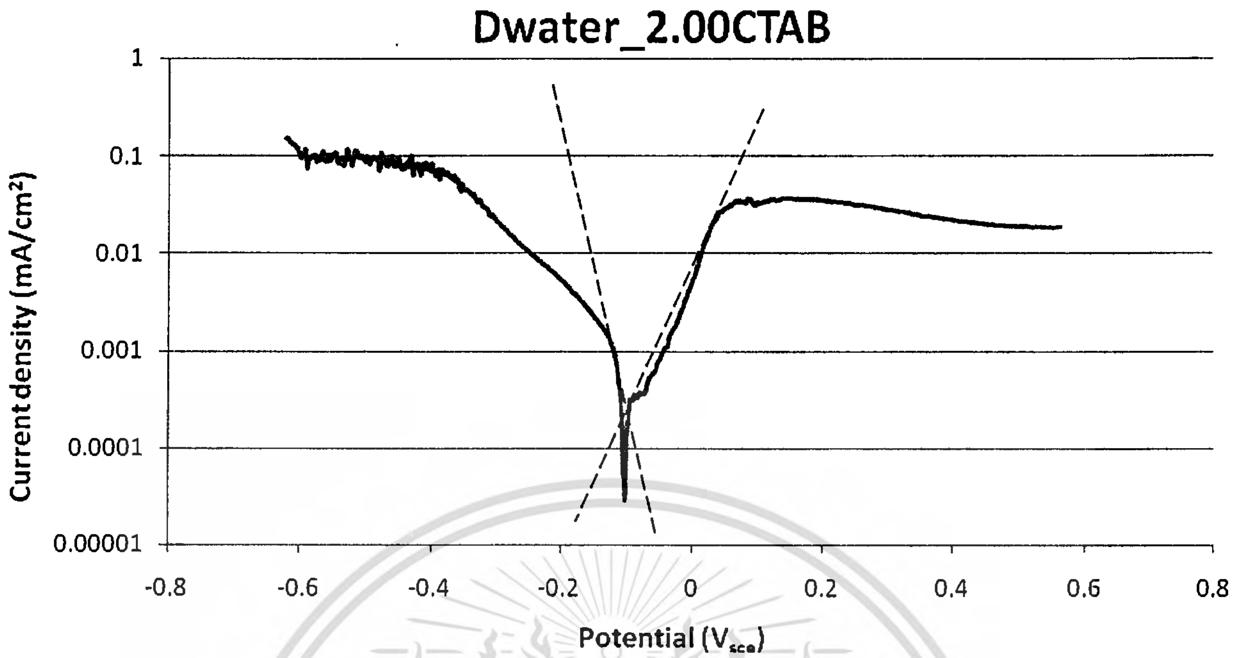


Figure A5 Anodic and cathodic Tafel slope extrapolation of copper in distilled water with 2.00 CMC of CTAB.

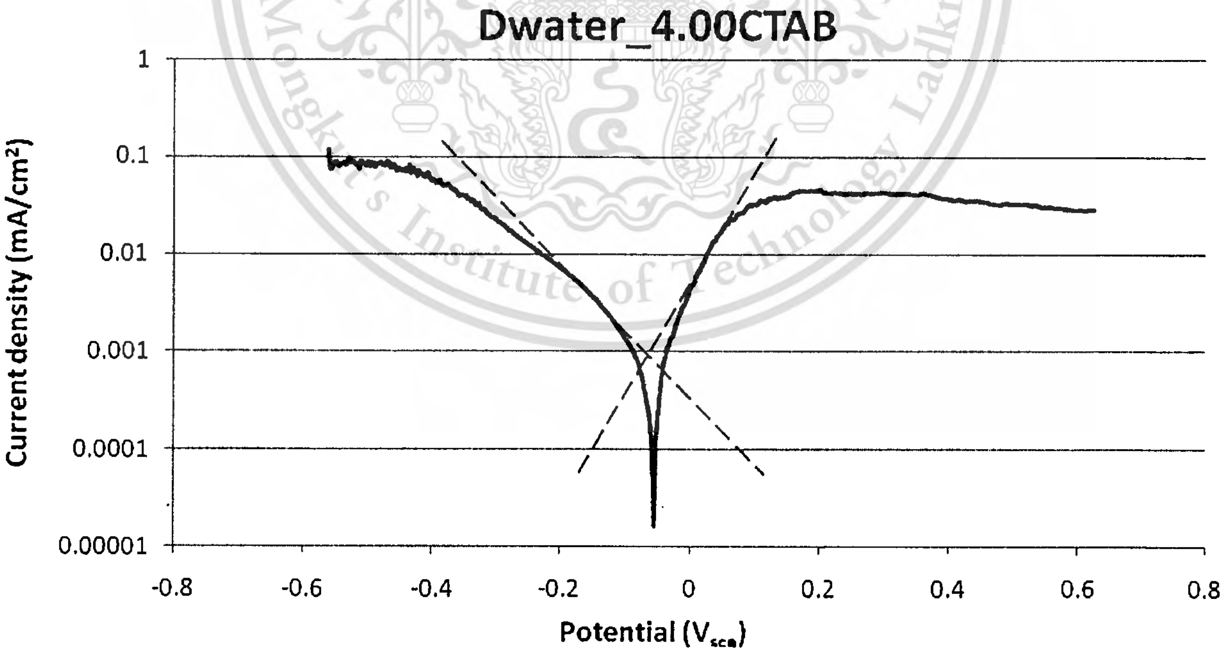


Figure A6 Anodic and cathodic Tafel slope extrapolation of copper in distilled water with 4.00 CMC of CTAB.

