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Corrosion rate study of mild steel in Aqueous 2-amino-2-ethyl-1,3-propanediol (AEPD)

by

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(MUHAMMAD RAIHAN BIN MOHD ISMAIL)

ABSTRACT

As there is growing concern that carbon dioxide (CO2) emissions are contributing to global climate change, it is critical to develop technologies to mitigate this problem. One very promising approach in reducing CO_2 emissions is CO_2 capture at a power plant, transport to an injection site, and sequestration for long-term storage in any of a variety of suitable geologic formations. Most common amine solutions used in absorbing CO_2 are the alkanolamines such as MEA, DEA and MDEA. Meanwhile, application of sterically hindered amines (SHA) such as AHPD, AEPD, and AMP in gas treating technology are also being studied , as to compare with alkanolamines, in terms of the feasibility of being applied for future application in CO_2 absorption approach. After all, all amine solutions whether it is lean or saturated with CO_2 are corrosive. Due to the effect, all plants that operate CO_2 absorption have to counter the case of corrosion effectively with the improved method, day by day. With this in mind, it is here to present as a research to minimize corrosion by taking into account of the emerging sterically hindered amines(SHA), as the chosen SHA is 2- amino-2-ethyl-1,3-propanediol (AEPD), due to the high uptake on CO_2 absorption , and stable form of carbamate formed during the reaction with CO_2.

In order to determine the corrosion rate in mild steel using aqueous solution of AEPD, the corrosion, the experiment is to be done on the factors of concentration of amines, temperature , and CO_2 loadings.

As the previous studies contained the data of solubility of carbon dioxide into 2- amino-2-ethyl-1,3-propanediol (AEPD), it is worthful to continue the research in terms on the corrosion studies of mild steel in the aqueous AEPD, since the corrosion rate study on AEPD has not been carried out.

Suggesting 2- amino-2-ethyl-1,3-propanediol (AEPD), the experiment is to be carried out with the chosen parameters of the experiment such as **concentrations** (amine) : 0.3 M, 0.6 M, 0.9 M; **Temperature** : 50 °C, 70 °C, 90 °C; **Mixed Amines**: Mixing of AEPD and DEA at 0.3 M , 0.6 M, and 0.9 M respectively. Also could be referred is also the corrosion rate for the alkanolamines, Diethanolamine (DEA) itself.

ACKNOWLEDGEMENT

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1. INTRODUCTION

1.1 Background Studies

Intensive human activities and economic development have been contributing a significantly rise of the concentration of greenhouse gases, nowadays. As far as what are being concerned, a major component, CO2 is mainly emitted from fossil fuels such as coal and oil, used for generating energy.(Bougie & Iliuta, 2012) Plus, important emissions come from different industrial processes connected to oil refineries, cement works, and even iron production.

As industrially, alkanolamines are more often used for gas absorption process for CO_2 absorption. Among them are such monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and others. Choice of certain amines are based on the absorption capacity, reaction kinetics, regenerative potential and facility.(Bougie & Iliuta, 2012) As for the primary and secondary alkanoamines like MEA and DEA, their fast reactivity due to the stabilized carbamate formation are one of the key advantages for the amine type. Conversely, this will much lead to very high solvent regeneration costs. Plus, they have the drawback of a relatively low CO2 loading(limited to 0.5 mol CO_2/mol amine). Tertiary alkanolamines on the other side, like MDEA, have low reactivity with respect to CO2, due to exclusive formation of bicarbonates by CO2 hydrolysis. However, this leads to a very low solvent regeneration cost, plus another advantage is the high CO2 theoretical loading capacity of 1 mol of CO2/mol of amine.(Veawab, Tontiwachwuthikul, & Chakma, 1999a) However, those conventional alkanolamine contains some disadvantages and not efficient. With the emergine research of sterically hindered amines, the alkanoamines used for corrosion inhibitors can be improved.

The application of sterically hindered amines (SHAs), for example, AMP, in gas-treating technology offers absorption capacity, absorption rate, selectivity, and degradation resistance advantages over conventional amines for CO2 removal from gases. Due to the hindrance of the bulky group adjacent to the amino group, sterically hindered amines form unstable carbamates. Significantly, higher reaction kinetics in respect to tertiary

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amines, coupled with low solvent regeneration cost offer to SHA important industrial advantages for corrosion inhibitors.

The use of blended alkanolamine has also become very attractive , as combination of each amine advantage, fast reactivity from a primary or secondary alkanolamines (e.g, MEA,DEA) coupled with high absorption capacity and low solvent regeneration cost from a tertiary or sterically hindered alkanolamine.(Veawab, Tontiwachwuthikul, & Chakma, 1999a)

From history, CO2 absorption process using aqueous amine solution has faced corrosion problems in many plants(Rooney & DuPart, 2000). The corrosion problems causes a huge impact directly on the plant's economy since it causes unplanned downtime, production losses, reduced equipment life, and even injury or death, as a major problem for alkanoamine-based plants, since metal failure could be resulted, especially in heat-exchanger tubes and absorber/regenerator trays, equipment fouling, and foaming.(Blomen, Hendriks, & Neele, 2009) Diethanolamine(DEA) plants generally experience less corrosion than monoethanolamine plants, but corrosion is also a concern for DEA plants.(Mofarahi, Khojasteh, Khaledi, & Farahnak, 2008)

1.2 Problem Statement

Among the available methods for control of corrosion, the use of inhibitors is one of the most reliable and cost effective . development of new amines with higher chemical stability has become essential, as the function as good alternative solvents because of their increased CO2 absorption capacity(MARTIN et al., 2012). So far , many works have been done to determine the corrosion rate of amine solutions, in terms of finding the better amine solution with least corrosion problems. This include the above conventional alkanolamines, and also the sterically hindered amines(SHA).

Current data on on sterically hindered amines are very limited since much research are still going on in determining the ability of them as corrosion inhibitors. Previous works and research which done have focused about the solubility data for AEPD, kinetic adsorption of CO_2, and the involvement of activator into the solubility of CO_2 into AEPD. Since the data of the solubility of CO_2 into AEPD are present, it is beneficial to determine the corrosion rate studies involving AEPD as corrosion inhibitors

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for mild steel, As there is no corrosion rate studies that had been done using AEPD, plus there is the availability of CO_2 solubility, these factors have led to an interest in carrying out this study.

1.3 Objective And Scope Of Study

Objective

1. To determine the corrosion rate in mild steel , using aqueous solution of AEPD.
2. To compare the corrosion rate in mild steel in AEPD based on different parameters which is concentration of amines, temperature , and CO_2 loadings.

Scope of Study

The research study will be make use the fundamental understandings throughout the chemical engineering studies and will eventually expose the corrosion plus electrochemistry basic knowledge.

1. Study on the amines type, the usage of amines in corrosion inhibitors in industries.
2. Carrying out experiments for corrosion of mild steel in aqueous amine solution at different concentration, temperature, and different amine types.

   i.   Concentrations, M (Molarity): 0.3, 0.6 , 0.9

   ii.   Temperature : 50 $^\circ$C, 70 $^\circ$C, 90 $^\circ$C

   iii.   Mixtures of AEPD and DEA at Concentrations, M (Molarity) : 0.3,0.6,0.9
3. Research and study on the electrochemistry , which relates the corrosion experiment and the current density which obtained from

   i.   Tafel Plot

   ii.   Linear Polarization Resistance

   iii.   Polarization
4. Analyzing results based on the observed graphs and relate the corrosion rate study to the factors consisted by AEPD.

The project is relevant to be carried out in the time frame of two semesters, as it will be done in Ionic Lab , Chemical Engineering Department, and the experiment setup involves corrosion cells, which mainly consists of different type of electrodes,

i.   Steel sample for corrosion test

ii.   Graphite electrode, as Counter electrode

iii.   Reference electrode

Datas are tabulated as plot of graphs, which is Tafel Plot, Linear Polarization Resistance, and Potentiodynamic. The graphs varies according to the experiment parameters, such as **concentrations of amine, temperature of amine solution, and mixtures of AEPD and DEA(diethanolamine-conventional amine) aqueous solution.**
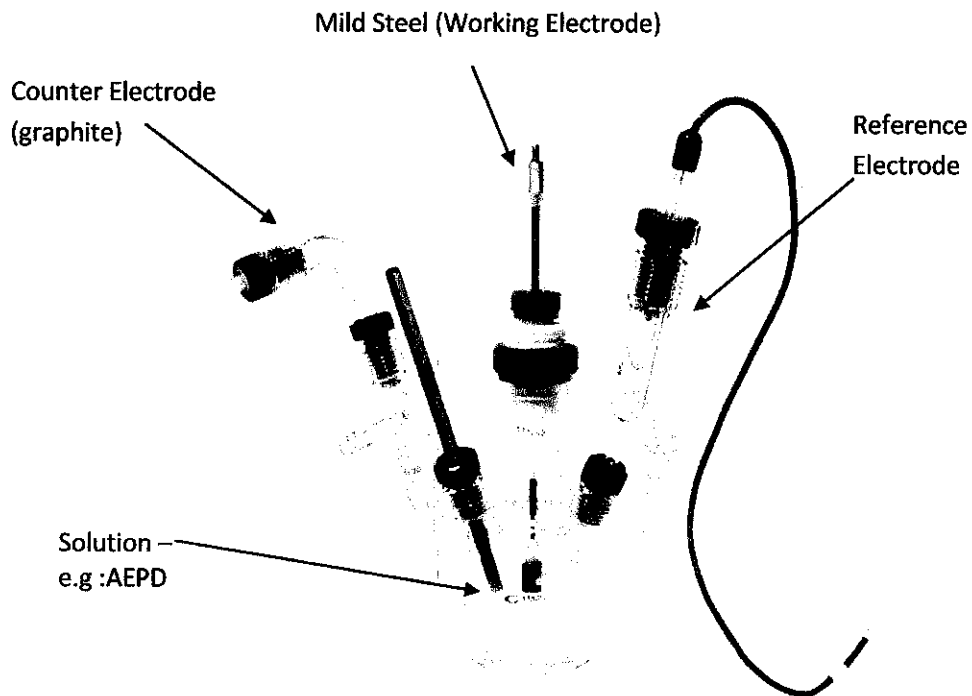
Mild Steel (Working Electrode)

Figure 1 Corrosion Cell

2. LITERATURE REVIEW

As corrosion in alkanolamine plants can be caused by a number of factors, guidelines are given in terms of maintaining solvent(amine) cleanliness, acid gas loadings, to minimize effects of corrosion. The topic of corrosion plays an important role in the design and successful operation of commercial gas plant. From a materials degradation and corrosion point of view, there is a wide range of environments amongst the different carbon-capture processes. In general, the high CO2 levels mean that wet process environments tend to be acidic, resulting in high corrosion rates for unprotected carbon steel. In some cases, there is an interaction between choices in the details of the process design and the corrosivity of the environment, and consequently the demands on materials. In particular cases, high-performance, expensive materials may have to be used if the environment is not controlled within suitable limits. (McGraw-Hill,2008)

But first, it is essential in determining the electrochemical reaction in detail and understanding the reactions that take place , thus leading to the corrosion case. Basically, an electrochemical reaction is defined as a chemical reaction involving the transfer of electrons. It is also a chemical reaction which involves oxidation and reduction. Since metallic corrosion is almost always an electrochemical process, it is important to understand the basic nature of electrochemical reactions. (McGraw-Hill,2008) Most metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution.Corrosion normally occurs at a rate determined by an equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The other is the cathodic reaction, in which a solution species (often O_2 or H^+) is reduced, removing electrons from the metal. When these two reactions are in equilibrium, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs. (Kobe, 1952)

Briefly then, for corrosion to take place, there must be formation of ions and release of electrons at anodic surface where oxidation or deterioration of the metal occurs. There must be a simultaneous reaction at the cathodic surface to consume the electrons that are generated at the anode part. (McGraw-Hill,2008)

2.1 Type of Steel Used

The type of steel used is mild steel. It is the most common form of steel. While it is not brittle but consist the hardness attributes, it is widely used when large amount of steels are needed(- *Effects of multiphase flow on internal CO2 corrosion of mild steel pipelines*). As an example, for the purpose of many equipments in the chemicals process plants which consist huge amount of steels. Mild steel is a carbon steel typically with average percentage of 0.25% Carbon and 0.4%-0.7% manganese, 0.1%-0.5% Silicon and some + traces of other elements such as phosphorous.

Mild steel (a so-called carbon steel) is a general term for a range of low carbon (a maximum of about 0.3%) steels that have good strength and can be bent, worked or can be welded into an endless variety of shapes for uses from vehicles (like cars and ships) to building materials.(- *Iron gets a new coat*)

As for the experiment, approximately, the sample type of mild steel consists the fraction of C - 0.20,Mn - 0.51,P – 0.013.S – 0.039,Si – 0.17 and Fe - balance .

