TION EXCIPIENTS AS CORROSION INHIBITORS UERED TIN PLATED STEEL

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A research dissertation submitted in partial fulfillment for the degree of Master of Pharmacy in Industrial Pharmacy in the School of Pharmacy, University of Nairobi.

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I hereby declare that this research dissertation is my original work and has not been presented to any other academic institution for evaluation for research and examination.

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Supervisors' Approval

This research proposal has been submitted for evaluation for research and examination with our approval as university supervisors.

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I dedicate this work to the love of my life, Beatrice Nailantei Yiaile and my daughters Sasha Wanjiku and Lynn Njoki for their unwavering support, prayers and sacrifices made to enable me complete my studies.

To my parents Mr. and Mrs. David K. W. Kariuki and my family for instilling hard work in me and encouraging me to pursue the noble course of pharmacy.

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LIST OF TABLES

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ACRONYMS AND ABBREVIATIONS

E^0	Standard Electrode/Equilibrium Potential
SHE	Standard Hydrogen Electrode
φG	Chemical driving force of an electrochemical reaction
SCE	Standard Calomel Electrode
μ^o	Standard Chemical Potential
EDTA	Ethylenediaminetetraacetic Acid
Avicel	Microcrystalline Cellulose

ABSTRACT

Background: The use of metals in packaging is widespread in both pharmaceutical and food industries. The most commonly used metals are tin plated steel and aluminium. About 80% of food cans are made of tin plated steel with increasing use of tin plated steel canisters in the packaging of pharmaceuticals. Tin is incorporated onto steel because it is non toxic, it acts as a low friction surface during manufacturing, it resists seam welding, it is recyclable and the fact that it provides mild atmospheric resistance to corrosion. Tin plated steel cans can rust when in contact with water. The rate of corrosion/rust varies with the composition of media in contact with the container.

Objectives: To develop a model system to study corrosion of tin plated steel and to test selected pharmaceutical excipients for corrosion inhibition properties.

Methodology: Commercially available lacquered tin plated steel sheets obtained from a container ready for packing pharmaceuticals were cut into 30*30*0.2 mm pieces. The external side of the tin plated sheet contained clear vanish lacquer rendering it waterproof. The internal part of the sheet contained an epoxy phenolic lacquer. The amount of tin was 2.8 mg per metre squared of steel. The pieces were mechanically polished using filter paper, washed with distilled water, dried between clean filter papers and finally weighed. The tin plated pieces were immersed in 100 mL of test solution with or without the inhibitor for 72 hours for all excipients except solvents. After the test, the pieces were removed, washed with distilled water, dried as before and weighed again. To test for the effect of substitution of distilled water with other solvents the procedure was as above, but the duration was 14 days. For every concentration of test solution, only one concentration of pharmaceutical excipient was investigated.

The weight loss of the metal was calculated as follows:

$\varphi W = W_1 - W_2$

Where $W_1$and W_2 are the weights of the metal before and after exposure to corrosive solution respectively.

) was calculated from the equation below:

$$\%IE = [1-(\varphi W_{inh}/\varphi W_{free})]*100$$

Where φW_{free} and φW_{inh} are weight losses of metal in grams per 9 cm^2 in the absence and presence of inhibitor at a given time, period and temperature respectively.

Results: Substitution of distilled water as the vehicle of formulation with Isopropyl alcohol (IPA) and ethanol at concentration of 20% and 50% for each resulted in substantial corrosion inhibition. The results obtained indicate that IPA is slightly more effective both at 20% and 50% concentrations as compared to ethanol at the same concentrations.

In alkaline media of 0.01N NaOH, 0.1N NaOH and 1N NaOH, the inclusion of ascorbic acid (0.1% and 0.5%), EDTA (0.5% and 2%) Avicel (2% and 5%) and gelatin (2% and 5%) in each of the concentrations resulted in corrosion inhibition to varying degrees. An increase in concentration of the excipients resulted in an increase in Percentage Inhibitor Efficiency (% IE). The above excipients when incorporated in alkaline formulation packed in tin plated steel can be of help in inhibiting corrosion of tin plated steel.

