THE SYNERGISTIC EFFECT OF TANNINS AND IODIDE IONS ON THE CORROSION INHIBITION OF MILD STEEL IN CORROSIVE MEDIA

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by

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LIST OF ABBREVIATIONS

CnT	Chestnut tannin
CPE	Constant phase element
CR	Corrosion rate
EIS	Electrochemical impedance spectroscopy
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared
MgT	Mangrove tannin
MmT	Mimosa tannin
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy

LIST OF SYMBOLS

ΔH	Activated enthalpy
ΔS	Activated entropy
E_a	Activation energy
β_a	Anodic Tafel slope
N	Avogadro's number
C_{dl}	Capacitance of double layer
B_c	Cathodic Tafel slope
R_{ct}	Charge transfer resistance
R^2	Coefficient of determination
i_{corr}	Corrosion current density
E_{corr}	Corrosion potential
ΔG_{ads}	Change of Gibbs free energy of adsorption
S_1	Parameter of synergism
% IE	Percentage inhibition efficiency
h	Planck's constant
R_p	Polarisation resistance
R_s	Solution resistance
θ	Surface coverage
R	Universal gas constant

KESAN SINERGI TANIN DAN ION IODIDA TERHADAP PERENCATAN KAKISAN KELULI LEMBUT DI DALAM MEDIA KAKISAN

ABSTRAK

Kesan perencatan tanin bakau (MgT), tanin mimosa (MmT) dan tanin berangan (CnT) terhadap sifat kakisan keluli lembut di dalam larutan 0.5 M HCl, 0.25 M H_2SO_4 dan 3.5 % NaCl telah dikaji menggunakan kaedah kehilangan berat, kekutuban potensiodinamik dan spektroskopi impedans elektrokimia (EIS). Keputusan bagi semua kaedah kajian menunjukkan MgT telah memberikan kecekapan perencatan yang memuaskan bagi keluli lembut. Prestasi MgT didapati telah meningkat setelah ion iodida ditambahkan ke dalam media kakisan yang mengandungi perencat ini dan hal ini menunjukkan sinergisma telah wujud antara kedua-dua sebatian tersebut. Di dalam analisa kehilangan berat, nilai kecekapan perencatan bagi ketiga-tiga tanin didapati telah meningkat daripada 38-85 % kepada 82-97 % apabila ion iodida ditambahkan ke dalam larutan kakisan yang mengandungi tanin-tanin ini. Kecekapan perencatan bagi ketiga-tiga tanin ini juga didapati telah meningkat daripada 47-89 % kepada 83-94 % apabila digabungkan dengan ion iodida di dalam pengukuran kekutuban potensiodinamik. Di dalam pengukuran EIS, nilai kecekapan perencatan bagi ketiga-tiga tanin didapati telah meningkat daripada 69-84 % kepada 80-92 % apabila tanin-tanin ini disinergikan oleh ion iodida. Kecekapan perencatan yang diperoleh daripada pengukuran kehilangan berat dan elektrokimia adalah konsisten. Kajian kekutuban potensiodinamik menunjukkan secara jelas bahawa MgT bertindak sebagai perencat jenis campuran dengan kecenderungan keberkesanan anodik. Plot Nyquist yang diperoleh melalui analisis EIS menunjukkan proses perencatan

lebih dipengaruhi oleh proses pertukaran cas. Kajian morfologi permukaan menunjukkan ketahanan ketara permukaan keluli lembut dengan kehadiran kedua-dua perencat. Kajian isoterma penjerapan daripada semua kaedah pengukuran kakisan dalam larutan 0.5 M HCl menunjukkan gabungan tanin dan ion iodida adalah paling sepadan dengan isoterma penjerapan Langmuir dan mekanisma penjerapannya adalah melalui tindak balas penjerapan fizikal secara spontan. Kajian termodinamik dan kinetik menunjukkan proses pelarutan logam adalah proses endotermik. Kajian sinergisma antara MgT dan ion iodida menunjukkan mekanisme penjerapan secara membantu adalah lebih cenderung di dalam media HCl and H_2SO_4 manakala mekanisme penjerapan secara bersaing di dalam medium NaCl. Tambahan pula, MgT memberikan sifat perencatan yang setanding dengan tanin komersial MmT dan CnT di dalam semua kaedah pengukuran kakisan dan media kakisan yang dikaji.

THE SYNERGISTIC EFFECT OF TANNINS AND IODIDE IONS ON THE CORROSION INHIBITION OF MILD STEEL IN CORROSIVE MEDIA

ABSTRACT

The inhibition effect of mangrove tannin (MgT), mimosa tannin (MmT) and chestnut tannin (CnT) on the corrosion behaviour of mild steel in 0.5 M HCl, 0.25 M H_2SO_4 and 3.5 % NaCl solutions was studied using weight loss, potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) techniques. The results from all techniques studied showed that MgT gave satisfactory inhibition efficiencies on mild steel. The performance of MgT was further enhanced when iodide ions were added into the corrosive media containing this inhibitor, indicating the occurrence of synergism between these two compounds. In the weight loss analyses, the inhibition efficiencies for all three tannins have been increased from 38-85 % to 82-97 % when iodide ions were introduced into the corrosive media containing these inhibitors. The inhibition efficiencies for all three tannins were enhanced from 47-89 % to 83-94 % when combined with iodide ions in the potentiodynamic polarisation measurements. In the EIS measurements, the inhibition efficiencies for all three tannins were further increased from 69-84 % to 80-92 % when these tannins were synergised by the iodide ions. The inhibition efficiencies obtained from the weight loss and electrochemical measurements were in good agreement. Potentiodynamic polarisation studies clearly revealed that MgT behaved as mixed-type inhibitor with predominant anodic effectiveness. The Nyquist plots obtained from the EIS analyses showed that the inhibition process was mainly controlled by a charge transfer process. Surface morphological studies show significant

improvement on mild steel surface in the presence of both inhibitors. The adsorption isotherm studies from all corrosion measurements in 0.5 M HCl revealed that the combined MgT and iodide ions best fitted the Langmuir adsorption isotherm and the adsorption mechanism was predominantly a spontaneous physisorption reaction. The thermodynamic and kinetic studies revealed that the metal dissolution process was an endothermic process. The synergism studies between MgT and iodide ions revealed that the co-operative adsorption mechanism was favoured in HCl and H_2SO_4 media while competitive adsorption mechanism was favoured in NaCl medium. In addition, MgT gave comparable inhibitive properties to that of commercial MmT and CnT tannins in all corrosion measurement techniques for all corrosive media studied.