Exposed area of Steel
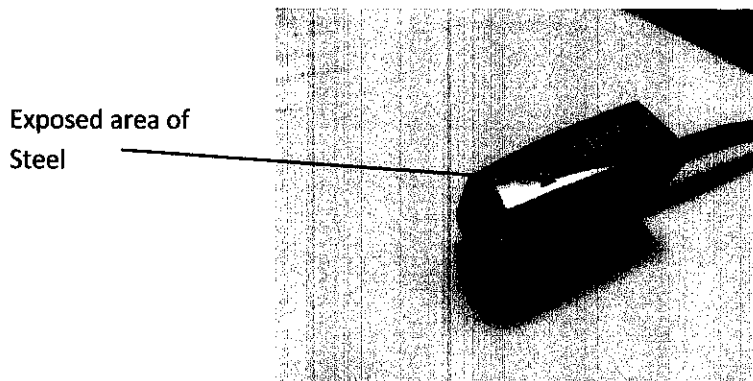
Figure 2 Sample-Mild Steel

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2.2 Anode Process

Anodic reaction occurring during corrosion can be written in the general form:

General anodic reaction: $M(s) \rightarrow M^{n+} + ne^-$
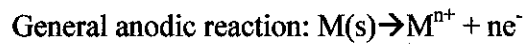
That is, the corrosion of metal M results in the oxidation of metal M to an ion with a valence charge of n+ and the release of n electrons. The value of n, of course, depends primarily on the nature of the metal. As current generated by one of anodic reactions expressed, it is possible to convert the current to an equivalent mass loss, or corrosion penetration rate.

Faraday's law states that reaction with 1 mol of silver would require 1 mol of electrons, or 1 Avogadro's number of electrons. Charge carried by 1 mol of electrons is known as 1 Faraday (F). Multiplying electronic charge by Avogadro number means 1F equals 96485 C/mol of electrons. Combining the principles with specific electrochemical reactions of known stoichiometry leads to

$$Q = F . \Delta N . n$$

N is the number of moles and ΔN the change in that amount
n is the number of electrons per molecule of the species being reacted

Q can be defined in terms of electric current

$$Q = \int_0^t I . dt$$

I is the total current in amperes (A)
t is the duration of the electrochemical process in seconds (s)

2.3 Cathodic Process

When hydrogen ions are reduced to their atomic form, they often combine , to produce hydrogen gas through reaction with electrons at cathodic surface. Reduction of hydrogen ions at cathodic surface will disturb the balance between acidic hydrogen ions and hydroxyl ions, and make less acidic or more alkaline or basic at the corroding interface.

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The change in concentration of hydrogen ions or increase in hydroxyl ions can be shown by use of pH indicators. Several other cathodic reactions encountered during corrosion of metals are such :

i.   Acid solutions : $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

ii.   Neutral or basic solutions : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

iii. Metal ion reduction : $Fe^{3+} + e^- \rightarrow Fe^{2+}$

iv.   Metal deposition : $Cu^{2+} + 2e^- \rightarrow Cu(s)$

Above all, the reactions are similar in one respect, which is they consume electrons. All corrosion reactions are simply combinations of one or more of the above cathodic reactions, together with an anodic reaction. During corrosion , more than one oxidation and one reduction reaction may occur. For example, during the corrosion of an alloy, its component metal atoms go into solution. (McGraw-Hill,2008)

2.4 Relationship with the Amine System

To relate, in industries, amine solvents are mostly used to remove CO2 gas in the process gas which will be passed to the downstream. Specifically in alkanolamine treating unit, feed gas containing CO2 flows into column where it contacts amine solution. Acid gas components are removed from gas by chemical reaction with the amine.(Kohl, Nielsen 1997). Purified gas is the overhead product while rich amine solution flows at the bottom, which is then will be treated. Treated in flash drum, rich amine is flashed to a lower pressure to remove dissolved and entrained hydrocarbons. Rich amine then flows to amine regenerator, in which acid gas are stripped from the solution by using heat. Acid gas as the overhead product and lean amine solution as bottom product.(Correa, Gomes, Sllveira, Baptista, & Vigo, 2000)
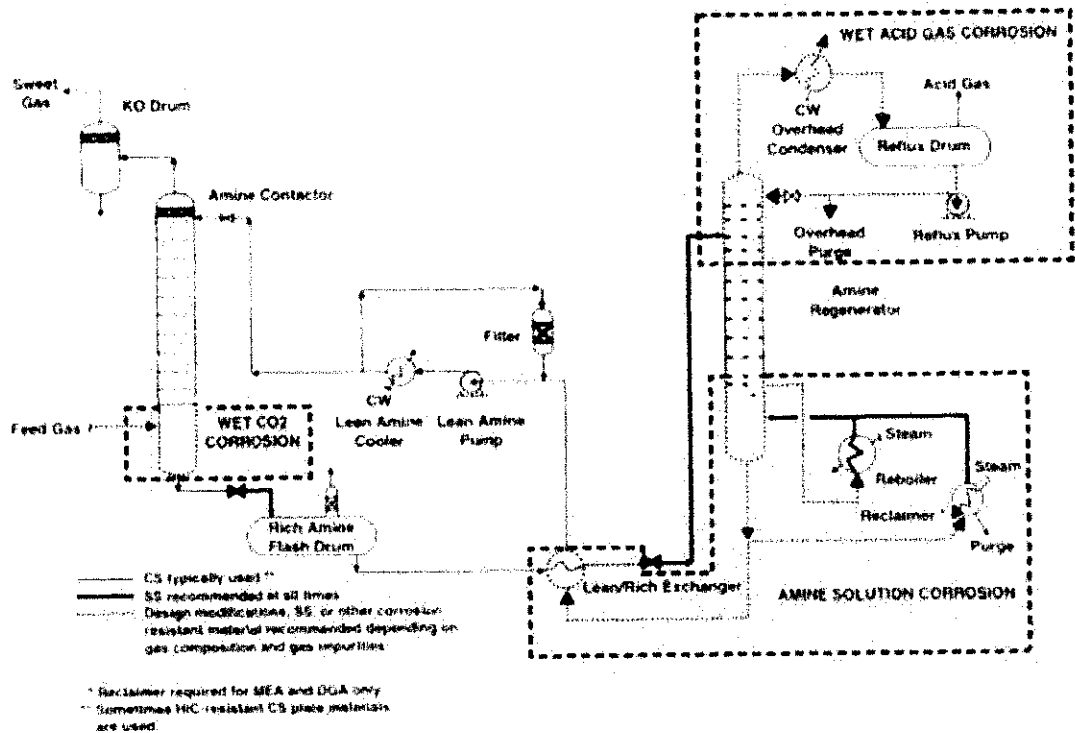
Figure 3 Flow diagram of typical amine plant

As most of equipment and piping in an alkanolamine plant are constructed of carbon steel, it is possible that corrosion should take place.

The anodic half reaction is the oxidation of iron to ferrous ion :

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
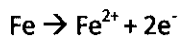
Cathodic half reaction is reduction of hydrogen ion , H+

$$2H^{+} + 2e^{-} \rightarrow H_2$$
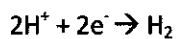
As indicated in the figure , corrosion in amine plants are said to be as Amine Solution Corrosion, which is the corrosion of carbon steel in the presence of aqueous amine. (F.Bosen, Dow)

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2.5 Chemistry of CO_2 Absorption by Amines

Various alkanolamines are used to absorb CO_2, from process such as monoethanolamine (MEA), diethanolamine(DEA), and N-methyldiethanolamine(MDEA). Conventional alkanolamines had their disadvantages, whether it is a primary amine(MEA), secondary amine(DEA), or tertiary amine (MDEA). In order to choose the best amine for the process of, several factors can be considered which are the absorption capacity, reaction kinetics and renegeration potential.(McCann, Maeder, & Attalla, 2008)

Amines are derivatives of ammonia, where in one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group (Lepaumier, Picq, & Carrette, 2009). All above three mentioned alkanolamines are widely used in the industry.

Basically, available amines in industry mainly consists of conventional alkanolamines and sterically hindered amines. Most of industrially used amines come from the class of conventional alkanolamines. Conventional amines are classified into primary amines, secondary amines, and tertiary amines.

Basically, easiest way to think of amines is as near relatives of ammonia, NH3. In amines, the hydrogen atoms in the ammonia have been replaced one at a time by hydrocarbon groups. In primary amines, only one of the hydrogen atoms in the ammonia molecule has been replaced. That means that the formula of the primary amine will be RNH2 where "R" is an alkyl group. One example of primary amines is Monoethanolamine (MEA)
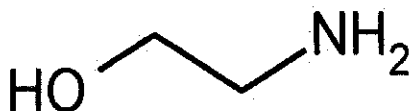
Figure 4 Monoethanolamine Structure

In a secondary amine, two of the hydrogens in an ammonia molecule have been replaced by hydrocarbon groups. At this level, it is only likely to come across simple ones where both of the hydrocarbon groups are alkyl groups and both are the same. One example of secondary amines is Diethanolamine(DEA)
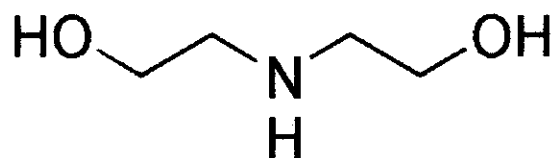
Figure 5 Diethanolamine Structure

Meanwhile for tertiary amine , all of hydrogens in an ammonia molecule have been replaced by hydrocarbon groups. Again, it is only likely to come across simple ones where all three of the hydrocarbon groups are alkyl groups and all three are the same. One example of tertiary amine is Methyldiethanolamine.
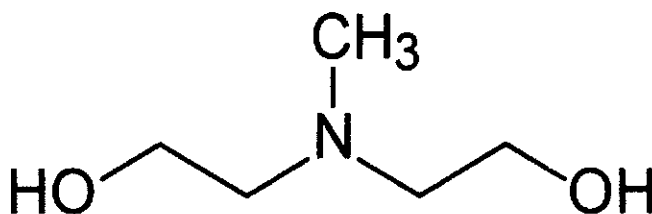
Figure 6 Methyldiethanolamine Structure

For **sterically hindered amine (SHA)**, it refers to a new type of amine which is derived from the conventional amine by addition of other functional group such as methyl and hydroxyl. The addition of these functional groups will create a steric effect which can improve the absorption capability of the amine. Steric effect refers to the fact that each atom within a molecule occupies a cetain amount of spaces.(Lorenz, Dr. Günter 2008). Steric hindrance refers to a situation where the size of a group within the molecule are preventing the chemical reaction that are supposed to happen in related smaller molecule.(Bougie & Iliuta, 2012)

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2-amino-2 methyl -1- propanol(AMP)	
2-Amino-2-methyl-1,3-propanediol(AMPD)	
2-Amino-2-(hydroxymethyl)-1,3-propanediol(AHPD)	
2-amino 2-ethyl-1,3-propanediol(AEPD)	

Figure 7 Sterical Hindered Amine and Molecular Structures

The key advantage of the primary and secondary alkanolamines such as MEA and DEA is their fast reactivity due to the formaton of stable carbamates. Conversely, this will lead to very high solvent regeneration cost. As for the absorption capacity side, they have the drawback of a relatively low CO_2 loading (limited to 0.5 mol CO_2/mole amile). Tertiary alkanolamines like MDEA, have low reactivity with respect to CO_2, due

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to the exclusive formation of bicarbonates by CO_2 hydrolysis. Hydrolysis is a slower than direct reaction. Therefore tertiary have low CO2, absorption rates.(Rinker,Sandall 2000) . However, this will lead to a very low solvent regeneration cost. Another advantage of these amines is the high CO_2 theoretical loading capacity of 1 mol of CO_2/mol of amine. .(Bougie & Iliuta, 2012). It was suggested that absorption rate of tertiary amines can be improved by the addition of a small amount of primary or secondary amines (MEA,DEA). For the amount of energy necessary for solvent regeneration ; primary and secondary amines require high amounts of energy for solvent regeneration compared to tertiary amines. (Nuchitprasittichai & Cremaschi, 2011)

The reactions of primary and secondary alkanolamines with CO_2 can be described by zwitterions equation. Zwitterion refers to neutral molecule with a positive and a negative electrical charge at different locations within that molecule. Zwitterions are sometimes also called inner salts.(Bougie & Iliuta, 2009)

$$CO_2 + RNH_2 \leftrightarrow RNH_2^+ COO^-$$
$$RNH_2 + COO^- + B \rightarrow RNHCOO^- + BH^+$$
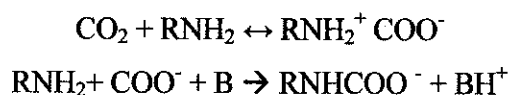
For case of primary and secondary alkanolamines, formation of carbamate is the main reaction. This due to stability of the carbamate compound , caused by unrestricted rotation of aliphatic carbon atom around aminocarbamate group.(Veawab, Tontiwachwuthikul, & Chakma, 1999b) Based on second reaction, B can be the amine, water or hydroxyl ion. These three substances can contribute to deprotonation of zwitterions in aqueous solution.

$$RNH_2 + COO^- + RNH_2 \rightarrow RNHCOO^- + RNH_3^+$$
$$RNH_2 + H_2O + RNH_2 \rightarrow RNHCOO^- + H_3O^+$$
$$RNH_2 + COO^- + OH^- \rightarrow RNHCOO^- + H_2O$$
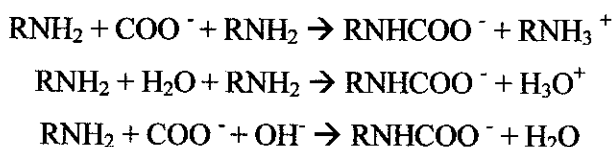
Overall reactions for alkanolamines is written as
$$2RNH_2 + CO_2 \rightarrow RNHCOO^- + RNH_3^+$$

Meanwhile for the sterically hindered amines (SHA), they mainly carry the higher absorption capacity, absorption rate, selectivity and degradation resistance advantages over conventional alkanolamines for CO_2 removal from gases. Due to the hindrance of the bulky group adjacent to the amino group, sterically hindered amines form unstable carbamates. Hydrolysis of the carbamates lead to a preferential bicarbonate formation process, resulting in theoretical loading capacity up to 1.0. Reaction kinetics significantly higher than those related to tertiary amines, coupled with a low solvent regeneration cost offer to SHA. (Bougie & Iliuta, 2012)

For reaction of sterically hindered amines, in contrast with alkanolamines, low stability of carbamate compound is produced. Carbamate compound likely to react with water and forms free amine and bicarbonate ions. Due to the **occurrence of free amine formation, only 1 mol of sterically hindered amine instead of 2 mol of alkanolamine** is required to react with 1 mol of CO_2.