Anodic and cathodic Tafel slope extrapolation of copper in 0.01 N H_2SO_4 with different concentrations of CTAB.

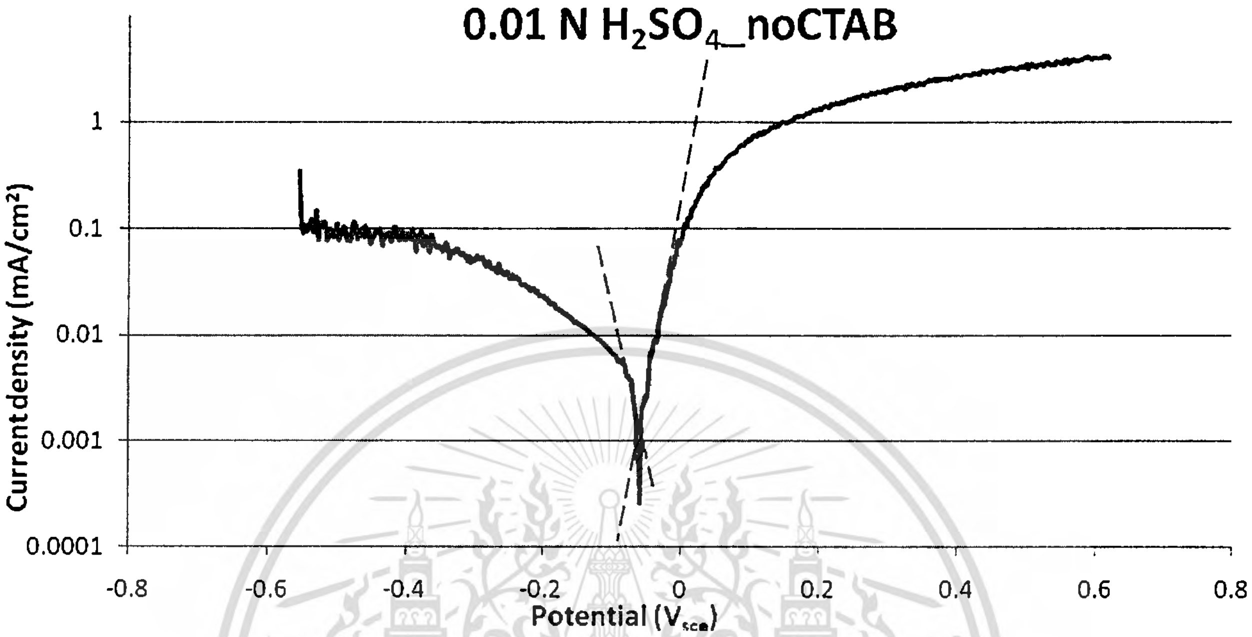


Figure A7 Anodic and cathodic Tafel slope extrapolation of copper in 0.01 N H_2SO_4.