CHAPTER 1

INTRODUCTION

1.1   Iron and its alloy

Iron is not found in the pure form as it is a reactive metal and thermodynamically unstable in its pure form. The tendency of a metal such as iron to form oxide, sulfides, silicates, carbonates or other metal ore is a natural process of forming a more stable compound. This natural formation process is best known as corrosion process. The extraction of metals from their ores are very costly and requires very high energy (around 1,500 °C). The extracted metals used in service will revert back to their more stable ore forms when they are exposed to the corrosive environment as shown in Figure 1.1 (Fontana, 1986).
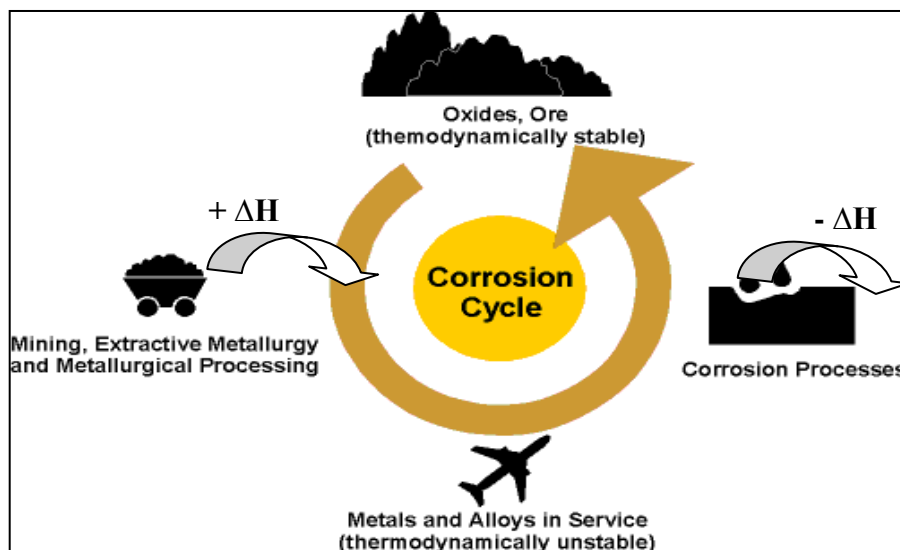
Figure 1.1: The corrosion cycle of metals (Fontana, 1986)

The alloying of metals is the process of metal properties improvement. Iron metal itself is easier to corrode and has poor mechanical properties. The addition of other elements in a metal is for the purpose of mechanical improvement of the metal. Iron is alloyed with carbon and other metals such as chromium, phosphorus, nickel, manganese, silicon and tungsten in order to produce steel. Steel is mechanically better than pure iron in terms of hardness, ductility as well as tensile strength since the added metals in steel act as hardening agents (Shreir *et al.*, 1994). The classification of steel as mild, medium or carbon types depends on the amount of carbon added into it (Garrison Jr, 2001).

Mild steel is an iron alloy with ~0.25 % carbon content. It is an excellent option of construction material due to its high flexibility and compressive strength as compared to other types of steels. Besides its high strength and flexibility, mild steel also has other advantages such as lighter, more durable and ductile, and more corrosive resistant (Edwards, 1953). However, mild steel is vulnerable to corrosion especially when exposed to aggressive media due to its thermodynamic instability in such media (Prabhu *et al.*, 2008). In the presence of water and oxygen, mild steel tends to form iron oxide as the rust product.

Mild steel is one of the most used metal alloys in industries. The special properties of mild steels make it as a favourite alloy in many fields such as automobile, water treatment, construction etc. However, the long exposures of this metal into the corrosive medium such as acids and moist environment have led to the corrosion problem. As a consequence, the lifetime of mild steels will be less and this problem drives to other serious problems that includes the loss of life due to accidents. The corrosion scientists

have come out with many ideas to overcome this problem. One of the most practical ideas is the usage of corrosion inhibitors.

1.2 Metal corrosion

Corrosion is Latin in origin. The word *rodere* in Latin means "gnawing" and *corrodere* means "gnawing into pieces" (Davis, 2000). This phenomenon is a costly materials science problem since metals were first put to use. Besides of just an inevitable natural phenomenon, corrosion is also important in view of economics and social wellbeing since it can cause tragic accidents involving loss of life.

Corrosion of metal is a common and serious problem in our daily life. Metals and alloys are normally used in wide range of purposes and are designed for long-term operations. The corrosion processes are usually caused by the interaction between the metal and its surrounding. This problem has caused the consideration of many corrosion control programmes and research in various fields around the world.

There are many forms of corrosion in our daily life which is caused by the aggressive environment. Materials that are exposed to corrosion include plastic, rubber, composite as well as wood. One of the most common examples of corrosion is the metal corrosion. Corrosion of metals is an electrochemical reaction which can cause the damage and deterioration of the physical and chemical properties of the attacked metal or alloy.