Overall reaction for sterically hindered amines can be written as

$$CO_2 + RNH_2 + H_2O \leftrightarrow RNH_2^+ \; HCO_3^-$$

2.6 Effect of Operating Parameters to Corrosion

a. CO_2 loading

Corrosion rate increases with increasing CO_2 loading in the amine system. Effect of CO_2 loading on corrosion is due to an increase in concentration of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) that can induce the corrosion of iron. (Heuer,Stubbins 1999)Formation of carbonic acid and bicarbonate are explained as:

$$H_2O + CO2 \rightarrow H_2CO_3$$
$$2H_2CO_3 + 2e^- \leftrightarrow H_2 + 2HCO_3^-$$
$$2HCO_3^- + 2e^- \leftrightarrow H_2 + 2\,CO_3\,2^-$$
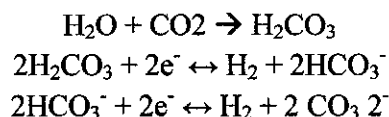
Reduction-oxidation of iron with carbonic acid and bicarbonate ion are such

$$Fe + 2\,H_2CO_3 \leftrightarrow H_2 + Fe(HCO_3)_2$$
$$Fe + 2HCO_3 - \leftrightarrow H_2 + FeCO_3 + CO_3^{2-}$$
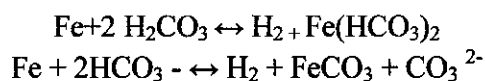
Also found that amounts of bicarbonate and hydronium ions generally increase,

$$2RR'NH + CO_2 \leftrightarrow RR'NCOO\text{-} + RR'NH_2^+$$
$$RR'NCOO^- + 2H_2O \leftrightarrow RR'NH + HCO_3^-$$
$$RR'NH_2^+ + H_2O \leftrightarrow H_3O^+ \, RR'NH$$
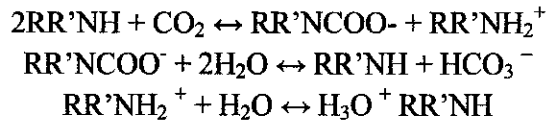
It is seen from CE that carbonate and bicarbonate anions increase with increasing CO_2 loading. This is attributed to the increase in the amount of dissolved CO_2 in the system. The amounts of carbonate/bicarbonate anions are dominant in this system causing significant difference in corrosion rates of these systems.

b. Operating Temperature

A higher temperature increases the corrosion rate of the system. The reason for the increase in corrosiveness with operating temperature can be explained on the basis of reaction kinetics that temperature generally accelerates the rate of any reaction (Wiley, 1999). All reactions mentioned in the previous section can go faster. The dissolved oxygen, H^+ or H_3O^+, H_2CO3, and $HCO3^-$ enhance the reduction rate, and then, more metal is dissolved into the solution, thus leading to a higher corrosion rate.

c. Oxygen Concentration

The corrosion rate increases as oxygen concentration increases. This is because the higher the oxygen concentrations, the higher the dissolved oxygen present in the tested solution resulting in the dissolution of iron. The reduction-oxidation reaction among iron, dissolved oxygen, and water occurs as in reaction

$$2\,Fe + O_2 + 2H_2O \leftrightarrow 2Fe(OH)_2$$
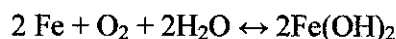
The produced ferrous hydroxide component ($Fe(OH)_2$) is unstable in systems containing oxygen and thus is oxidized to the ferric salt ($Fe(OH)_3$) or rust (Fontana, 1986)

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$$2Fe(OH)_2 + \tfrac{1}{2} O_2 + H_2O \leftrightarrow 2Fe(OH)_3$$
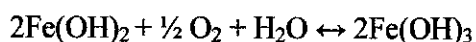
2.7 2-Amino-2-Ethyl-1-3-Propanediol

As mentioned in the problem statement, chosen SHA for the project is AEPD. AEPD is the derivation of AMPD , which addition of one methyl group into AMPD structure.
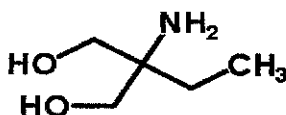
Figure 8 AEPD Molecular Structure

Formula for AEPD is $C_5H_{13}NO_2$. Density of AEPD is 1.099 and molecular weight is 119.16. AEPD is soluble in water and can cause irritations if get in contact with skin or eye. AEPD will react with CO_2 to absorb the CO_2 from gas stream.

As previously done on the research regarding solubility data for aqueous AEPD, it is worthful to carry out the corrosion rate studies as we could determine the level of mole of CO_2 absorbance per mole of AEPD, thus analyzing the corrosion data based on different parameters, such as CO_2 loadings, temperature , and concentrations of AEPD to be used.

Table 1 Solubility data for Aqueous AEPD

Type of amine	Concentration	Pressure	Temperature (K)	Solubility = mole CO_2/mole Amine
Aqueous AEPD	10 mass % AEPD	1-3000 kPa	313.151	Highest : 1.289 Lowest : 0.632
		1-3000 kPa	323.15	Highest : 1.189 Lowest : 0.664 Highest : 1.108 Lowest : 0.179
	30 mass % AEPD	1.3000 kPa	333.15	Highest : 1.026 Lowest : 0.206

As the solubility data for AEPD which was done previously consist of several parameters including different pressure drop,CO_2 loading, and effect of different AEPD concentration on absorption of CO_2, those data might be helpful in assisting the study of corrosion rate behavior on mild steel, by using aqueous AEPD. Plus, there is no available study on the corrosion rate that has being done using aqueous AEPD, so far. This is why AEPD is being selected as the amine solution for the study, plus the available data on CO_2 solubility is already produced.

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3. METHODOLOGY

3.1 Research Methodology

a

b

c

d

e

a. Sample mounting – Prepare mounting into approximately justified space for the steel sample, by using aluminum foil. Epoxy and hardener is poured into mountings, with the mild steel already put inside.

b. Grinder and Polisher machine – Sample is grinded and polished using the machine. According to acceptable speed (rpm, rotation per minute, normally 160 – 180)

c. Grinding – Sample is grinded to make it into smaller size. Plus, Grind the sample until one side of the mild steel is exposed.

d. Polishing – Polish the exposed area of the mild steel for corrosion test

e. Sample steel with exposed area – Exposed sample steel which is ready for corrosion test.
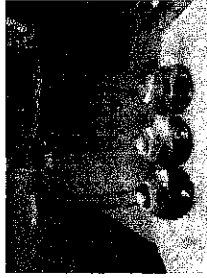
f
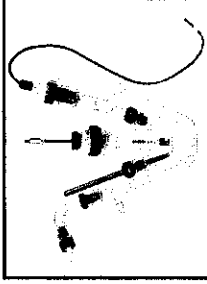
g

h

i

f. Diluted AEPD – diluted AEPD with distilled water, from left, 0.9 , 0.6, and 0.3 M.

g. Corrosion cell setup – three working electrodes , e.g : counter electrode, reference electrode, working electrode (sample steel). Solution (AEPD) is poured into the corrosion cell container, and the all the electrodes are immersed into it.

h. EIS machine – the machine (wires) are connected to the corrosion cell, and the EIS machine is connected to the WEIS application in the computer.

i. Sample Corrosion Cell – Complete setup of the corrosion cell. Ready for testing.
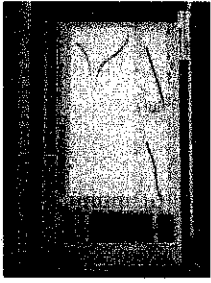
j
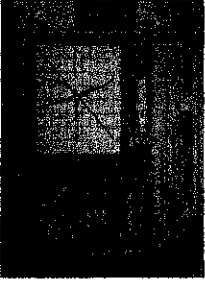
k

l

j. Tafel Plot – result, from WEIS software. The trend of the plot is observed for every trial, and other parameters such as voltage, current, are also monitored. Any abnormality is observed via Tafel Plot.

k. Data Storage IVMAN – the result from WEIS is exported into IVMAN application, in adjusting acceptable corrosion rate. Corrosion rate, corrosion coefficients are obtained from this application.

l. The corrosion product on the steel sample. Obvious corrosion products that happen on the sample are chosen, and sent to SEM(Scanning Electron Microscopy) for further analysis of the surface, in producing graphical results.

3.2 Project Activities-Preparation of steel sample for corrosion test

1. Mild steel is cut using abrasive cutter, to dimension – 19mm x 16mm
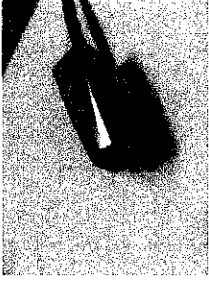
2. Prepare mounting into approximately justified space for the steel sample, by using aluminum foil.xz

3. Epoxy and hardener is poured into mountings, with the mild steel already put inside.

4. Immerse the mild steel with epoxy and hardener according to correct ratio 5:1 (epoxy:hardener)

5. Wait for 1 day, to give time the sample to dry and hardened.

6. Cut the hardened sample which is hardened with the epoxy, into small pieces.

7. Grind the sample until one side of the mild steel is exposed.

8. Polish the area of the exposed mild steel, for corrosion test.

9. Measure the area of exposed mild steel for further measurement.
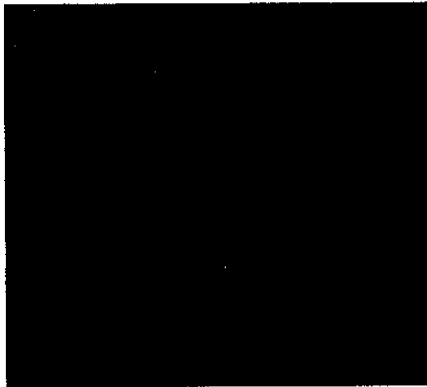
Figure 7 Metal sample inside epoxy 3mounting
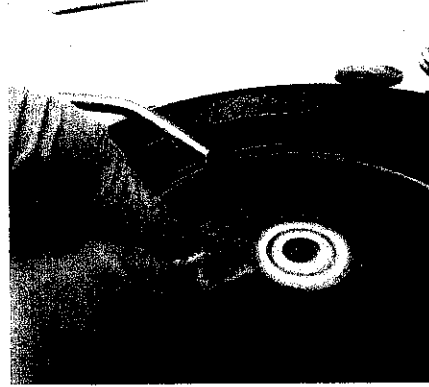
Figure 8 Grinding the sample into desired shape

3.3 Corrosion Cell

The three-electrode cell is the standard laboratory apparatus for the quantitative investigation of the corrosion properties of materials. It is a refined version of the basic wet corrosion cell. It can be used in many different types of corrosion experiments.

i.   The working electrode is the name given to the electrode being investigated. current measurements can be converted into current densities for further analysis and calculation. The working electrode is the steel sample which we intend to observe and measure the corrosion rate.
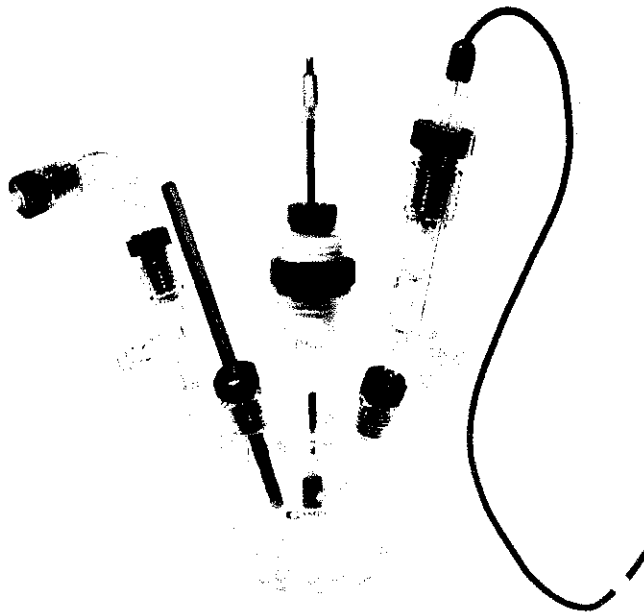
Figure 9 Corrosion Cell

Source- *http://www.gamry.com/products/cells/eurocell-corrosion-cell/*

ii. Second, "Counter (auxiliary) electrode" is the name given to the second electrode which is present specifically to carry the current in the circuit created by the investigation: it is not required for measurements of potential. Graphite is always used.

iii. Third, the "reference electrode" is present to provide a very stable datum point against which the potential of the working electrode can be measured.

iv. Other essential components needed for the experiment is current measuring device, a potential measuring device and a source of potential.