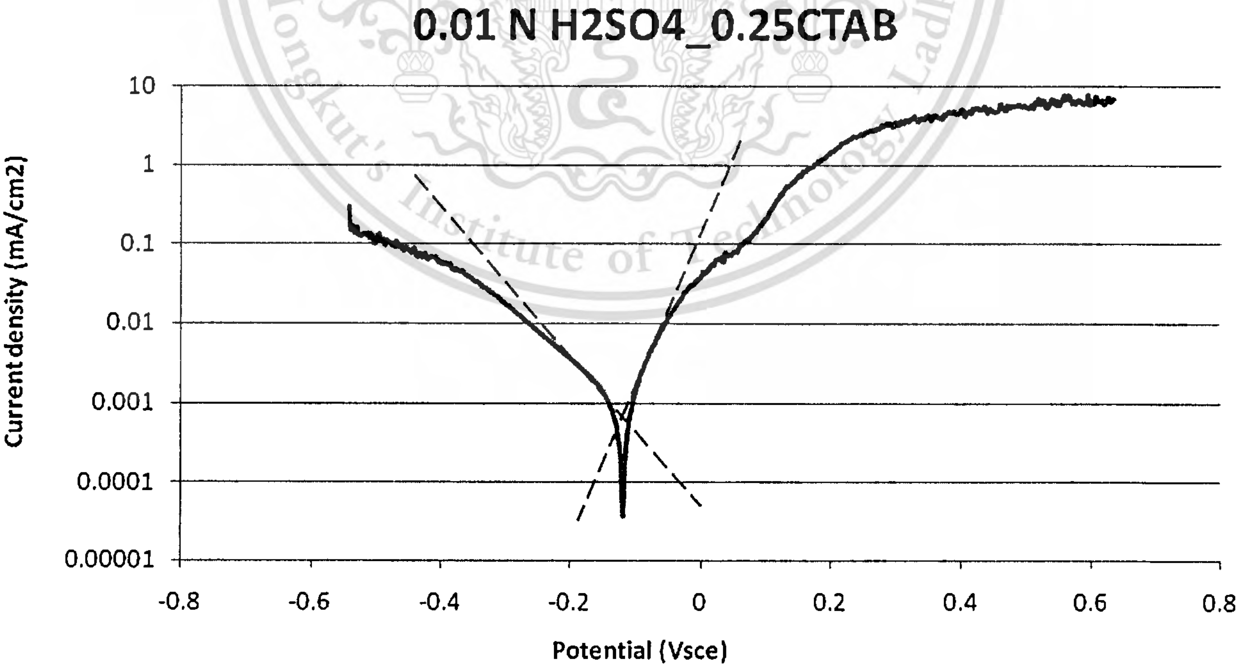


Figure A8 Anodic and cathodic Tafel slope extrapolation of copper in 0.01 N H_2SO_4 with 0.25 CMC of CTAB.

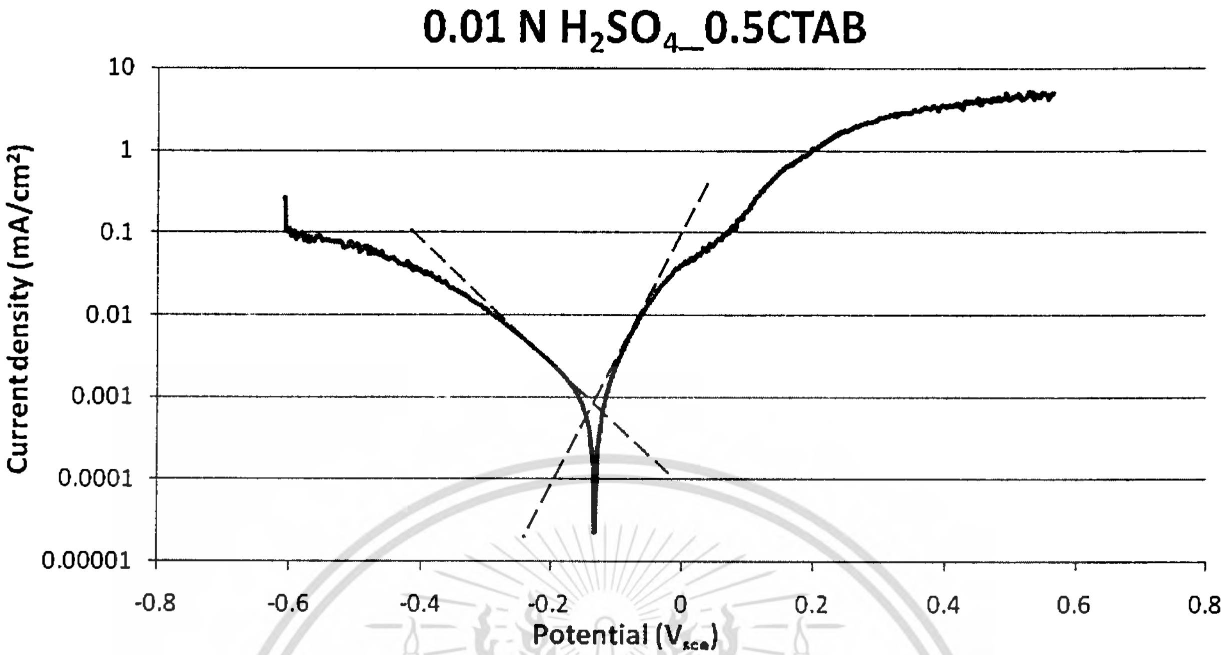


Figure A9 Anodic and cathodic Tafel slope extrapolation of copper in 0.01 N H_2SO_4 with 0.5 CMC of CTAB.