This natural process involves the ions transfer through the metal surface when exposed to the corrosive medium (Shreir *et al.*, 1994). In other words, the metal tends to form a more stable compound like metal oxides by reacting with the corrosive medium and this phenomenon will lead to metal loss as the corrosion products are formed (Raja & Sethuraman, 2008). When dealing with corrosion, it can be very expensive as well as unsafe. The elements of costs related to corrosion are shown in Table 1.1 as follows (Sastri, 2011):

Table 1.1: The elements of cost related to corrosion

Cost	Processes
Capital	Replacement of corroded component of equipment and buildings, excess equipment, extra capacity, safety considerations and environmental regulation
Control	Maintenance and service and corrosion monitoring
Design	Materials of construction selection and special processing
Associated	Loss of production during downtime, insurance, equipment inventory, technical support and chemical expenses

There are many factors contributing towards the corrosion problems. Some of the typical corrosive media are air and humidity, water (fresh, distilled, salted and marine), acids and alkalines as well as soil, steam and gases. Besides the natural factors such as air humidity and wetness time, the usage of acid is found to be one of the major factors that accelerates corrosion problem. Strong acids such as hydrochloric and sulphuric acids are

widely used in industries for many purposes especially cleaning, de-scaling, pickling, etc.

1.3 Corrosion of iron

Corrosion is an electrochemical process involving redox reactions of the metal surface. According to Whitman (1926) and reported elsewhere (Huang *et al.*, 2013) , when a corrosion process takes place, the metal ions which get into the solution at the anodic site is chemically equivalent to the amount of reaction that occurs at the cathodic site (Figure 1.2).
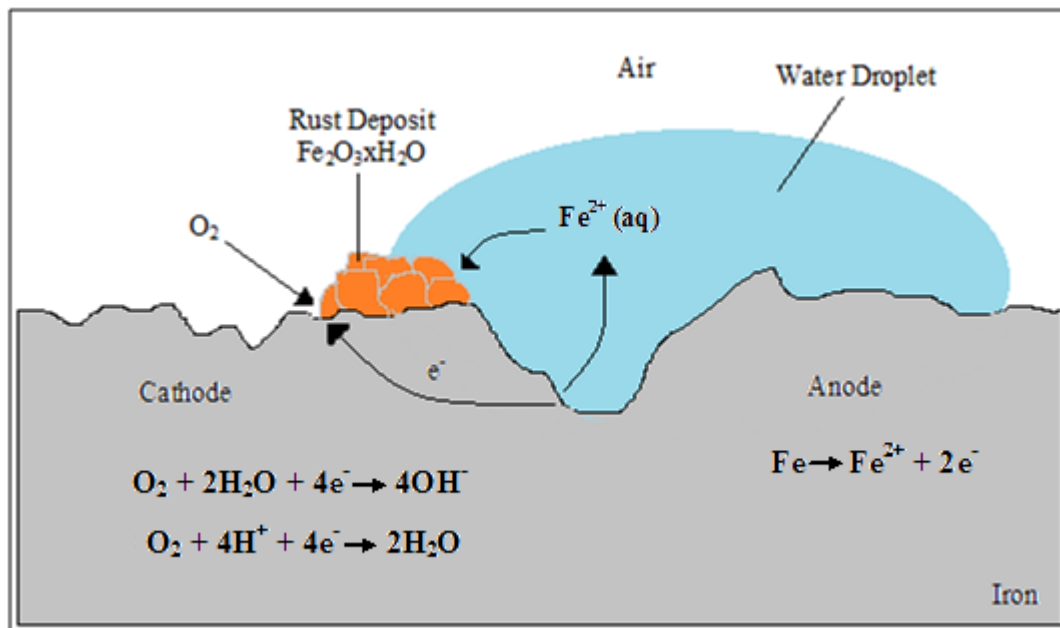
Figure 1.2: Electrochemical mechanism of corrosion of iron

Generally, at the anodic areas, the oxidation reaction of iron will take place as follows;

Anodic reaction

$$Fe \rightarrow Fe^{2+} + 2e^-$$ (1.1)

The oxidation of iron metal into iron (II) leads to the dissolution of the metal. This rapid reaction is mainly controlled by the cathodic reaction which is much slower. In de-aerated or acidic condition, the reduction of hydrogen ions will occur at the cathodic terminal which will lead to the hydrogen gas evolution as follows (Shreir *et al.*, 1994);

Cathodic reaction (de-aerated)

$$2H^+ + 2e^- \rightarrow H_2$$ (1.2)

The lower the pH (more acidic) of the medium, the faster the cathodic reaction will be. This phenomenon is due to the equilibrium potential of the hydrogen electrode becoming more noble, leading to an increase in corrosion current.

On the other hand, in the presence of oxygen molecules (aerated) and in alkaline or natural environment where the corrosion occurs at nearly neutral pH values, the cathodic reaction is represented as follows (Kruger, 2001);

Cathodic reaction (aerated)

$$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$$ (1.3)

The oxygen from the atmosphere and the water molecules in the medium solution will be reduced into hydoxyl anions at the cathodic terminal.

The corrosion process usually ends up with the formation of corrosion products. In the case of iron, the iron (II) ions will react chemically with the hydroxyl ions that are formed at the opposite terminal. The reaction will result in the formation of insoluble iron (II) hydroxide or known as green rust. The formation of the product is as follows;

$$Fe^{2+} + 2\,OH^- \rightarrow Fe(OH)_2 \tag{1.4}$$

The pure $Fe(OH)_2$ is normally white in colour. However, the partial oxidation of air will result in the greenish blue colour of the compound. The iron (II) ions are unstable. It tends to form more stable ions (iron (III) ions). This could happen when the dissolved oxygen molecules immediately oxidise iron (II) ions into iron (III) ions as shown below;

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O \tag{1.5}$$

The Fe^{3+} will furher react with the hydroxyl anions at the cathodic site and form iron (III) hydroxides that is also known as ferric hydroxides or rust which is reddish bown in colour;

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \tag{1.6}$$

Ferric (III) hydroxide can exist in various forms. The slow formation of ferric (III) hydroxide results in crystallised form of $Fe_2O_3.H_2O$ which is red-brown in colour. In addition, the most common forms of ferric (III) compounds in nature are hematite (α-Fe_2O_3) and geothite (α-FeOOH). However, maghemite (γ-Fe_2O_3) and lepidocrocite (γ-FeOOH) are also found. The formation of hematite is favoured at low or neutral pH that resulted from high temperature and higher suspension concentration. However, geothite formation is favoured by high pH (Fischer & Schwertmann, 1975). Further hydration and oxidation of ferric (III) hydroxide will produce other forms of compounds such as magnetite (Fe_3O_4), akaganite (β-FeOOH) and so forth.