3.4 EIS

Electrochemical Impedance Spectroscopy (EIS) consists of many advantages compared to other electrochemical techniques. During EIS experiments, small amplitude of AC signal is applied to the system or condition that is being studied. It is a non destructive method for evaluation of wide range of materials, including coatings, films, and corrosion inhibitors. It possesses the ability of delivering information such as corrosion rate, electrochemical mechanisms and reaction kinetics, and detection of localized corrosion.

In this experiment, electrochemical impedance is measured by applying AC potential to an electrochemical cell and then measuring the current through the cell.

Measurement takes place as

i. Observation of the Tafel plot, (Electromotive force vs Log I(current), together with current vs time, and voltage vs time, in the WEIS software.

ii. Tafel analysis, which is adjusting the tafel plot obtained to the extent which it follows the normal tafel plot fitting provided by the IVMAN software, in calculating corrosion rate.

iii. Linear Polarization Method which is adjusting the graph obtained, fitting it to the linear line provided by IVMAN software in calculating corrosion rate.

Potentiodynamic, same pattern like Tafel, but to produce a qualitative picture of the metal sample, in the solution. It follows the trend of normal

Schematic Diagram

Tafel

Voltage

Fitted

Anodic

Cathodic

Corrosion Potential

Corrosion Current

Ecorr[V]   -348.501m

Icorr[A]   368.807n

b_a [V/div]   0.206

b_c [V/div]   0.089

Rp[Ohm]   73.391K

CR[MPY]   312.872m

CR[mmPY]   7.948m

XScale
Format
Engineering Notation
Precision
0
Autoscale
LooseFit
Major Grid   Minor Grid   Flip Axis

YScale
Format
Engineering Notation
Precision
0
Autoscale
LooseFit
Major Grid   Minor Grid   Flip Axis

b_a – anodic coefficient

b_c -- cathodic coefficient

Corrosion
Rate obtained

Resistance

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3.5 Tafel Plot

i.   A very useful electrochemical technique used for corrosion studies is the
      Tafel plot, where the corrosion current and the corrosion potential can be
      determined.
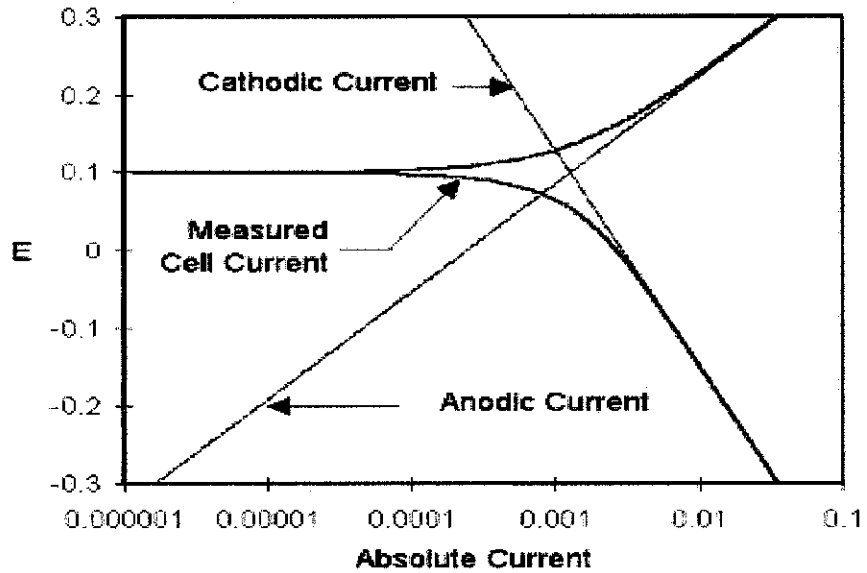
Figure 10 Tafel Plot

Source: J.R. Scully and R.G. Kelly, Methods for Determining Aqueous Corrosion Reaction Rates, *Corrosion:*

Fundamentals, Testing, and Protection, Vol 13A, ASM Handbook, ASM International, 2003, p 68–86

ii. $CR = \dfrac{0.13 \times I_c \times E_w}{A \times D}$

I_c – corrosion current (microamperes per squared centimeters)

E_w – Equivalent weight of the specimen (grams)

A – Surface area of the specimen (squared centimeters)

D – Density of the specimen (grams per centimeter cube)

CR - corrosion rate (mili-inch per year)

3.6 Linear Polarization Resistance

Linear Polarization Resistance monitoring is an effective electrochemical method of measuring corrosion. Monitoring the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream allows the calculation of the corrosion rate.

Small, externally-imposed, potential shifts (ΔE) will construct quantifiable current flow (ΔI) at the corroding electrode. The manners of the externally imposed current are managed, as is that of I_{corr} by the degree of difficulty with which the anodic and cathodic corrosion processes take place. Therefore, the superior intricacy will provide lesser value of I_{corr} and ΔI for a particular potential shift. At small value of ΔE, ΔI is directly proportional to I_{corr} and hence to the corrosion rate. This equation is embodied in the theoretically derived Stern-Geary equation:

$$\frac{\Delta E}{\Delta I} = \frac{\beta_a \beta_c}{2.3 \, (I_{corr} \, (\beta_a \beta_c)}$$
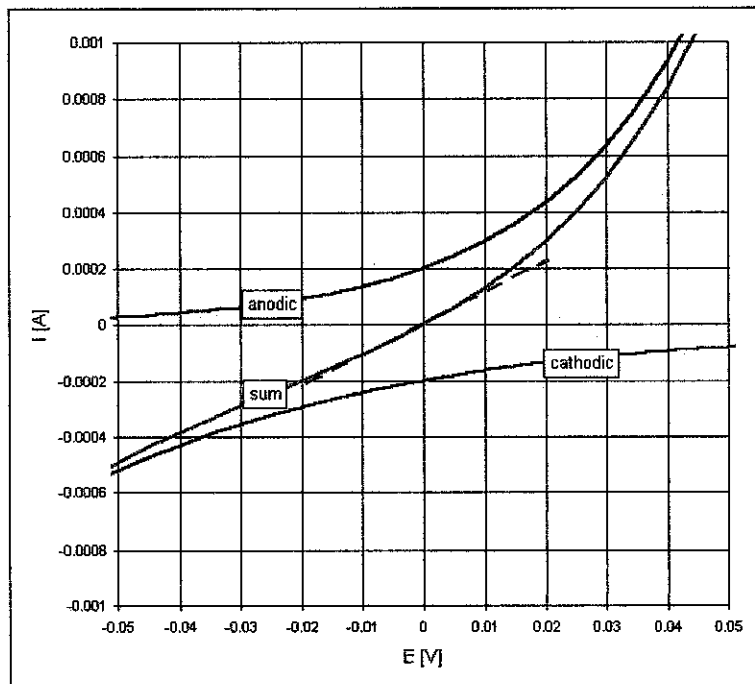
Figure 11 Example of LPR plotting

3.7 Potentiodynamic Polarization

The potentiodynamic polarization technique is generally used to produce a qualitative picture or "fingerprint" of a substance in a given solution. It detects important information just like Tafel Plot such as:

i. The potential region over which the specimen remains passive.

ii. The corrosion rate in the passive region.

iii. The ability of the material to spontaneously passivate in the particular medium

The potential is ramped at a fixed rate per second in a potentiostat and the current response of the working electrode measured. The potential is then plotted as a function of the log of the current density to produce polarization curves. From the data, back extrapolation of the straight line portion of the anodic and cathodic semi logarithmic behavior enables the calculation of the current density at open circuit for input into the Faraday equation to calculate corrosion rate.
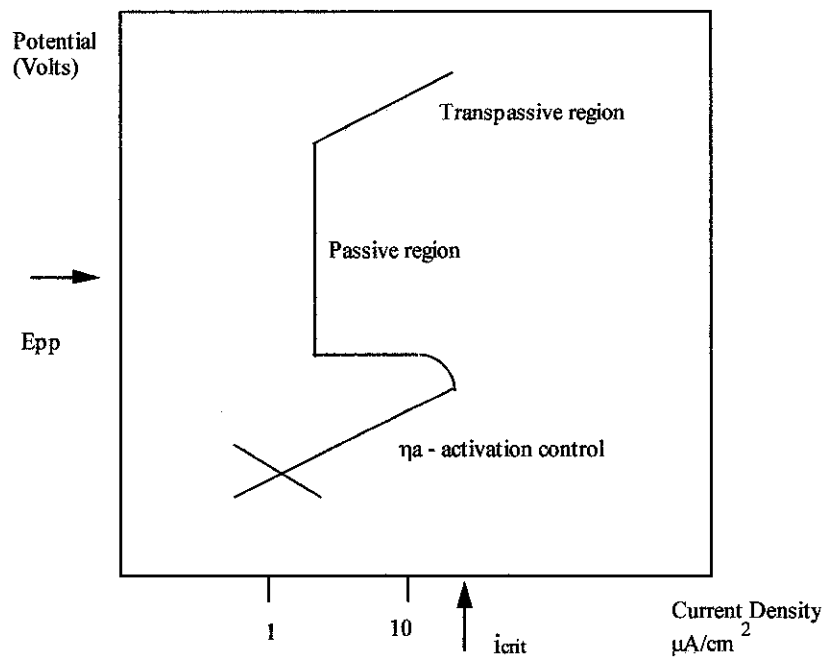
Figure 12 Typical common pattern of Potentiodynamic

3.8 Gantt Chart

Figure 13 Summary of Methodology

Activities	Week 1	2	3	4	5	6	7	8	9	10	11	12	13	14
Searching on journals regarding CO_2 absorption and Corrosion	■	■	■	■	■									
Preparation of Metal Sample		■	■											
Cutting Metal Sample into certain measurement			■											
Attended Lab Briefing														
Preparation of Mounting/Epoxy-hardener for Mild Steel Sample				■	■	■								
Prepare Extended proposal														
Submission of Extended proposal						■								
Proposal Defence								■						
Continue with current progress, Grinding and preparation of corrosion sample									■	■	■	■	■	
Submission of interim report														■

Sem Break

Mid Sem Break

Activities	Week 1	2	3	4	5	6	7	8	9	10	11	12	13	14
Progress with the Electrochemical Corrosion Cell														
i. Selecting the appropriate Steel Sample for the purpose of testing the corrosion rate		■												
ii. Diluting the chemical (AEPD) for the solution for corrosion cell			■											

Mid Sem Break

Task													
iii. Producing different Concentration for the purpose of different condition testing on corrosion rate study		███											
iv. Corrosion test- using WEIS software(Electrochemical Impedance Spectrometer)		███	███										
v. Obtain the result and further result analysis using IVMAN for the corrosion rate data and graphic images		███	███										
Study based on i. Concentrations		███											
ii. Temperature					███								
Progress Report Submission						███							
Analysis on the bad data or results							███						
Further run on other conditions; mixtures of amines								███					
FYP Final Presentation									███				
Dissertation and Submission									███				

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4. RESULTS

4.1 Corrosion measurement

When a metal corrodes in an aqueous solution, anodic and cathodic sites are developed on the metal surface. A metal when it is plunged into an electrolyte, anodic and cathodic sites are generated on the metal surface and a current starts to flow between them after, perhaps some initial period during which surface oxide films are penetrated. This current flow represents a loss of metal as a result of dissolution.

As for in this experiment which involves the contact of mild steel with the solution of sterically hindered amine, **2-amino 2-ethyl-1,3-propanediol(AEPD)**, we measure the corrosion rate by using the corrosion current and the corrosion potential which are plotted by using Tafel plot. As for the next step, the corrosion rate is calculated by taking values of equivalent weight of specimen(g), surface area of the specimen(cm^2), density of the specimen(g/cm^2).

As the point of concern in the matter of calculation, we prefer the unit of **mm/year**(milimetre per year) or **mpy**(mili inch per year), as those two values are calculated in the software of corrosion calculation.

	$mA\ cm^{-2}$	$mm\ year^{-1}$	mpy	$g\ m^{-2}\ day^{-1}$
$mA\ cm^{-2}$	1	3.28 M/nd	129 M/nd	8.95 M/n
$mm\ year^{-1}$	0.306 nd/M	1	39.4	2.74 d
mpy	0.00777 nd/M	0.0254	1	0.0694 d
$g\ m^{-2}\ day^{-1}$	0.112 n/M	0.365 /d	14.4 /d	1

Table 2 Corrosion Rate Measurement

After the experiment occurs, the measurement takes place as

iv.   Observation of the Tafel plot, (Electromotive force vs Log I(current)), together with current vs time, and voltage vs time, in the WEIS software.

v.   Tafel analysis, which is adjusting the tafel plot obtained to the extent which it follows the normal tafel plot fitting provided by the IVMAN software, in calculating corrosion rate.

vi.   Linear Polarization Method which is adjusting the graph obtained, fitting it to the linear line provided by IVMAN software in calculating corrosion rate.

vii.   Potentiodynamic, same pattern like Tafel, but to produce a qualitative picture of the metal sample, in the solution. It follows the trend of normal Tafel plot,

but with extended trend at the later part of the run, provided by IVMAN software in calculating corrosion rate.