In acidic media, the inclusion of ascorbic acid (0.1% and 0.5%), EDTA (0.5% and 2%) Avicel (2% and 5%) and gelatin (2% and 5%) in test media resulted in corrosion inhibition to varying degrees. An increase in concentration of the excipients resulted in an increase in Percentage Inhibitor Efficiency (% IE). The above excipients when incorporated in acidic formulation packed in tin plated steel can be of help in inhibiting corrosion of tin plated steel.

In chloride solution, inclusion of ascorbic acid (0.1% and 0.5%), EDTA (0.5% and 2%), Avicel (2% and 5%) and gelatin (2% and 5%) in test media resulted in corrosion inhibition to varying degrees. An increase in concentration of the excipients resulted in an increase in Percentage Inhibitor Efficiency (% IE). The above excipients when incorporated in chloride containing formulations packed in tin plated steel can be of help in inhibiting corrosion of tin plated steel.

Conclusion: Ascorbic acid (0.1% and 0.5%), EDTA (0.5% and 2%), Avicel (2% and 5%) and gelatin (2% and 5%) can be incorporated in acidic formulations, alkaline formulations or formulations containing chloride ions in tin plated steel containers as corrosion inhibitors. Substitution of distilled water with ethanol or isopropyl alcohol as vehicle for formulation, where inhibition of corrosion of tin plated steel. Sodium idic, alkaline or chloride containing formulations that are to be packed in tin plated steel. Sodium Lauryl Sulphate has minimal value as a corrosion inhibitor for tin plated steel in acidic, alkaline or chloride containing formulations.

Recommendations: Combinations of EDTA, Avicel, Gelatin and Ascorbic acid should be tested for synergistic corrosion inhibition activity of tin plated steel in acidic, basic and chloride systems .These combinations may also be tested in systems containing mixtures of acidic, basic and chloride ions.

1.1 Background

Packaging of finished products is amongst the last processes in the manufacture of any product. Packaging is very critical as it affects the final quality of the product. The use of metals in packaging is widespread in both pharmaceutical and food production industries. The most commonly used metals for packaging are tin plated steel and aluminium.

The commercially available form of tin plated steel is electrolytic tin plate. It is a low carbon steel coated on both sides with tin using an electrode position method. Tin plated steel is used for all types of cans, including Drawn and Walled Ironed (DWI) and Draw Redraw (DRD) cans making it suitable for all market segments (1).

The USA is the biggest market for all types of cans, using almost 100 billion cans per year for drinks and about 30 billion cans for food, industrial products and aerosols. All cans for drinks are made of aluminium and this represents about 20% of the total aluminium requirement worldwide. In the food industry, 80% of food cans are made of tin plated steel with the rest being aluminium (2).

Tin is usually preferred to be incorporated onto steel because it is non toxic, acts as a low friction surface during manufacturing, facilitates the resistance seam welding process, recycling is possible and it provides mild atmospheric resistance to corrosion of steel during storage. The major problem with tin-plate coating is that it is not continuous and thus exhibits some degree of porosity. The degree of porosity is a function of the applied tin coating weight. The typical thickness of tin plating on steel for most aerosol cans is 0.254µm. When ordinary tin plated aerosol cans are stored under wet conditions they will rust. Tin is cathodic to iron in the presence of moisture and oxygen and as such tin plated steel containers are susceptible to accelerated corrosion due to the electrolytic-ally applied tin coating. Sometimes, chromium surface treatment is applied to the tin plate as protection. The tendency for galvanic corrosion or protection at the can interior is a function of the chemical composition of the product being packed. When pH values are basic (pH greater than 9) tin is anodic to steel. However, it is the chemical composition of the contents that plays the biggest role in determining whether corrosion will take place. One approach to stop corrosion has been the use of interior linings to prevent interactions

ctions include malodors, excessive metal ion pick up and ve the disadvantage in that they do not completely cover metal surfaces of components and hence the need to for inhibitors to prevent internal corrosion. In the can structure, the metal used for the bottom has a thin organic coating in addition to the tin plate to facilitate end forming process. This organic coating also provides localized corrosion inhibition even though it is not continuous. Aluminium is also widely used as a material for making cans; it is considered the only other structural metal other than steel that can be considered practical for fabrication into cans for general use. Aluminium does not rust, but it is readily corroded by aqueous media having pH less than 4 or greater than 8.5. It is cheaper than steel but has less strength. Aluminium can be used for specialized products, but generally lacks the utility of steel required for most aerosol applications (3).