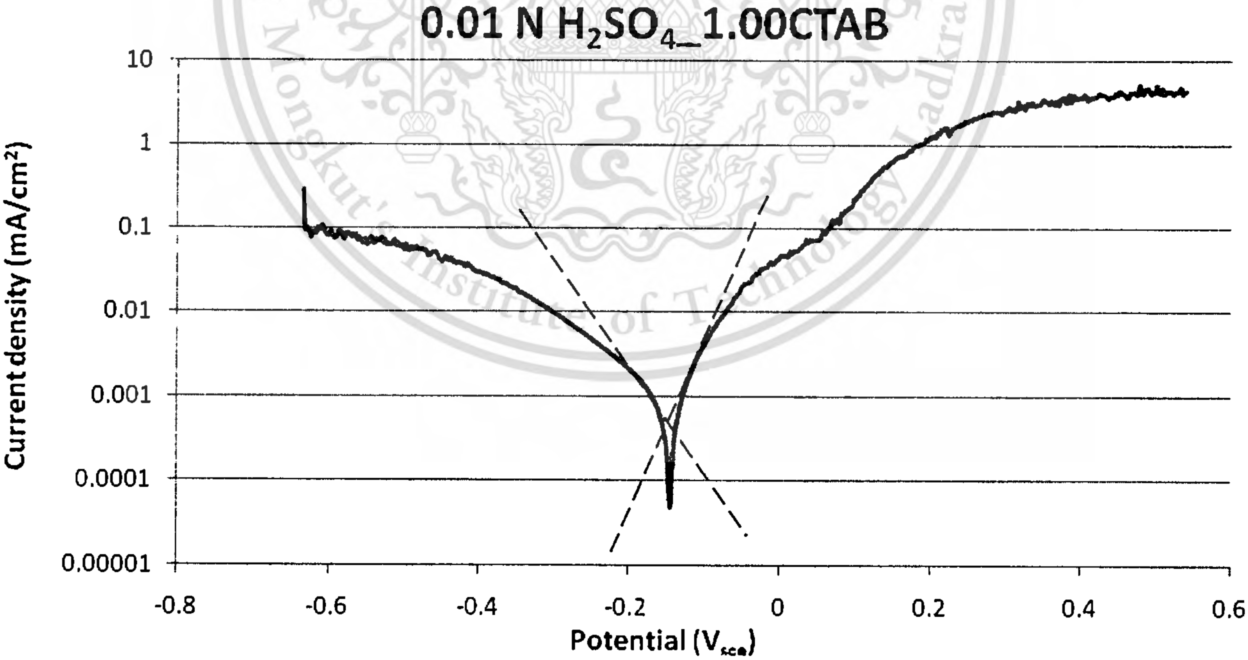


Figure A10 Anodic and cathodic Tafel slope extrapolation of copper in 0.01 N H_2SO_4 with 1.00 CMC of CTAB.

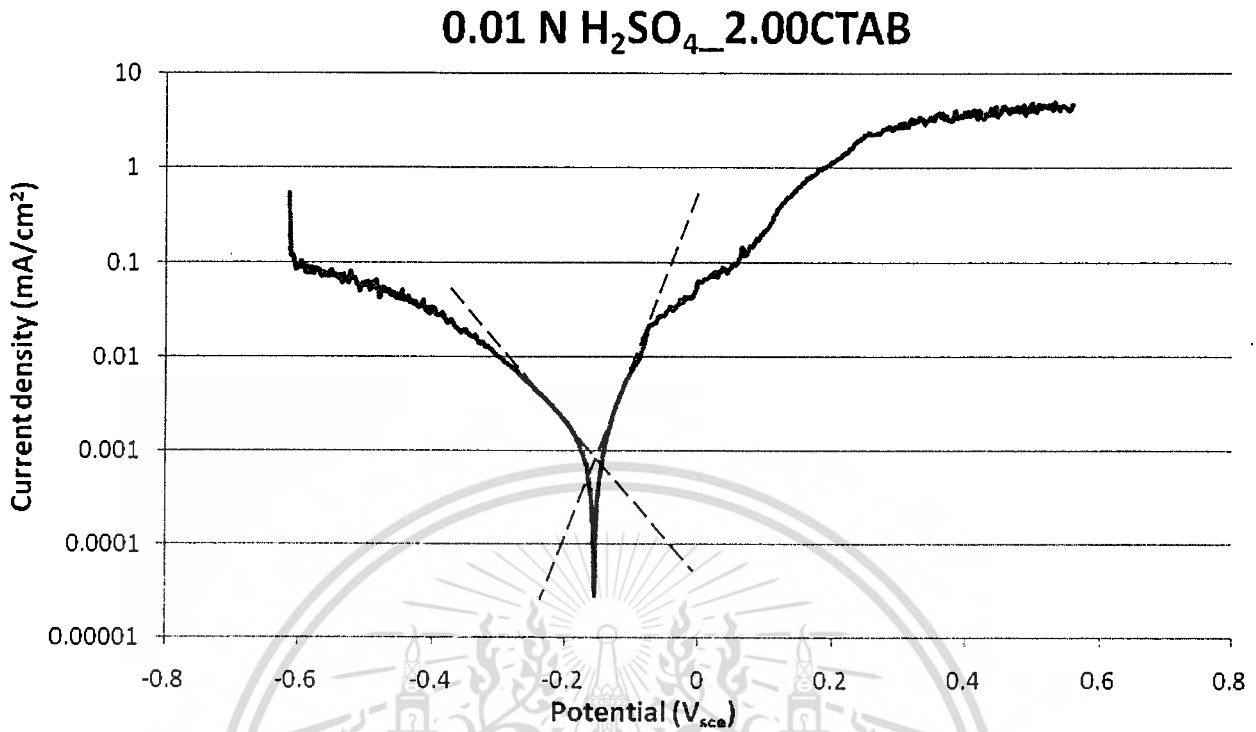


Figure A11 Anodic and cathodic Tafel slope extrapolation of copper in 0.01 N H_2SO_4 with 2.00 CMC of CTAB.