The anodic dissolution of iron in HCl medium is according to the following steps (Oguzie *et al.*, 2010);

$$Fe + Cl^- \rightleftharpoons [FeCl^-]_{ads} \tag{1.7}$$

$$[FeCl^-]_{ads} \rightleftharpoons [FeCl]_{ads} + e^- \tag{1.8}$$

$$[FeCl]_{ads} \rightleftharpoons FeCl^+ + e^- \tag{1.9}$$

$$FeCl^+ \rightleftharpoons Fe^{2+} + Cl^- \tag{1.10}$$

Meanwhile, the anodic dissolution of iron in H_2SO_4 medium is as follows;

$$Fe + SO_4^{2-} \rightleftharpoons [FeSO_4^-]_{ads} + e^- \tag{1.11}$$

$$[FeSO_4^-]_{ads} \rightleftharpoons [FeSO_4]_{ads} + e^- \tag{1.12}$$

$$[FeSO_4]_{ads} \rightleftharpoons FeSO_4^+ + e^- \tag{1.13}$$

$$FeSO_4^+ + e^- \rightleftharpoons Fe^{2+} + SO_4^{2-} \tag{1.14}$$

In aqueous solution containing Cl^- ions such as NaCl solution, the mechanisms of iron dissolution are as follows (Noor and Al-Moubaraki, 2008);

$$Fe + Cl^- + H_2O \rightleftharpoons [FeClOH]^- + H^+ + e^- \tag{1.15}$$

$$[FeClOH]^- \rightleftharpoons FeClOH + e^- \tag{1.16}$$

$$FeClOH + H^+ \rightleftharpoons Fe^{2+} + Cl^- + H_2O \tag{1.17}$$
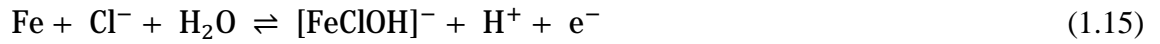
where $[FeClOH]^-$ is the adsorbed intermediate in which it is involved in the rate setermining step (1.16) of steel dissolution according to the above mechanisms.

1.4 Corrosion measurement techniques

There are many techniques used in determining and measuring the corrosion rate of metals. Previously, the weight loss method or sometimes known as gravimetric method was the only conventional method used for corrosion measurement. However, as the research world become more sophisticated, modern technology has lead to the development of electrochemical measurements. These time saving measurements have produced some comparitive results to the conventional method.

1.4.1   Weight loss technique

Weight loss measurement or also known as gravimetric technique is the simplest way of corrosion monitoring (Bendahou *et al*., 2006). This method involves direct immersion of the metal specimen in the corrosive medium in the absence and presence of studied inhibitor. The corrosion measurement by this technique is due to the loss of the specimen's weight after corrosion process. The specimen size for this technique can vary depending on the amount of electrolyte and the size of the electrolyte's container.

The pre-treatment of sample or specimen is crucial in order to get precise analysis. The specimen must undergo two main steps namely the mechanical and chemical treatments. For the mechanical treatment, the specimen will be polished using different grades of emery papers in order to get rid of any passive layer on the surface. The mirror-like

polished surface will be chemically treated using chemical solution such as acetone or alcohol to remove water and other materials that can cause atmospheric corosion.

The advantage of this technique is that it can be carried out in various environments including liquid, solid or even gases. Besides in stagnant conditions, this technique is also applicable in any particulate flow systems. The weight loss of the specimen can be analysed, leading to corrosion rate calculation as well as inhibitor efficiency calculations.

1.4.2   Potentiodynamic polarisation

Potentiodynamic polarisation is one of the most popular electrochemical measurement techniques commonly used in corrosion studies until today. According to Mansfeld (1976), this technique measures the corrosion rate of the metal based on the current-potential relationships. This technique is mainly due to the induction of the corrosion process by applying the electrical current through the elctrochemical cells that results in changes in the working electrodes (Perez, 2004).

Results from this technique are represented in a logarithm plot called Tafel plot. The Tafel plot can be obtained by polarising the sample to about 300 mV anodically (towards more positive potential value) and 300 mV cathodically (more negative potential value) from the point of corrosion potential, E_{corr}. From the plot abtained, the values of corosion current density, i_{corr} can be determined by extrapolating the linear

curves (anodic and cathodic) toward the point of $E_{corr.}$ The general curve of a Tafel plot is shown in Figure 1.3.