Since the experiment consists of 3 parameters of interest which are :

i.   Concentrations, M (Molarity): 0.3, 0.6 , 0.9

ii.   Temperature : 50 °C, 70 °C, 90 °C

iii.   Mixtures of AEPD and DEA at Concentrations, M (Molarity) : 0.3,0.6,0.9

The results are plotted using three techniques, by **Tafel, Linear Polarization**, and **Potentiodynamic**. After all, the Tafel plots show positive display and appropriate trending for all the parameters. Linear Polarization does not really show the proper trending for certain parameters, meanwhile the Potentiodynamic technique shows a good trend on the high concentration of amine solution for the corrosion cell, only at 0.6M and 0.9M.

Since Tafel plot shows the acceptable trending for the condition of concentration of amine solution and temperature, only Tafel method is used for the Mixtures of AEPD and DEA at the desired concentration (0.3,0.6,0.9 M) .

Apart from that, due to time limitations and limited sample steels (4 sample mountings), it is also regarded as one of the reason for the use of Tafel method only.

Plus, as reference, also concluded in the results is the Tafel plots and data for the corrosion rate of sample steels, with using **only DEA as the corrosion cell solution.**

Here, as an additional information, it is desirable to analyze and compare the results between the conventional alkanolamine (DEA) and the sterically hindered amines (AEPD). The Tafel plots for the DEA solution, are based on the parameters of concentration 0.3 , 0.6, and 0.9 M, and also temperature 50,70 and 90 °C.

Summary of the obtained data

For **(i) concentration** and **(ii) temperature** variations

	Concentration(M)	Temperature (° C)	Tafel	Linear Polarization	Potentiodynamic
AEPD	0.3	50	/	/	
		70	/	/	
		90	/	/	
	0.6	50	/	/	
		70	/	/	
		90			
	0.9	50	/	/	/
		70	/	/	/
		90			

For (iii) Mixtures of AEPD and DEA

	Concentration(M)	Temperature (°C)	Tafel
Mixtures AEPD + DEA	0.3		/
	0.6	50	/
	0.9		/

For DEA alone

	Concentration(M)	Temperature (°C)	Tafel
DEA	0.3		/
	0.6	50	/
	0.9		/

4.2 Results

4.2.1 Discussion

Basically, during the corrosion rate measurement, the activity that happens in the corrosion cell is that,

i.   Anodic reaction – at the steel surface, it loses electrons dissolved and releases positive charged ions into the solution.

ii. Cathodic reaction – as the metal releases electron throught the electrical circuit. The aqueous solution which contains the water and oxygen molecules mostly, received the electron, and forming negatively charged hydroxide ions.

iii. The positively charged ions, will combine with the hydroxide ions and thus forming the corrosion layer on the steel surface.

iv. It can be observed that from the results table , that as lower the resistance recorded, the higher the corrosion rates will be. This might be justified by the higher transfer rate of electron throughout the reaction, higher combination rate of Fe^{2+} and OH^- to form ferrous hydroxide ,$Fe(OH)_2$. Later on the ferrous hydroxide wil be oxidized to ferric salt :

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}\ O_2 \rightarrow 2Fe(OH)_3$$
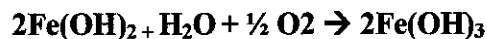
The final product is the familiar rust.

4.2.2 Tafel

The Tafel Plots for the mild steel in aqueous **2-amino 2-ethyl-1,3-propanediol(AEPD)** was measured in various temperatures of 50 °C, 70 °C, and 90 °C. The Tafel Plots were obtained at the potential range from -250 to +250 mV at a scan rate of 10 mV/minute and I Range (A) of 5 A. The kinetic parameters including corrosion current density, I_{corr} and corrosion rate are given in the table below.

4.2.2.1 Variation of Temperature

Concentration	Temp (°C)	E_{corr} [V]	I_{corr} [V]	b_a [V/div]	b_c [V/div]	Rp [ohm]	CR [MPY]	CR [mmPY]
0.3 M	50	-348.501m	368.80n	0.206	0.089	73.39k	312.87m	7.948m
	70	-183.812m	705.431	0.075	0.052	19.01k	598.44m	15.203m
	90	-177.858m	1.683u	0.144	0.078	12.99k	1.427	36.261m

Overall Plot for Variation of Temperature
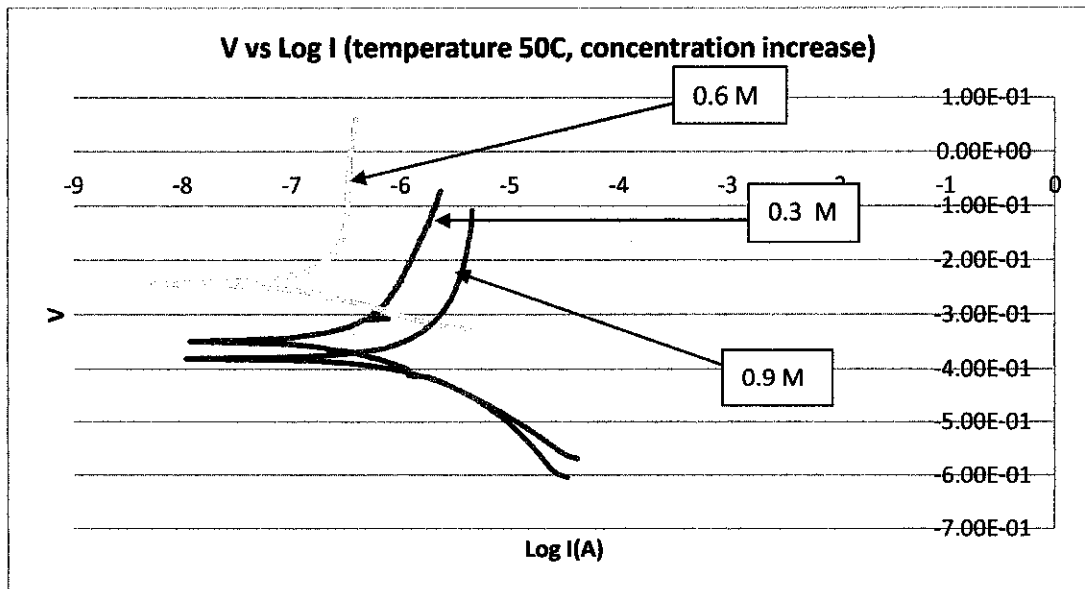
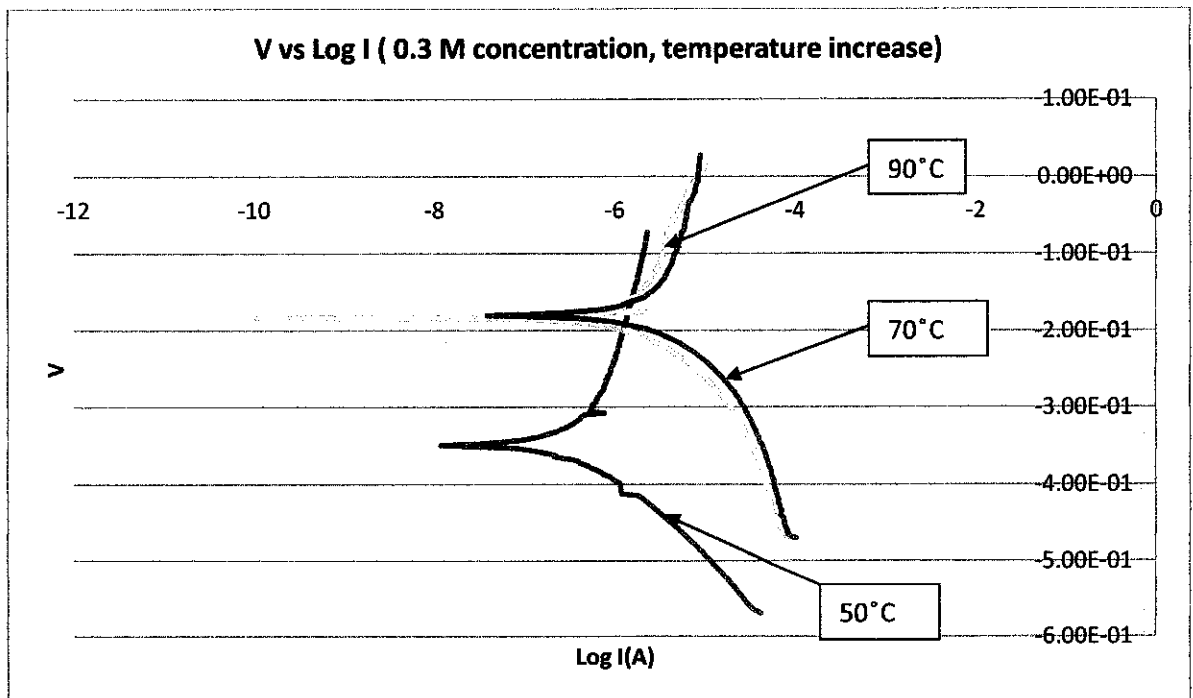### 4.2.2.2 Discussion – Variation of Temperature

- For the Tafel plot, as the temperature of the aqueous AEPD increase, it shows a higher slope on the current recorded for the cathodic part, for 50,70, and 90 ° C respectively.

- Due to the oxide formation , which leads to passivation on the exposed area of the metal, further corrosion is decreases, thus lead to decrease further corrosion current to be recorded on the Tafel plot. It happens on the cathodic current part.

- But, still according to the corrosion principal, as **temperature increases** , the corrosion rate increases. As the dissolved oxygen, and hydroxide enhance the reduction rate, it combines and forms the metal oxide on the exposed area of the steel on a higher rate.

- The result for temperature factor follows as increasing temperature, the corrosion rate yielded at about **7.498 x 10^{-3} mm/year, 15.203 x 10^{-3} mm/year , and 36.261 x 10^{-3} mm/year**, for the 50, 70, and 90 ° C respectively.

4.2.2.3 Variation of Concentration

Concentration	Temp (°C)	E_{corr} [V]	I_{corr} [V]	b_a [V/div]	b_c [V/div]	Rp [ohm]	CR [MPY]	CR [mmPY]
0.3 M		-348.501 mi	368.80n	0.206	0.089	73.39k	312.872 m	7.948m
0.6 M	50	-245.304 m	91.888n	0.125	0.052	172.46k	77.952m	1.980m
0.9 M		-380.607 m	1.664u	0.456	0.158	30.590k	1.412	35.867m

Overall Plot for Variation of Temperature

i.   For Variation of Concentration

V vs Log I (0.3 M concentration, temperature increase)

4.2.2.4 Discussion – Variation of Concentration

- For the graphs for Tafel, the pattern is almost the same for all of the concentration.

- As the temperature is maintained at 50° C, the increase of concentration results to a steeper slope for the upper part of the current recorded.

- It possibly due to the passivation layer that is formed onto the metal steel sample. As passivation layer is formed, the corrosion effect that is supposed to take place, begins to slow down.

- Thus , it displayed a steep slope at the upper part of the cathodic current. It means, the corrosion taking place at the metal has lowered down, and less current recording (eventhough the voltage increase).

- An unusual pattern is observed at the 0.6 M concentration as it yielded a lower corrosion rate than the 0.3 M, most probably to the quick formation of the passivation layer on to the metal surface.

- Afterall, increasing the concentration of the solution, still yield a higher rate of corrosion. This is due to the higher amounts of protonated ion which later on combine with the bicarbonate anion, thus producing iron carbonate, on the exposed steel area.

- The result for concentration factor follows as increasing temperature, the corrosion rate yielded at about **7.498 x 10^{-3} mm/year, 1.980 x 10^{-3} mm/year , and 35.867 x 10^{-3}mm/year**, for the 50, 70, and 90 ° C respectively.
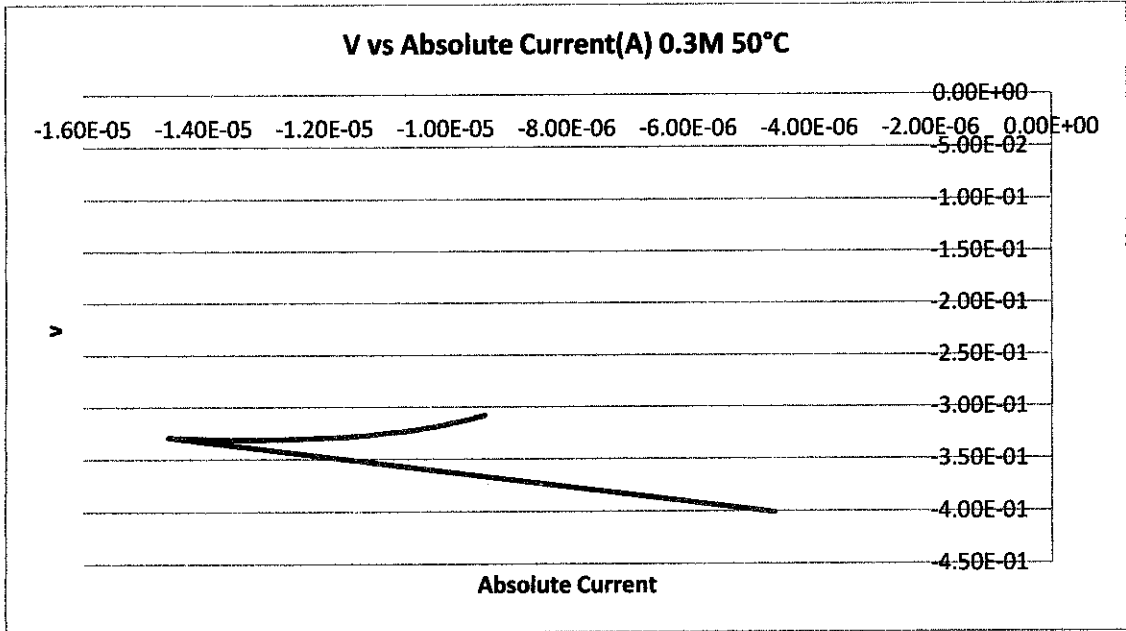
4.2.3 Linear Polarization Method

The linear polarization resistance (LPR) for the mild steel in aqueous **2-amino 2-ethyl-1,3-propanediol(AEPD)** was measured in various temperatures of 50 °C, 70 °C, and 90 °C. Therefore, the LPR plots were obtained at the potential range from -30 to +30 mV at a scan rate of 1 mV/minute and I Range (A) of 5 A. The kinetic parameters are recorded in the table below.