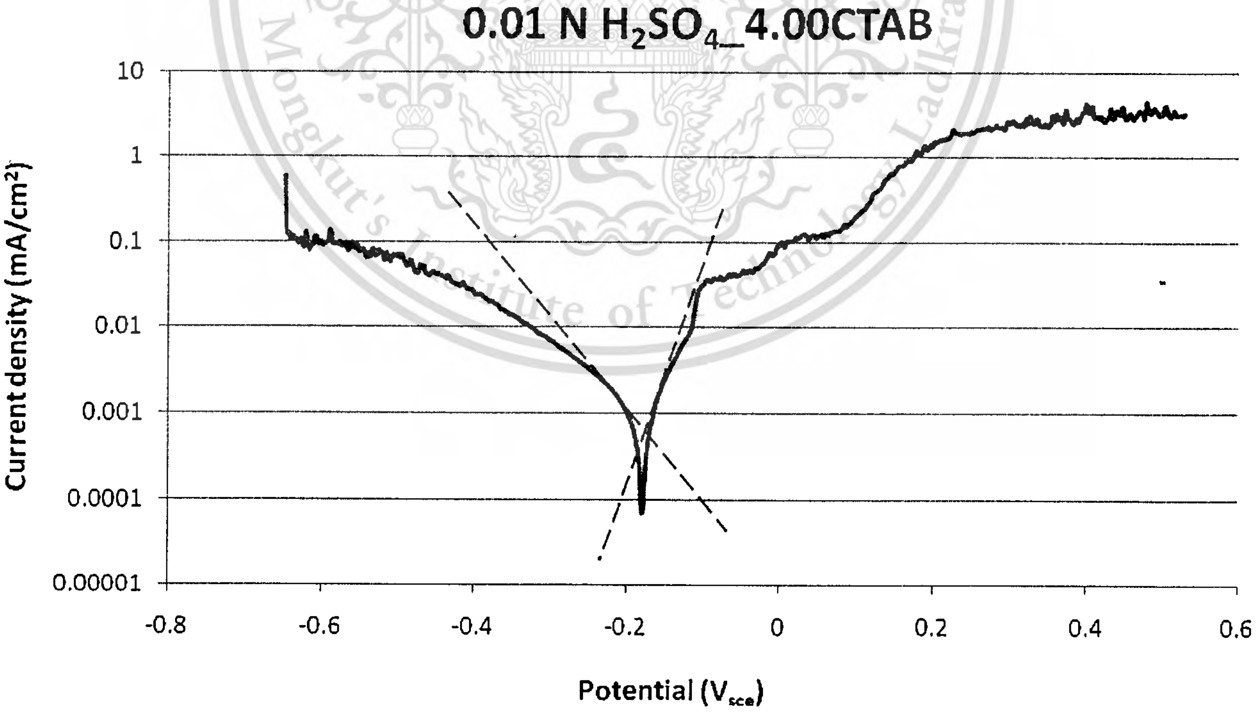


Figure A12 Anodic and cathodic Tafel slope extrapolation of copper in 0.01 N H_2SO_4 with 4.00 CMC of CTAB.

Anodic and cathodic Tafel slope extrapolation of copper in 1.00 N H_2SO_4 with different concentrations of CTAB

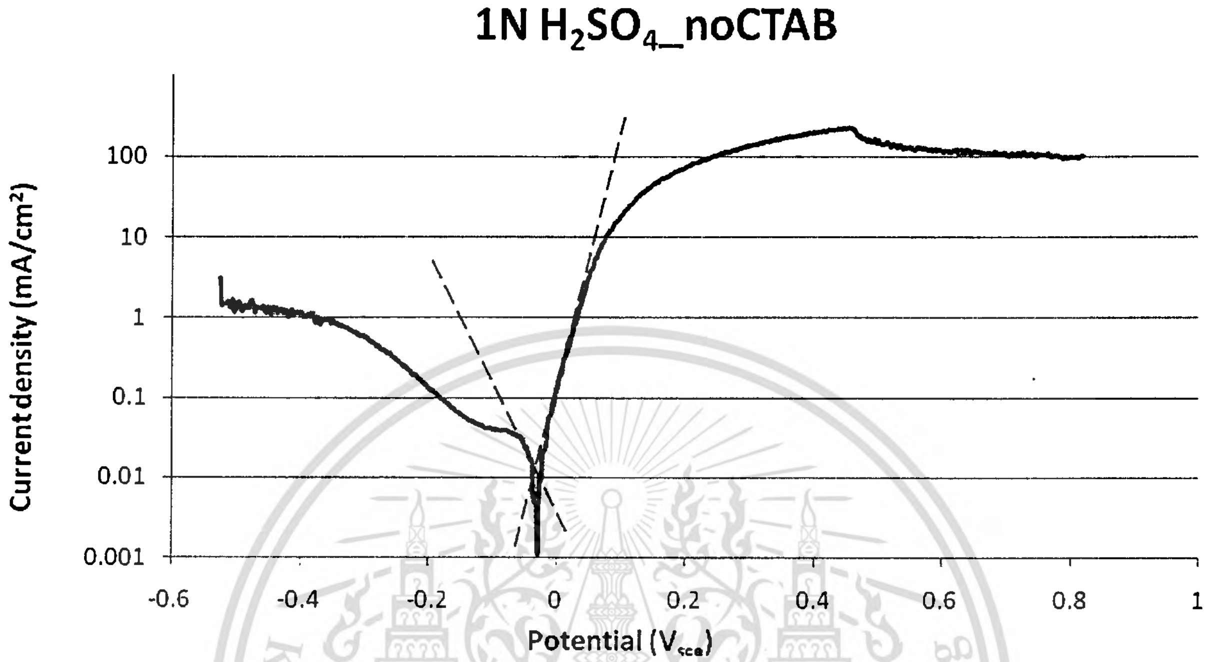


Figure A13 Anodic and cathodic Tafel slope extrapolation of copper in 1.00 N H_2SO_4.