Apart from corrosion rate determination, Tafel plot can also be used to describe the behaviour of the corrosion inhibition. As the electrode potential becomes more positive, the solution becomes more oxidising and results in the increase in the metal dissolution process. Meanwhile, if the electrode potential becomes more negative, the solution becomes more reducing and the hyrogen evolution process (for acidic media) in the cathodic site increases. In the presence of an inhibitor, the reduction in the current density of anode or/and cathode, will determine the type of inhibition process whether it is classified as anodic, cathodic or mixed-type inhibition (Stern, 1958; Jones, 1996; Davis, 2000).
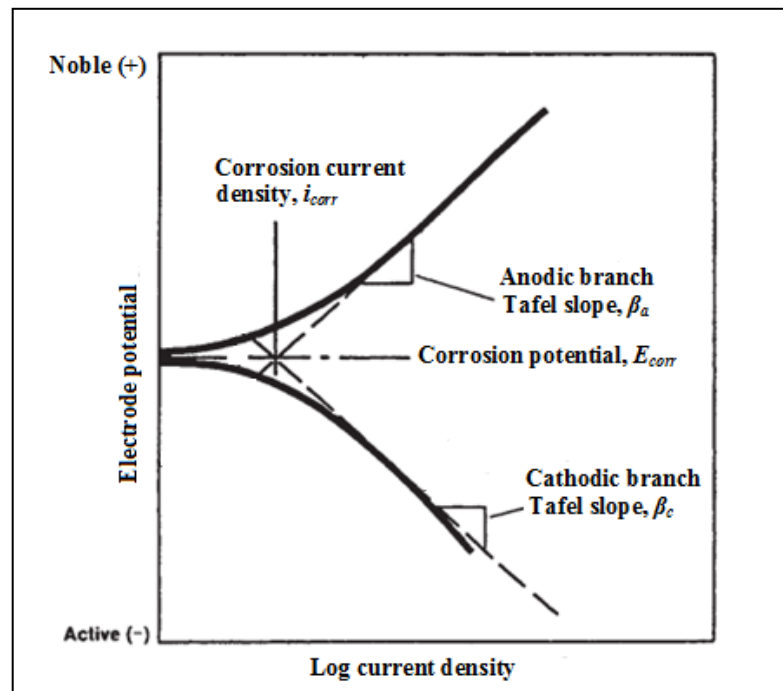
Figure 1.3: An example of a Tafel plot

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1.4.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is gaining popularity as another method of electrochemical measurement of corrosion studies. Impedance and resistance are the potential measurements of a component in a circuit. They will block or resist the electrical current flow of a circuit. Impedance measurements combine the effect of direct current (DC) resistance with capacitance and inductance. In a DC circuit, only resistance would block or resist the current flow whereas in alternating current (AC) circuit, all three components of resistance, capacitor and inductor will result in the blockage of the current flow. Furthermore, the AC impedance is useful in characterising comprehensively the corrosion behaviour of lower conductivity solution as well as high resistivity coatings (Revie & Uhlig, 2008). There are two components that are involved in impedance measurements namely real component (capacitance and inductance) and imaginary component (resistance).

The impedance results can be represented by Nyquist and Bode plots. In a Nyquist plot, the imaginary impedance components are plotted against the real impedance components for each exciting frequencies as shown in Figure 1.4. An example of an equivalent circuit that has been fitted to this plot is a Randles cirsuit (Figure 1.5) which represents a simple charge transfer circuit. The circuit consists of capacitance where the electron charges are stored and resistance which controls the the current flow by resisting the current flow throughout the circuit. Double layer capacitance, C_{dl} is where the electron transfer process takes place across the electrolyte and metal surface. The corresponding circuit represents the mechanism of the reaction that has occurred in the

electrochemical system. The Nyquist plot also shows the effect of solution resitance at the higher frequency. From Figure 1.4, it can be seen that at the higher frequency, almost all impedances are caused by the solvent resistance, R_s. As the frequency decreases, the real impedance is about to occur due to the polarisation resistace, R_p or sometimes denoted as charge transfer resistance, R_{ct}.
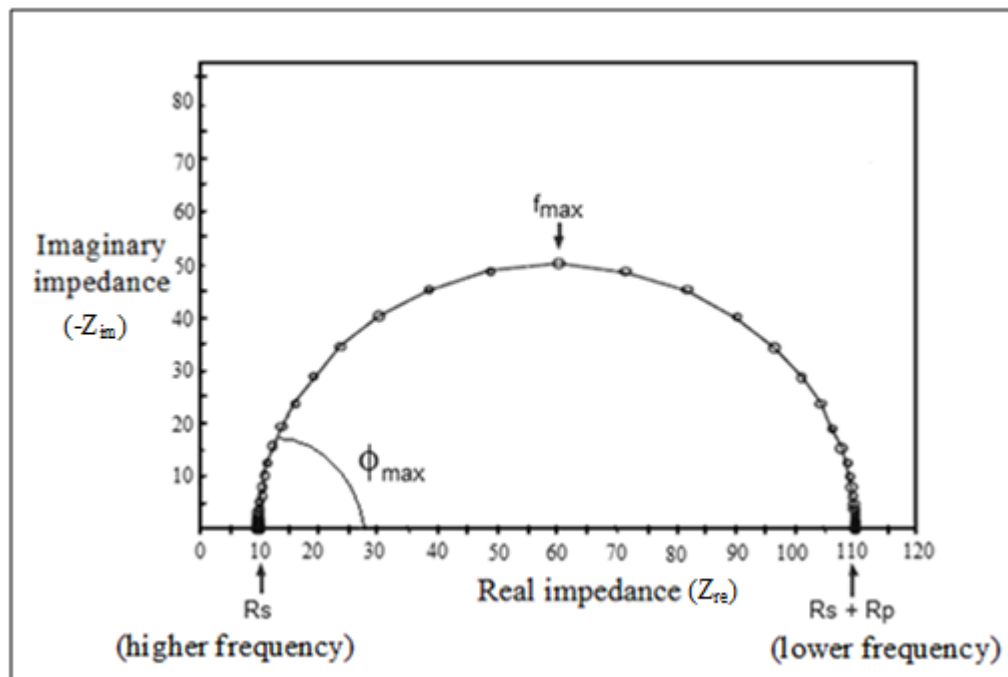
Figure 1.4: A typical Nyquist plot
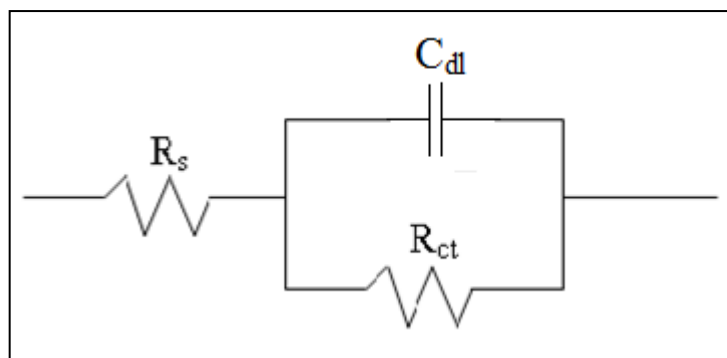
Figure 1.5: The electrochemical Randles equivalent circuit