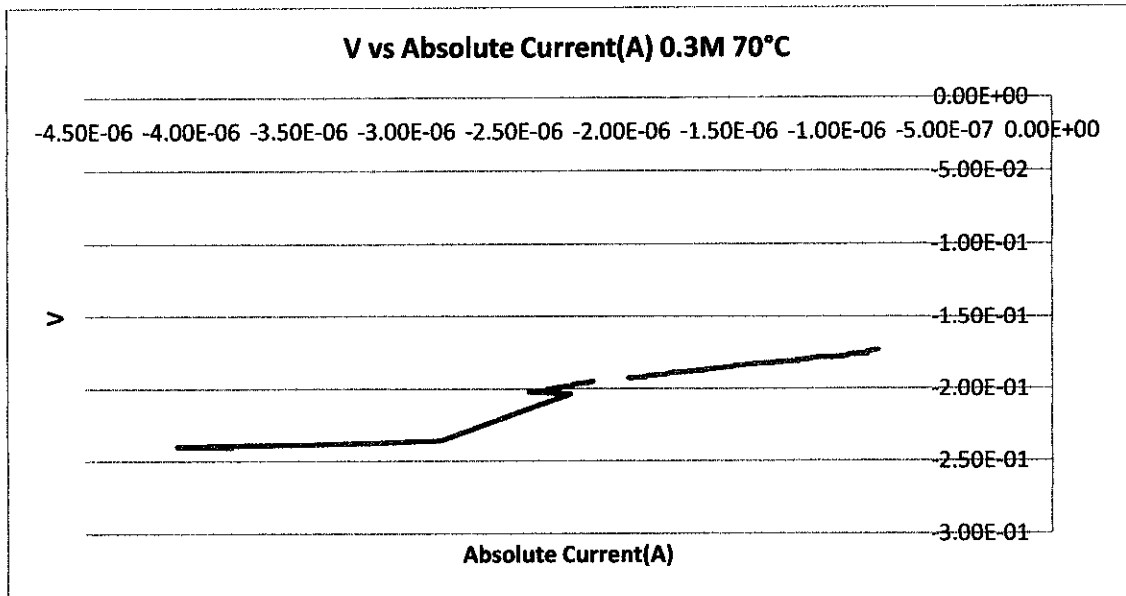| concentration	Temp. ($^\circ$C)	Rp [ohm]	b_a [V/div]	b_c [V/div]	CR [MPY]	CR [mmPY]
0.3 M	50	12.927k	0.12	0.12	1.71	43.435m
	70	16.540k	0.12	0.12	1.336	33.946m
	90	1.049k	0.12	0.12	21.079	535.474m
0.3M		12.927k	0.12	0.12	1.71	43.435m
0.6 M	50	4.489k	0.12	0.12	4.923	125.072m
0.9 M		56.206k	0.12	0.12	393.224m	9.989m

Though the graphs concerning to both parameters of interests which are the concentration and temperature are obtained, they have the inconsistency in the trend of the results plotted.

4.2.3.1 Variation of Temperature

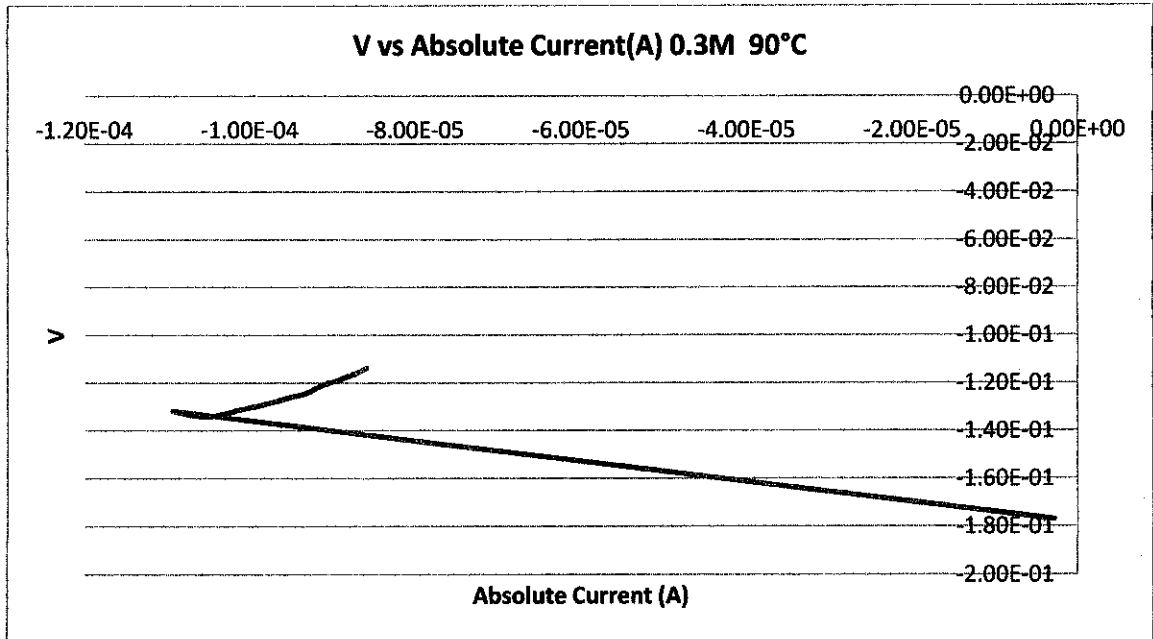i.   AEPD concentration **0.3 M** with temperature of solution **50 ° C**

V vs Absolute Current(A) 0.3M 50°C

Absolute Current

ii.   AEPD concentration **0.3 M** with temperature of solution **70 ° C**

V vs Absolute Current(A) 0.3M 70°C

Absolute Current(A)

AEPD concentration **0.3 M** with temperature of solution 90 ° C

V vs Absolute Current(A) 0.3M 90°C

Absolute Current (A)

4.2.3.2 Variation of Concentration

i. AEPD concentration **0.3 M** with temperature of solution **50 ° C**

V vs Absolute Current(A) 0.3M 50°C

Absolute Current
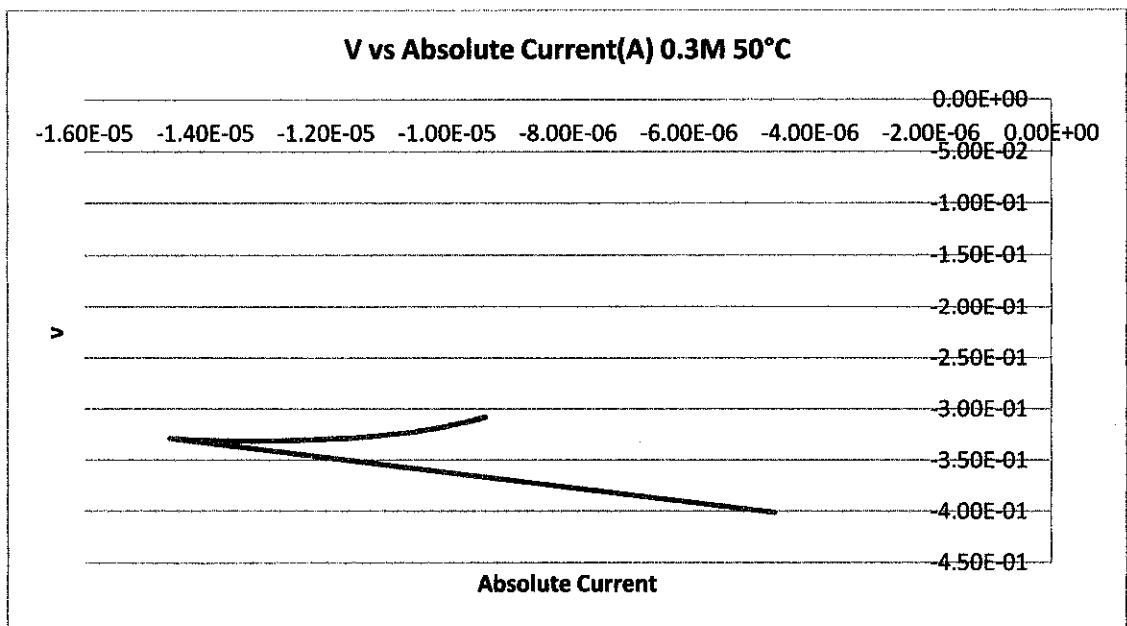
ii. AEPD concentration **0.6 M** with temperature of solution **50 ° C**

V vs Absolute Current(A) 0.6 M 50°C
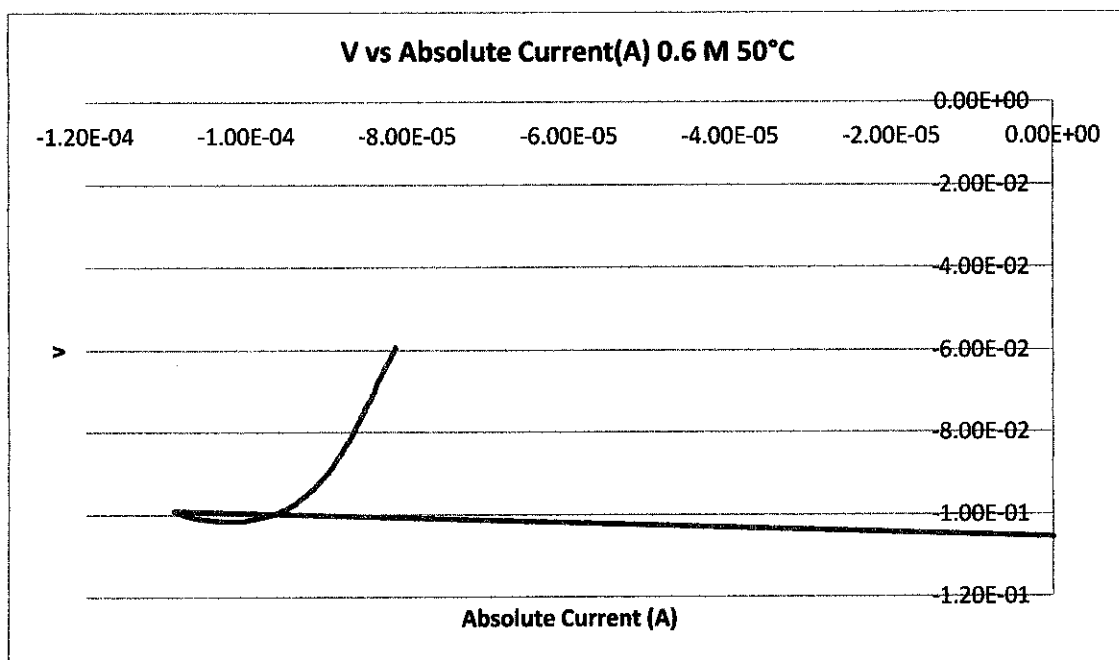
iii. AEPD concentration **0.9 M** with temperature of solution **50 ° C**

**V vs Absolute Current(A) 0.9 M 50°C**
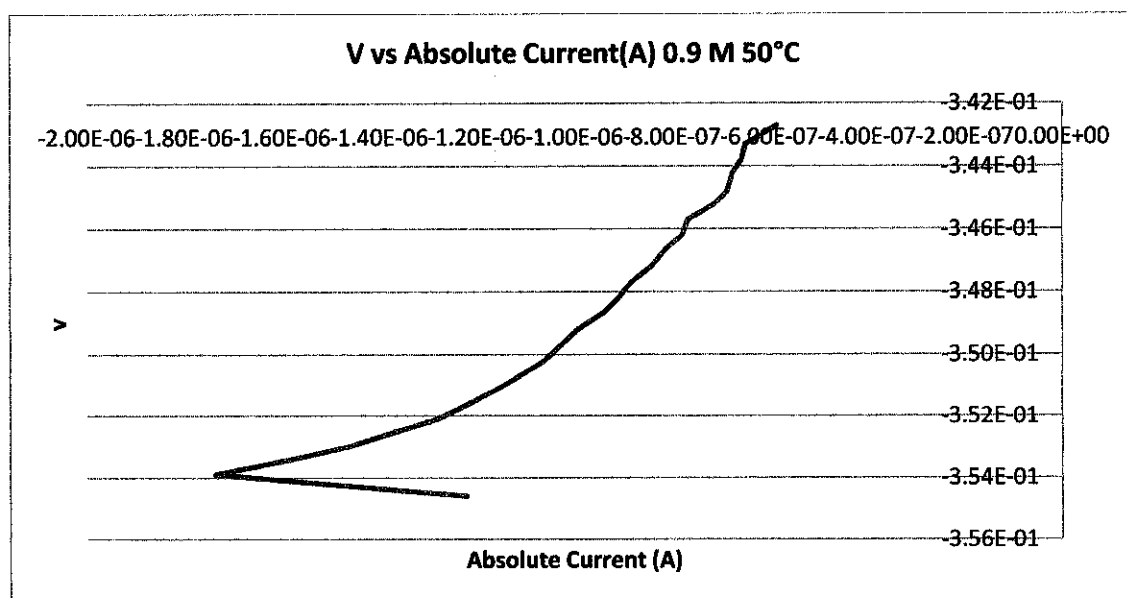
4.2.3.3 Discussion – Overall LPR Graphs

- For overall of the Linear Polarization technique, the plots are displayed in a pattern of abnormal, as random plotting are observed throughout all the trials.