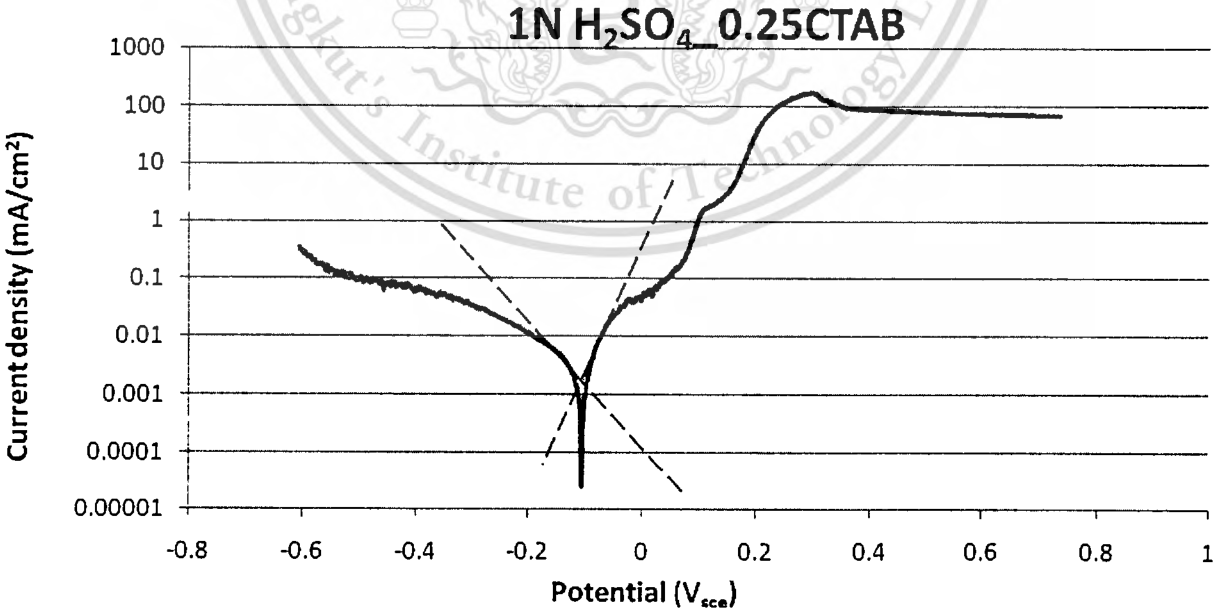


Figure A14 Anodic and cathodic Tafel slope extrapolation of copper in 1.00 N H_2SO_4 with 0.25 CMC of CTAB.

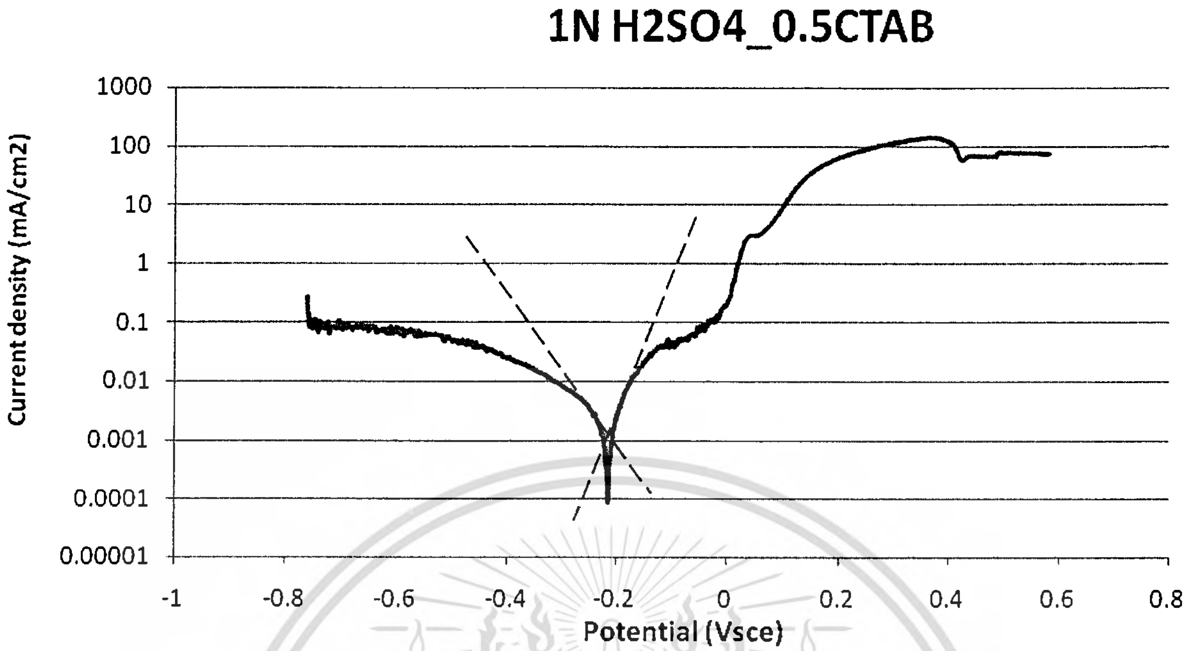


Figure A15 Anodic and cathodic Tafel slope extrapolation of copper in 1.00 N H_2SO_4 with 0.5 CMC of CTAB.