The Bode plots are divided into two different types that are impedance magnitude versus log frequency and phase angle versus log frequency. In the Bode plot, the frequency-dependent modulus, $|Z|$ and the phase angle, θ are considered as frequency functions. This plot consists of logarithm frequencies resulting in the high range of frequencies. This plot mainly shows the dependency of the impedance towards the frequencies. Similarly in this plot, the polarisation resistance, R_p and solvent resistance, R_s can be obtained. The log of R_s can be seen in the linear curve at the higher frequencies whereas the polarisation resistance can be determined from the log $(R_s + R_p)$ at the lower frequencies. Typical Bode plots are shown in Figure 1.6.
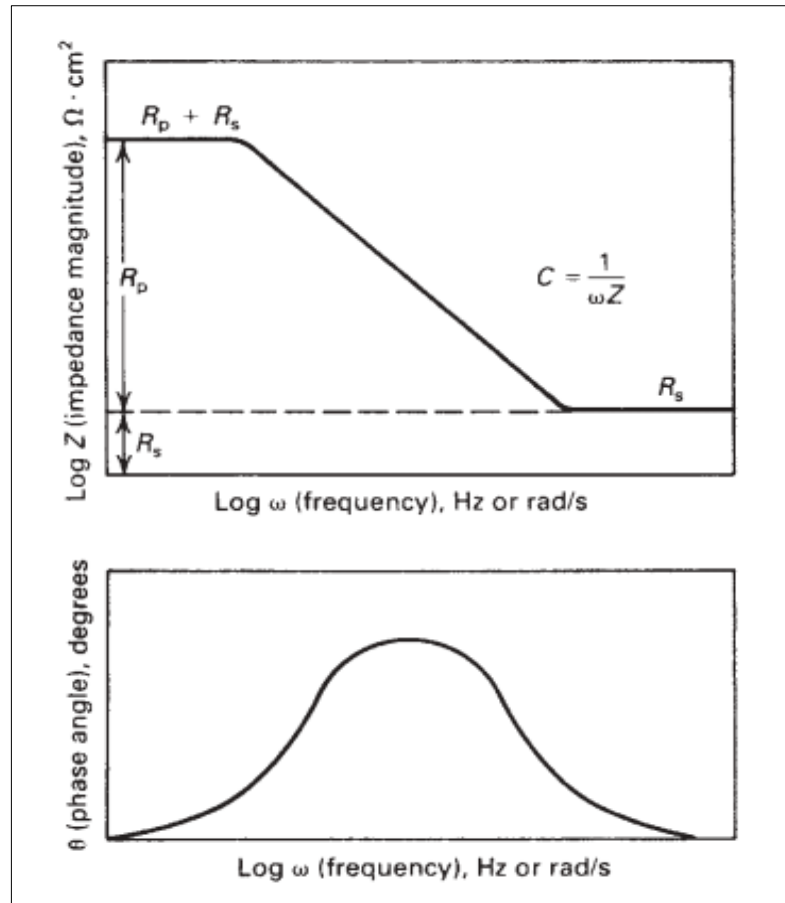
Figure 1.6: Bode plots for a typical electrochemical system (Revie & Uhlig, 2008)

1.5 Corrosion inhibitor

Several techniques have been investigated to prevent or control corrosion processes. Some attempt to change the properties of the metals in the corrosive environment while some try to modify the environment to be less corrosive to the metal. Table 1.2 lists some corrosion control techniques applied in industries.

Table 1.2: Corrosion control techniques used in industries

Technique	Industrial processes
Metal modification	Stainless metal-alloy
Surface reaction inhibition	Corrosion inhibitor and pH controlling
Surface electrochemical reaction retardant	Cathodic controlling (sacrificial anode) and anodic controlling
Surface and composition modification of metal and alloy	Corrosive agent removal control, modifying metal to avoid corrosion
Oxidation agent removal	Water-boiler treatment
Coating and plating	Paint and metal protective layer, electroplating

It can be clearly seen that most of the corrosion control processes involving plating, inhibiting, as well as electrochemical protecting. The use of inhibitors for corrosion prevention has been well established and more favoured due to its low production cost, undamage properties towards metal and sometimes it is environmental friendly.

Corrosion inhibitor is a chemical, when added in a small quantity in a corrosive medium, results in the reduction or inhibition of the corrosion process (Winston, 2000). Corrosion inhibitor can be classified into several types as shown in Figure 1.7.