- Those graphs clearly shown that due to the inconsistency in the trend of the results plotted , the method of Linear Polarization is **not a good way** in measuring the corrosion rate in this case, of involving sterically hindered amines.

- The results obtained for the Linear Polarization method did not actually match the theory of higher concentration and higher temperature, which should have shown a higher or increasing corrosion rate.

- Plus, this method also displayed the values of corrosion rate which are extremely high , taking example , at 0.3 M concentration and 90° C, the value showed 535.474 mm/year. Clearly this value is very high, but due to observation of the metal sample after the trial, the surface did not show the formation of particles of corrosion, and thus, it could be concluded that Linear Polarization method is **not the best way** in giving the satisfied and acceptable corrosion rate.

4.2.4 Potentiodynamic

Concentration	Temp. (°C)	E_{corr} [V]	I_{corr} [V]	b_a [V/div]	b_c [V/div]	Rp [ohm]	CR [MPY]	CR [mmPY]
0.9 M	50	-416.585m	5.360u	1.898	0.242	17.412k	4.547	115.505m
	70	-362.795m	9.182u	0.256	0.175	4.912k	7.789	197.880m

4.2.4.1 Overall plot of the Potentiodynamic

V vs Log I(A), Concentration 0.9 M, increasing temperature
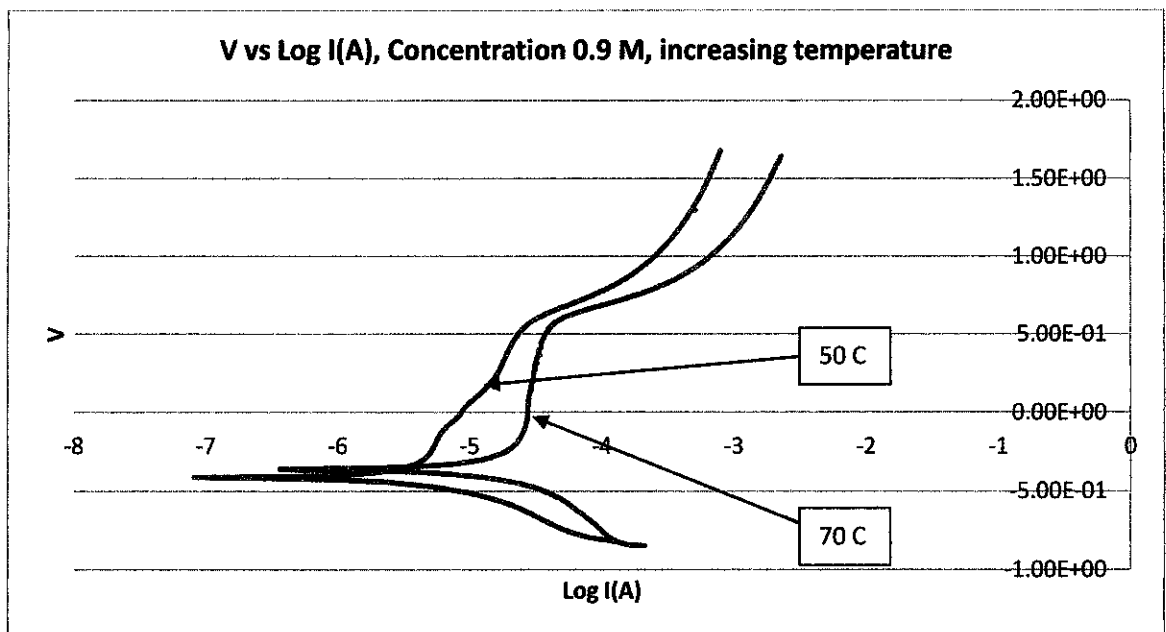
4.2.4.2 Discussion – Potentiodynamic

- For the potentiodynamic method, both graphs concerning to the temperature of 50 °C and 70° C respectively, show the similar trend at which they have the region where the metal sample corrodes, as the applied potential is more positive.

- At about the point where the cathodic current starts, the passivation begins. Passivation is probable due to the formation of a film on the surface on the steel.

- At the point where the slope is high(approaching vertical lines for both graphs), they display the decrease in the current rapidly, as the passivating film forms on the sample steel.

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- At the region where the current starts to increase back, the passivating film begins to break down in that period, known as the transpassive region , where oxygen evolution starts to occur.

- Afterall, from both graphs, they yield high corrosion rate value, only that due to the higher temperature at 70 ° C solution, it yielded much higher corrosion rate value, at **197.880 x 10^{-3}mm/year**, while the 50° C solution produces the corrosion rate value at **83.821 x 10^{-3}mm/year.**

4.2.5   Mixed AEPD and DEA (0.3 , 0.6 , 0.9 M)

The Tafel Plots for the mild steel in aqueous **2-amino 2-ethyl-1,3-propanediol(AEPD),** mixed with **Diethanolamine (DEA).** The concentration for each of the amines are set mixed at **0.3, 0.6** and **0.9 M** respectively of each amine. **Corrosion rates** were measured in temperature of 50 °C. The Tafel Plots were obtained at the potential range from -250 to +250 mV at a scan rate of 10 mV/minute and I Range (A) of 5 A. The kinetic parameters including corrosion current density, I_{corr} and corrosion rate are given in the table below.

Concentration	Temp (° C)	E_{corr} [V]	I_{corr} [V]	b_a [V/div]	b_c [V/div]	Rp [ohm]	CR [MPY]	CR [mmPY]
0.3 M		-255.518 m	882.735n	0.1	0.064	19.203k	748.86m	19.024m
0.6 M	50	-285.978m	2.456u	0.228	0.107	12.864k	2.083	52.920m
0.9 M		-303.071m	5.527u	0.116	0.089	3.959k	4.689	119.115m

4.2.5.1 Overall Tafel Plots of the mixing of amines

V vs Log I (increase concentration,50 C)[DEA+AEPD]

0.3 M
0.6 M
0.9 M

Voltage

Log I(A)
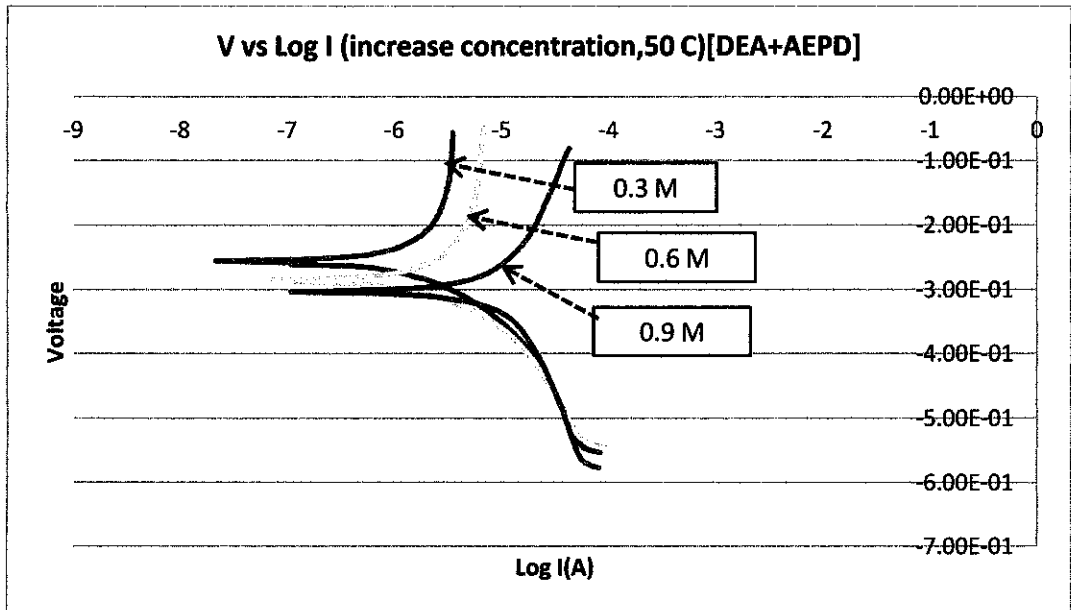
### 4.2.5.2 Discussion – Mixed Amine , AEPD & DEA

- From the Tafel plots, the trends obtained are similar to the previous trending happened on the concentration and temperature, parameter. They consist of the passivation patterns at the cathodic current, plus with the higher corrosion rate yielded for every concentration increment.

- In this parameter, the corrosion rate yielded for 0.3 M is recorded as 19.024 x 10^{-3} mm/year. As compared to the previous results (concentration and temperature), it shown a higher rate.

- The same results also occurred on the 0.6 M and 0.9 M, respectively. As compared to the previous results, for the mixed amines, **0.6 M** concentration yielded much higher rate at **52.920 x 10^{-3} mm/year**. Meanwhile, for the **0.9 M** concentration, it shown a much higher rate at **119.115 x 10^{-3} mm/year**.

- The higher rates obtained for all the concentrations for the mixed amines are due to the existence of the Diethanolamine (DEA), in the solutions. Eventhough DEA is rather used in the industry as the solvent in the CO2 absorption in gas sweetening plant, it still possesses the ability of yielding a higher corrosion rate.

4.2.6 DEA at 0.3, 0.6, and 0.9 M

The Tafel Plots for the mild steel in aqueous **2-amino 2-ethyl-1,3-propanediol(AEPD)**, in **Diethanolamine (DEA)**. The concentration are set mixed at **0.3, 0.6** and **0.9 M. Corrosion rates** were measured in temperature of 50 °C. The Tafel Plots were obtained at the potential range from -250 to +250 mV at a scan rate of 10 mV/minute and I Range (A) of 5 A. The kinetic parameters including corrosion current density, I_{corr} and corrosion rate are given in the table below.

Concentration	Temp. ($^{\circ}$C)	E_{corr} [V]	I_{corr} [V]	b_a [V/div]	b_c [V/div]	Rp [ohm]	CR [MPY]	CR [mmPY]
0.3 M		-231.57m	1.150u	0.013	0.067	16.504k	972.5m	24.704m
0.6 M	50	-223.49m	2.855u	0.208	0.102	10.428k	2.564	65.146m
0.9 M		-92.35m	15.67u	0.153	0.172	2.244k	13.294	337.721m

4.2.6.1 Overall Tafel Plots of the DEA

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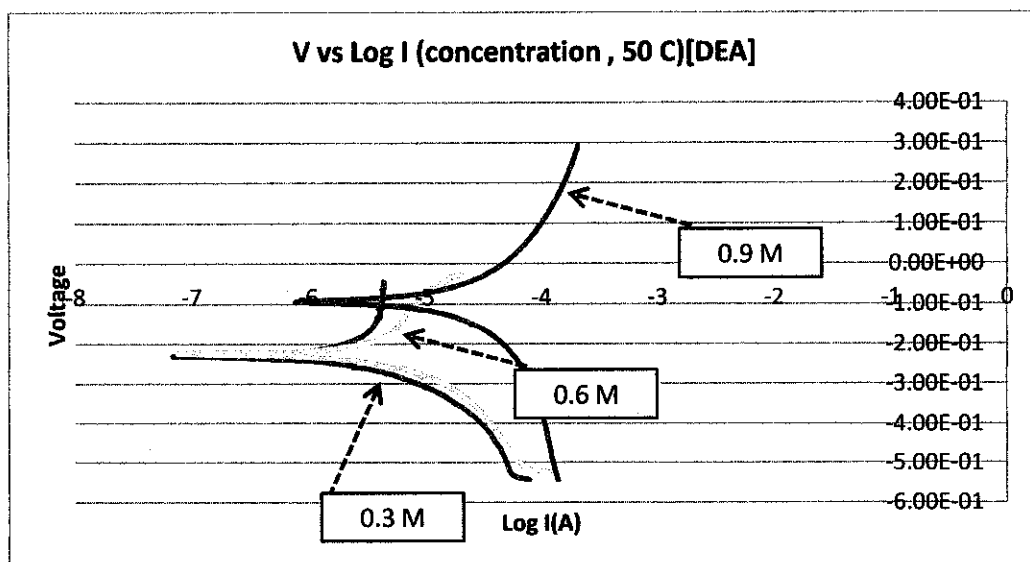
4.2.6.2 Discussion – DEA

- For the Tafel plots , trends obtained are better in the corrosion rate, by means that, all three graphs shown a pattern of signifying tendencies to corrode in higher rates. The cathodic part of the plot did not really show the passivation pattern, but to stress on, for the 0.9 M of DEA concentration, it clearly recorded the highest corrosion rate at **337.721 x 10^{-3}mm/year**. This is due to the high concentration of the DEA itself, which promotes to a system that corroded the steel well. The corrosion rates are followed by **65.146 x 10^{-3}mm/year**, and **24.704 x 10^{-3}mm/year**, for 0.6 M and 0.3 M concentration, respectively.