1.2 Problem Statement

Corrosion is a great problem worldwide. Consequences of corrosion can be classified into economic, health, safety, technological and cultural effects (4).

Economic effects of corrosion are very serious. It is estimated that corrosion of metals costs \$300bn per year in the USA. Of this amount about \$176 million to \$528 million is incurred in the pharmaceutical industry. In general terms, the most affected sectors are automotive, housing and manufacturing. Ten elements have been identified by National Institute of Standards and Technology, USA as contributing to the cost of corrosion. They include: replacement of equipment and buildings, loss of products, maintenance and repair, need for extra capacity to give allowance for corrosion, redundancy of equipment, costs associated with corrosion control such as inhibitors and coatings, the need for technical support, extra costs involved during design, increased insurance premium to cater for corrosion and the need to maintain parts and equipment inventory in case of breakdown associated with corrosion (5).

Health effects of corrosion arise from the leaching of metal ions into fluid, mainly water, which when consumed leads to serious health implications. The bursting of closed systems due to corrosion provides avenues for contamination of the contents of that system. Metal ions when consumed can cause mild to fatal health effects. Aluminium is thought to cause neurological disorders. Arsenic consumption causes weight loss, hair loss, nausea, depression and fatigue.

nd nervous system. Cadmium poisoning leads to kidney etic mutation. Chromium causes lung cancer while Iron though not hazardous to the body provides a good source of nutrients for the growth of microorganisms due to its central role in enzymatic processes, mitochondrial respiration and DNA synthesis. The presence of unwanted iron in a formulation would cause spoilage of product. Lead is a cumulative poison that leads to damage of the kidney, nerves and brain. Magnesium toxicity results in hypertension, confusion and muscle weakness. Manganese causes headaches, apathy and central nervous system disorders. Mercury poisoning causes muscle damage and brain damage. Selenium toxicity may result in growth inhibition, skin discoloration, bad teeth and gastrointestinal tract disorders. Silver poisoning is associated with blue-gray discoloration of skin, mucous membrane and death. Sodium is required in the body for physiological function but an excess in sodium consumption may lead to hypertension (6).

Safety effects result from failure of systems which rely on metals for their strength. They include collapse of bridges, damage to buildings, parking structures and highways. These incidents significantly endanger public safety. The collapse of Silver Bridge on Ohio River in 1967 which resulted from corrosion resulted in loss of 46 lives (5).

The corrosion of tin plated steel packaging may occur in pharmaceutical products. This is exhibited as rust within the container. Aerosols are used in pharmaceutical products for delivery of medication to the respiratory and topical systems. Corrosion in these systems has a number of adverse effects including loss of product quality and contamination. Furthermore since an aerosol is a pressurized system, significant corrosion will lead to a rupturing of the container and a loss of the contents (product concentrate and propellant).

Pharmaceutical excipients are inactive materials that may be incorporated into formulations for a number of reasons including facilitation of manufacturing, drug delivery, or enhance product stability. Pharmaceutical aerosols, in addition to the active pharmaceutical ingredient (API) will have a propellant and may also include solvents, surfactants, buffers, antioxidants, and chelating agents. Corrosion in these systems may result from the presence of API, salts, pH extremes, and solvents. Since corrosion results from the interactions of the contents and the container possible options to address its effects include: 1) utilizing a different type of container (e.g., aluminum instead of tin-plated steel; 2) utilizing a lacquered (internally inert coated) container; or 3) using ses it may not be feasible to obtain alternative types of constraints. Lacquering may not always be effective in uniformly coating the inside of the container. Consequently, it is of interest to evaluate whether there are excipients which can be used to address the problem by modification of the formulation so that interactions with the container are prevented. Such types of excipients can be termed as corrosion inhibitors.