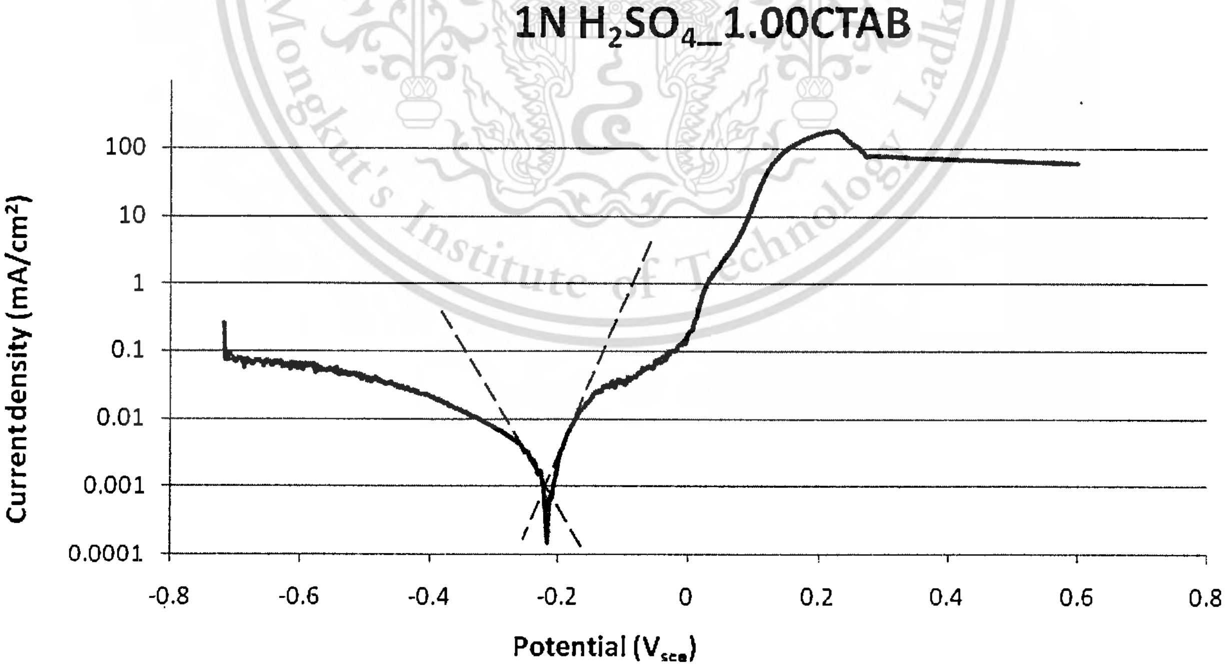


Figure A16 Anodic and cathodic Tafel slope extrapolation of copper in 1.00 N H_2SO_4 with 1.00 CMC of CTAB.

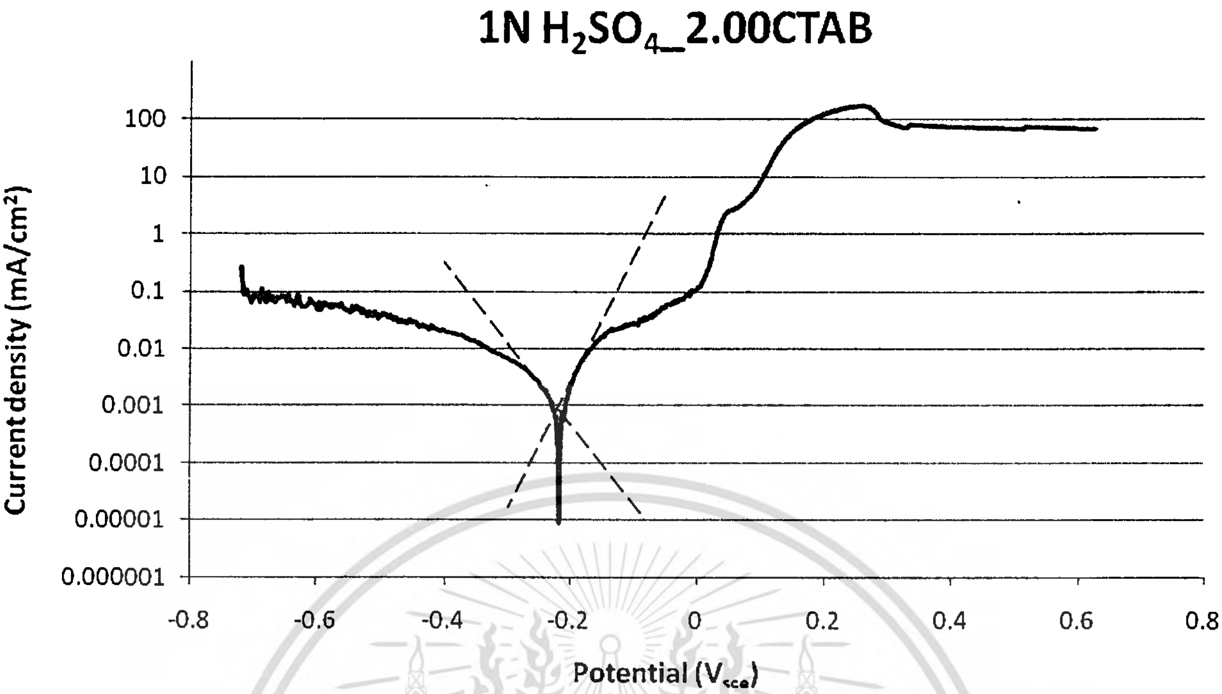


Figure A17Anodic and cathodic Tafel slope extrapolation of copper in 1.00 N H_2SO_4 with 2.00 CMC of CTAB.