- Overall, it follows that the higher the concentration of amine, in this case, Diethanolamine, the higher the corrosion rates obtained.

4.3 Scanning Electron Microscopy (SEM)

SEM is a method of getting images of the surface structure of the sample. The electrons beam will be attracted to the atoms and creates the patterns and images of the structure. Two samples were tested.

First sample is the control sample which A36 mild steel which was immersed in the Diethanolamine solution, with concentration 0.9 M and temperature 60 ℃.

Second sample is the A36 mild steel which was immersed in the AEPD solution at concentration 0.9 M and temperature 60 ℃

4.3.1 First Sample , in Diethanolamine(DEA) (0.9 M , 60 ℃)

From the analysis of the sample, it can be observed from the SEM images , shwing the pattern of corrosion on the steel. Roughly at lower magnification, it shown the images of holes happened to be on the surface of the metal. At higher magnification, it shown a clearer view, in which it displays obvious images of holes, signifying that the corrosion of the steel has taken place, specifically in the case of pitting. It also indicates serious corrosion attack on the steel sample. Also found are the element composition that exist on the scanned surface, with iron, Fe being the major component that is recorded.
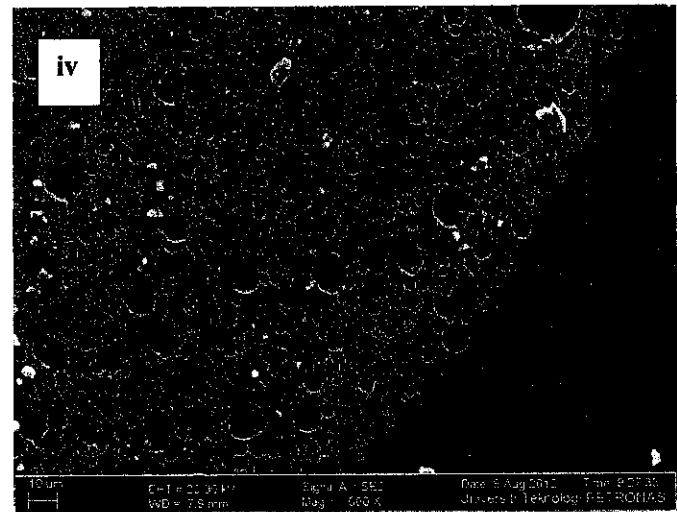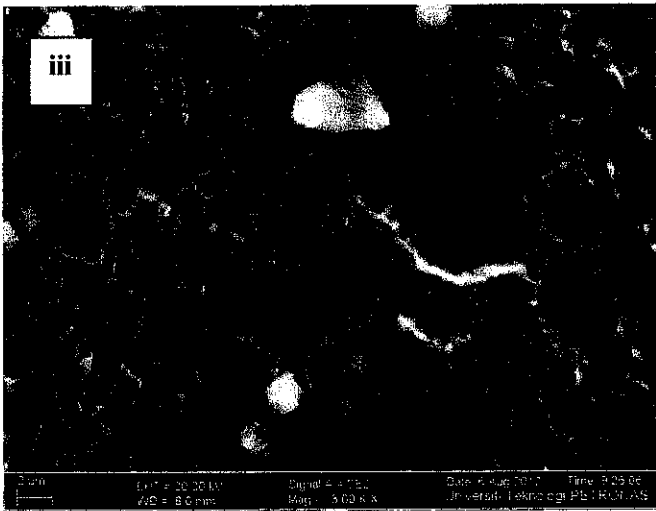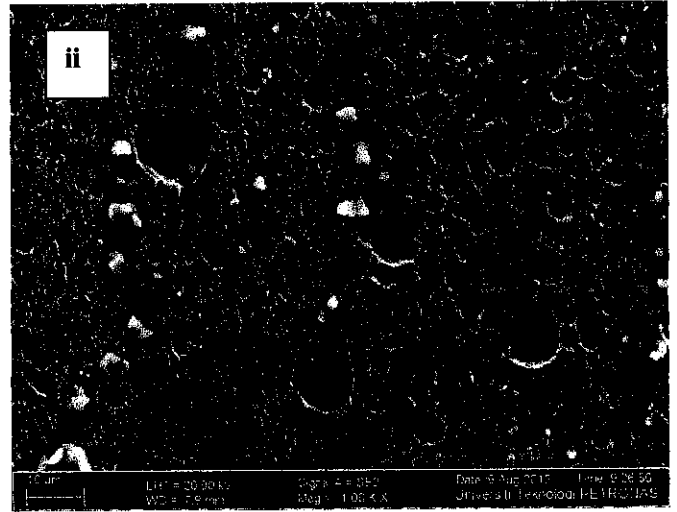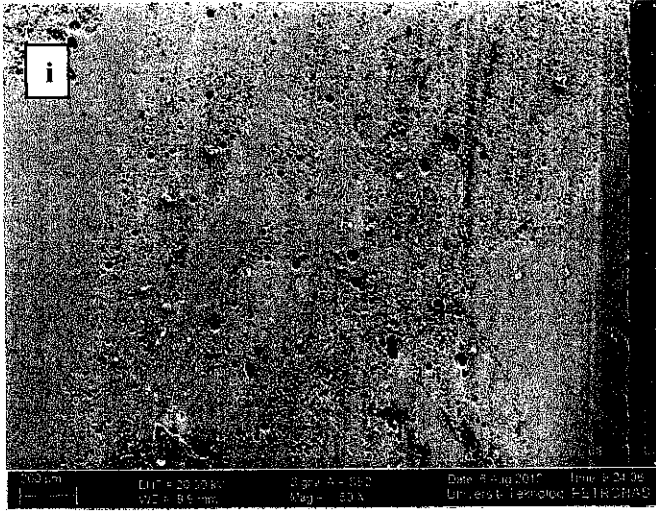
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Figure 14 SEM images, for the mild steel which immersed
in the DEA, at 0.9 M, 60°C (i)50x (ii)1000x (iii)3000x
(iv)500x

4.3.2 Second Sample, in 2-amino 2-ethyl-1,3-propanediol(AEPD) (0.9 M, 60℃)

For the second sample, observed is the several parts of the sample steel which is focused to show the corrosion that has taken place. Ferrite microstructure are formed at the sample surface, looks more obvious compared to the first sample. element composition that exist on the scanned surface, with iron, Fe being the major component that is recorded. *(attachment of the Table in the Appendix)*
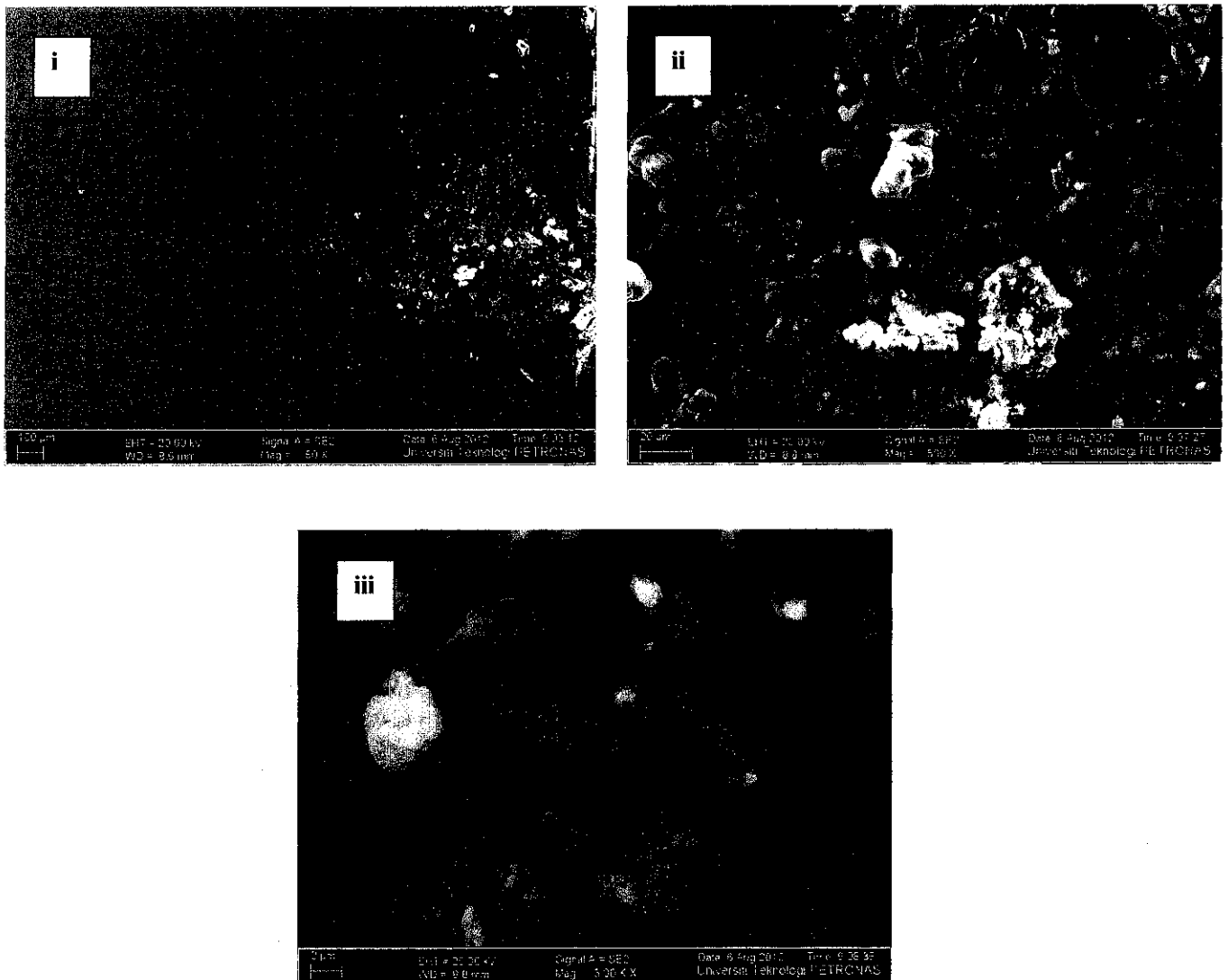
Second Sample Images

Figure 15 : SEM images, for the mild steel which immersed in the AEPD, at 0.9 M, 60℃ (i)50x (ii)500x (iii)3000x

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based from the process parameters, which is (i) temperature of the amine solution, (ii) concentration of the amine solution, and (iii) mixtures of amines, the corrosion rate for the mild steel in Aqueous 2-amino 2-ethyl-1,3-propanediol(AEPD) have been determined.

As temperature increases, the corrosion rate increases. Temperature increases induces higher rate of dissolved oxygen, and hydroxide to combine, thus enhancing the reduction rate. It combines and forms the metal oxide on the exposed area of the steel on a higher rate. The highest rate for this factor is at 90° C at **36.261 x 10^{-3} mm/year.**

For the concentration, as it increases, corrosion rate increases. This is due the higher the oxygen concentrations, the higher the dissolved oxygen present in the tested solution, later on yielded higher rate of ferrous hydroxide and ferric salt(rust) on the steel, at 0.9 M, it values at **35.867 x 10^{-3} mm/year.**

As for the mixtures of amines, the mixture of AEPD and DEA solution produced a corrosion rate which is rather lower than DEA solution alone. But, due to the existence of DEA, the corrosion rate is still higher. Mixture of AEPD and DEA yields highest value at **119.115 x 10^{-3} mm/year**, compared to the DEA alone, yields much higher rate at **337.721 x 10^{-3} mm/year**.

From this result, it can be concluded that sterically hindered amines, specifically in this research, Aqueous 2-amino 2-ethyl-1,3-propanediol(AEPD), yields a lower corrosion rate, and regarded as one of the promising corrosion inhibitor for future, for the benefit of the plant economical reason and not forgetting as the CO_2 absorption solvent.

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5.2 Recommendations

- The steel sample need to be cleaned frequently just after each corrosion testing, to ensure a clear surface area for the next trial of test. Fresh, cleaned steel sample might help in obtaining good Tafel, Linear Polarization, and Potentiodynamic Plot, in determining corrosion rate.
- Fresh solution condition is very much needed for the testing of Potentiodynamic in investigating the corrosion rate study. It is because Potentiodynamic method takes longer time in providing the results, and it is advised to not use solution after running Tafel or Linear Polarization, for the purpose of Potentiodynamic.
- Prepare adequate steel samples for the purpose of testing, in determining the corrosion rate.
- Make several trials for each parameters to obtain the precise results for the corrosion rate. This is to ensure the precision of all trials, so that it is easier to determine the corrosion rate in the acceptable values.
- Try comparing the corrosion rate by taking consideration of more different types of amines for better comparison of corrosion rate.
- Ensure proper wires for the connection to the corrosion cell so that results are obtained smoothly.

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APPENDIX

Table 3 Elements Found on the Scanned Sample 1

Element	Weight (%)	Atomic (%)
Carbon, C	10.08	23.05
Oxygen, O	26.63	45.69
Chlorine, Cl	0.55	0.42
Iron, Fe	62.74	30.84

Table 4 Elements Found on the Scanned Sample 2

Element	Weight (%)	Atomic (%)
Carbon, C	4.14	13.94
Oxygen, O	9.20	23.24
Chlorine, Cl	0.39	0.44
Iron, Fe	86.26	62.38