Inhibitors can be divided into two main categories depending on the interaction of the inhibitor. Some inhibitors tend to alter or modify the corrosive environment to become non-corrosive or less corrosive. This type of inhibitor is classified as environment

modifier. It controls the corrosion process by removing the aggresive ions in the corrosive medium. As a consequence, the metal will be less attacked by the aggresive species present in the medium. One of the common phenomenon that occurs in neutral and alkaline solution is the reduction of oxygen at the cathodic terminal. This environment modifier inhibitor will reduce the amount of oxygen present in the medium.
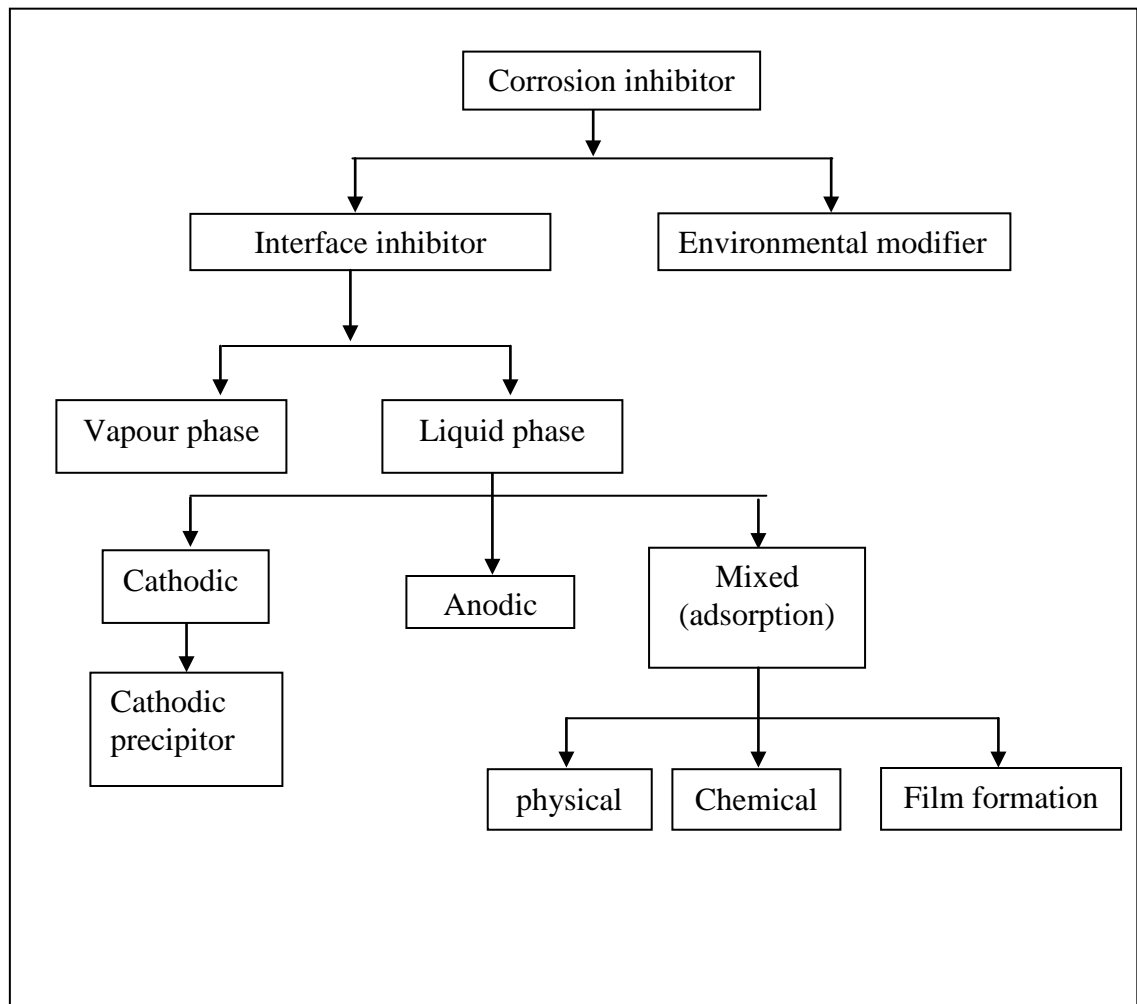
Figure 1.7: Classification of corrosion inhibitors

The other type of inhibitor is the interface inhibitor. This inhibitor inhibits the corrosion process by forming a protective film at the metal/environment interface (corrosive medium). In order to form a protective film, the inhibitor will be adsorbed on the metal surface and prevent the corrosion process from occuring. This process of inhbition consists of two steps which are the transportation of the inhibitor to the metal surface and the interaction of the inhibitor and metal surface. This inhibitor can be divided into two main groups which are liqiud phase and vapour phase interface inhibitors (Winston, 2000).

Vapour phase corrosion inhibitors are also known as volatile corrosion inhibitors. These inhibitors are chemical compounds having significant vapour pressures which allow the vaporisation of the compounds and are subsequently adsorbed on the metallic surface. The main purpose of vapour phase inhibitors are to avoid the corrosion process caused by oxygen moisture and atmospheric pollutants. The inhibitors are normally used in a closed system or chamber where it can be vapourised and adsorbed onto the metal surface and protects the metals from atmospheric corrosion. This type if inhibitor is normally applied in a storage or shipping purposes (Miksic, 1983).

In contrast, liquid phase inhibitor is associated with the corrosion caused by the liquid form of corrosive media. The inhibitors can be divided into three types that are anodic, cathodic or mixed type inhibitor. The classification of liquid phase inhibitors is mainly from the inhibitive effect of the inhibitor whether it inhibits anodic oxidation reaction, cathodic reduction or both reactions.

Anodic inhibitors are usually used in neutral solutions where the corroded surface will be covered by soluble or partially soluble corrosion products such as oxides, hydroxides or salts. Anodic inhibitors are generally effective in the pH of 6.5 to 10.5 (Sastri, 2011). The formation of a protective film on the metal surface, causing a large anodic shift of the corrosion potential. This shifts force the metal surface into the passivation region and inhibits the metal dissolution in the anodic reaction. They are also known as passivators. Some anodic inhibitors are chromates, nitrates and molybdates (Stratmann and Frankel, 2003).