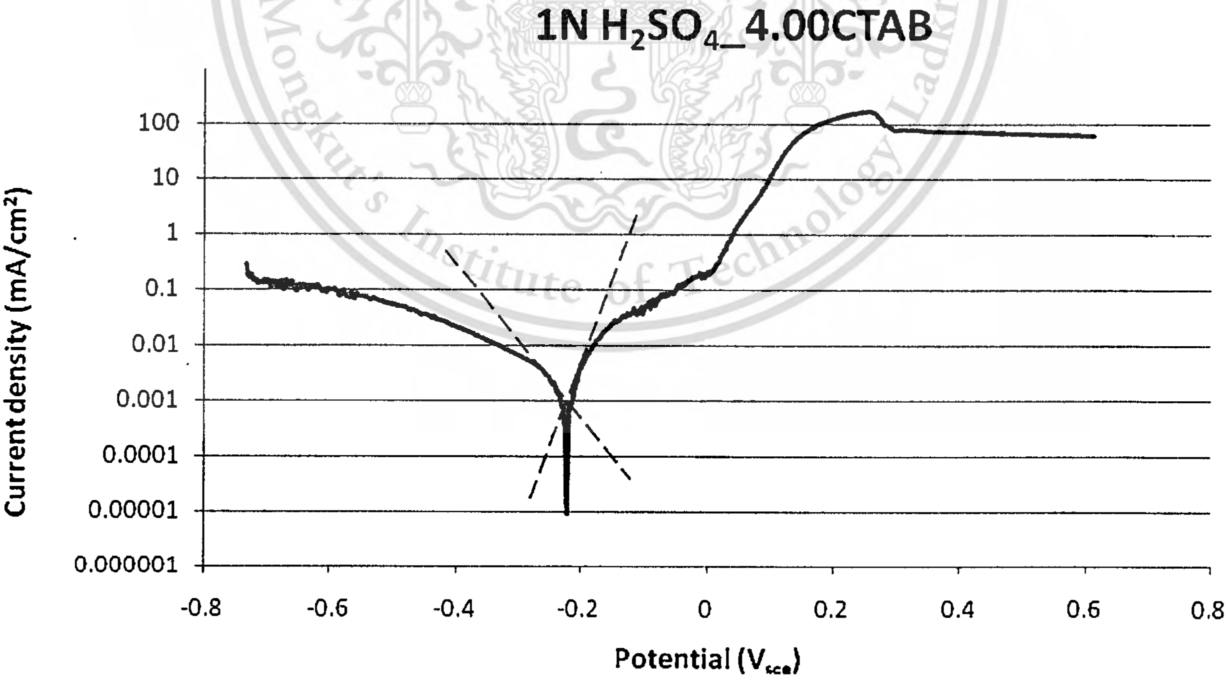


Figure A18 Anodic and cathodic Tafel slope extrapolation of copper in 1.00 N H_2SO_4 with 4.00 CMC of CTAB.

Appendix B

Calculation

1. Atomic weight of copper

As the 4N copper that we use has 99.99% purity, so the other 0.001% is considered to be negligible.

Atomic mass: Cu 99.99 % = 63.55 g/mol (shown in the periodic table)

2. Corrosion rate

According to Faraday's Law;

$$W = iAtM/nF$$

Where; W = weight loss at instant second time (g)

I = current (A)

M = atomic weight of metal (g/mol)

i = current density (A/cm^2)

n = number of electron moles during corrosion

F = Faraday's constant (96,500 C/mol)

A = average surface area (cm^2)

t = time (s)

The example of corrosion rate calculation for copper in an absence and presence of CTAB is shown below.

From Table 4.6, the value of i_{corr} of copper in 1 N H_2SO_4 in absence of CTAB is $1.926\text{x}10^{-5}$ A/cm^2.

$$\frac{W}{At} = \begin{array}{c|c|c|c} 1.926\text{x}10^{-2}\ \text{mA} & & 63.55\text{g} & \text{mol} \\ \hline \text{cm}^2 & 2 & \text{mol} & 96{,}500\ \text{A.s} \end{array}$$

$$= \begin{array}{c|c|c|c|c} 6.342\text{x}10^{-6}\ \text{mg} & 60\text{s} & 60\ \text{min} & 24\ \text{hr} & 365\ \text{days} \\ \hline \text{cm}^2\text{.s} & 1\text{min} & 1\ \text{hr} & 1\ \text{day} & 1 \end{array}$$

$$= 1.999\times10^{-1}\text{g/cm}^2\text{.y}$$

The calculation that shown above is only the example, same calculation method can be used for calculating corrosion rate in other samples.