Cathodic inhibitors inhibits the cathodic reduction reaction that occurs at the cathodic terminal. It inhibits the hydrogen evolution in acidic solutions or the reduction of oxygen in neutral or alkaline solutions. An effective cathodic inhibitors are substances with high overpotential for hydrogen in acidic solutions and form insoluble products in alkaline solutions. It acts by slowing the cathodic reaction (cathodic poison) or precipitating on cathodic areas (cathodic precipitator) to limit the diffusion of reducing agents to the surface. The usage of cathodic poison will reduce the reduction process by getting adsorbed on the metal surface and form a metallic layer. In the case of aerated and neutral solution, the reduction of oxygen is limited by reducing the diffusion of oxyen to the metal surface using the oxygen scavengers. Meanwhile the cathodic precipitor reacts by increasing the alkalinity of cathodic site and forms insoluble precipitate on the metal surface (Hackerman & Makrides, 1954).

Mixed type inhibitors, generally are organic compounds, retard both anodic oxidation and cathodic reduction reactions. The organic inhibitors are adsorbed on the metal surface and formed a barrier to dissolution at the anodic site and a barrier to oxygen reduction or hydrogen evolution at the cathodic site. Mixed type inhibitors prevent the corrosion process by three approaches; physical and chemical adsorptions and film formation. Physical adsorption involves the electrostatic interaction between the inhibitor molecules and the metal surface. In other words, if the metal surface is positively charged, the adsorption of the inhibitor anions (negatively charge) will occur. On the other hand, chemical adsorption involves the charge sharing or charge transfer between the inhibitor molecules and the metal surface. The interaction will then result in the formation of coordinate-type bond which gives stronger and more efficient inhibition. The protective layer formation occurs as a result of a complex formation by the corrosion product itself.

1.5.1 Organic and inorganic inhibitors

Organic inhibitors normally contain polar groups such as nitrogen, oxygen and sulphur. Normally, the efficiency of the inhibitor depends on the amount of the inhibitor present in the medium. Organic inhibitor is more favourable in industrial applications. This is because the compounds have the ability to form complexes with the metal by getting adsorbed onto it (Morales *et al.*, 2004). Generally, the organic inhibitors are known as film forming inhibitors. This is due to the formation of hydrophobic layer on the metal surface which gives protection to the metal from water adsorption. The replacement of

water molecules by inhibitor molecules results in the prevention of the corrosion process. Natural occurring organic inhibitors are safer choice since it gives less harm to the environment and less toxic (Raja & Sethuraman, 2008). Several investigations on the preformance of the organic inhibitors have been reported. Most of the researches have used different parts of plants such as bark, leaves, seeds, roots and fruits. The inhibition efficiencies of the plant extracts are normally due to the presence of complex organic constituents such as tannins, alkaloids, flavonoids, carbohydrates, proteins as well as nitrogen bases (Oguzie, 2008). Moreover, the efficiency of such inhibitors strongly depends on the concentration of inhibitors, type and concentration of anions in the corrosive medium, chemical structure of the inhibitor molecules and its functional groups, size of molecules as well as the modes of adsorption.

Likewise, inorganic inhibitors are inhibitors such as chromates, molybdates and phosphates that are not friendly to the environment and can be extremely toxic. In most cases, it has been reported that the inorganic inhibitors are toxic and are harmful toward the environment and human being itself (Stratmann & Frankel, 2003). Previously, chromates have been widely used in indutries since the application of zinc and chromates give an effective inhibition in the inhibitor formulation. However, zinc chomate have been declared as toxic and carcinogen chemical. An exposure to the zinc chromate can cause lung cancer (Langård, 1990).

1.5.2   Corrosion inhibitor mechanism

The corrosion inhibition of metals by organic inhibitors is known to involve two steps which are transport of the inhibitor to the metal surface and the adsorption of the inhibitor on the surface (Sastri *et al.* 2008). The corrosion of metals can be inhibited by the anions weak acids. However, anions of strong acids can cause the breakdown of the passive protective oxide film. The inhibitive actions of such species are strongly dependent on several aspects including the anions concentration, pH of the corrosive medium, concentration of the dissolved oxygen, nature of the metal as well as the temperature (Brasher, 1969).

According to Mansfield (1987), the corrosion inhibition mechanism of metals by organic and inorganic inhibitor consist of;

- Ø   repassivation of metal surface by rebuilding the oxide film
- Ø   prevention of aggressive anions adsorption by creating competition during the adsorption process
- Ø   rebuilding of passive oxide layer by forming insoluble layer on the metal surface
- Ø   stabilise the oxide passive layer by reducing the solubility of the layer

In the case of neutral and alkaline environments, the inhibitive effect of inhibitors are based on the reaction of the inhibitor molecules with the hydroxide ions that are produced at the cathode terminal. This reaction will result in the precipitate formation on

the metal surface which consequently will prevent further reduction of oxygen and retard the corrosion process.

1.6 Mangrove (*Rhizophora Apiculata sp.*)

Mangrove which is scientifically known as *Rhizophora apiculata sp.* or locally known as "Bakau Minyak" is a plant found to live on deep soft mud of estuaries flooded by high tides. These plants are mostly found in Asia especially in India, Bangladesh as well as Southeast Asia. In Peninsular Malaysia, about 92,300 ha are reserved as forest and another 15,400 ha are commercialised planted mangrove. According to Clough (1993), Perak is the biggest state planted with mangrove. About 19 reserve forests are located in Matang, Perak. The main purpose of mangrove planting is as timber (charcoal). Since 1902, mangrove also been used in construction area as poles and piling purposes (Kairo *et al*., 2001). Besides that, mangrove plants also play an important role for the local ecosystem since it acts as natural flood retention and also serve as filter to hold sediment along the riverbank in order to avoid erosion from happening. Moreover, it is useful to reduce the water pollution by trapping the debris and rubbish floated in the river stream. In terms of ecological sustainability, mangrove plants serve as a safe breeding and nursery ground for various species of birds such as egrets, herons, storks, shore birds terns and gulls as well as kingfishers.