1.3 Objectives

1.3.1 General Objectives

The general objective was to test if selected pharmaceutical excipients had corrosion inhibition properties on tin plated steel.

1.3.2 Specific Objectives

The specific objectives of this study were as outlined below.

1. Develop a model system to study corrosion of tin plated steel
2. To test the effect of pharmaceutical excipients specifically solvents, surfactants, antioxidants and polysaccharides as corrosion inhibitors. The surfactant used was Sodium Lauryl Sulphate (SLS). Antioxidants included ascorbic acid, EDTA and Sodium Metabisulphite while the solvents used were Ethanol and Isopropyl alcohol. Gelatin and Avicel are the polysaccharides that were used.

EW

2.1 Introduction

Corrosion has been defined as ña physicochemical interaction between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the metal, the environment or the technical system of which these form a partò (7).

Corrosion has also been defined as ñan irreversible interfacial reaction of a material (metal ceramic, polymer) with its environment which results in consumption of the material or dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusive physical or mechanical processes such as melting, evaporation, abrasion or mechanical fracture are not included in the term corrosion (8).

In simpler terms, corrosion has been defined as deterioration of physical properties of a material due to its reaction with the environment (9).

2.2 How Corrosion Occurs

The basic source of corrosion is the instability of a metal in its refined form. The process of corrosion is therefore the tendency of a metal to revert to its natural state.(10) For example, metals such as gold and silver are found in their natural metallic state and have little tendency to corrode. Iron is moderately active and corrodes readily in the presence of water. The natural state of iron is iron III oxide and the common ore is hematite. Rust, the most common corrosion product of iron is iron III oxide (11).

The level of corrosion is the combination of the material type and the environment it is exposed to (9). There are 4 major categories of corrosion environments: liquid, underground, atmospheric and high temperature. In practice, a material is exposed to more than one of the corrosion environments (10).

All forms of corrosion with the exception of some form of high temperature corrosion (10) occur through the action of an electrochemical cell. A metallic surface exposed to an aqueous electrolyte possesses sites for an oxidation reaction (anodic chemical reaction) that produces n reaction (cathodic chemical reaction) that consumes s. These two sites form the basis of the electrochemical cell. The anodic reaction is the dissolution of the metal to form soluble ionic products or an insoluble compound of a metal usually an oxide. Possible cathodic reactions include reduction of oxygen gas or the reduction of water to produce hydrogen gas. Anodic and cathodic reactions occur simultaneously in a metal surface creating an electrochemical cell. The process of dissolution of the metal results in metal ions in the electrolyte or conversion of these ions to insoluble products such as rust. This is in essence the destructive process called corrosion. The difference in potential between the anodic and cathodic sites provides the driving force for electrons flow between the anode and the cathode (12).

The electrode potential, E, of a metal refers to the potential difference (measured in volts) between a metal electrode and a reference electrode. E_e is the equilibrium potential or reversible potential and it describes the equilibrium between two different oxidation states of the same element at whatever concentration or pressure they occur. Equilibrium potential denotes the electrode potential when the components of the reaction are in equilibrium.

In a reaction such as:

$Bz^{+} + ze^{-} = B$,   where B represents metal and Bz^{+} is the ionized form of metal B.

A concentration of C_{BZ+} of B^{2+} is in equilibrium with solid B. The reaction moves away from the equilibrium only if there is a source or sink for electrons.

E^{o} denotes the standard equilibrium potential or standard electrode potential. It is defined as the equilibrium potential of an electrode reaction when all components are in their standard states measured against the standard hydrogen electrode (SHE). It describes the equilibrium between two different oxidation states of the same element. E^{o} is a constant for any given reaction at 298K.

φG denotes the chemical driving force for an electrochemical reaction. At equilibrium φG is equal to the electrical driving force E_e. φG corresponds to a charge zF, taken through the potential E_e. The measured potential for an electrochemical reaction is therefore directly proportional to its free energy change (ΔG) as shown below.

Where z is the number of moles of electrons exchanged in the reaction and F is faradays constant (96485 coulombs per mole of electrons).

The diagram below denotes how aqueous corrosion occurs:

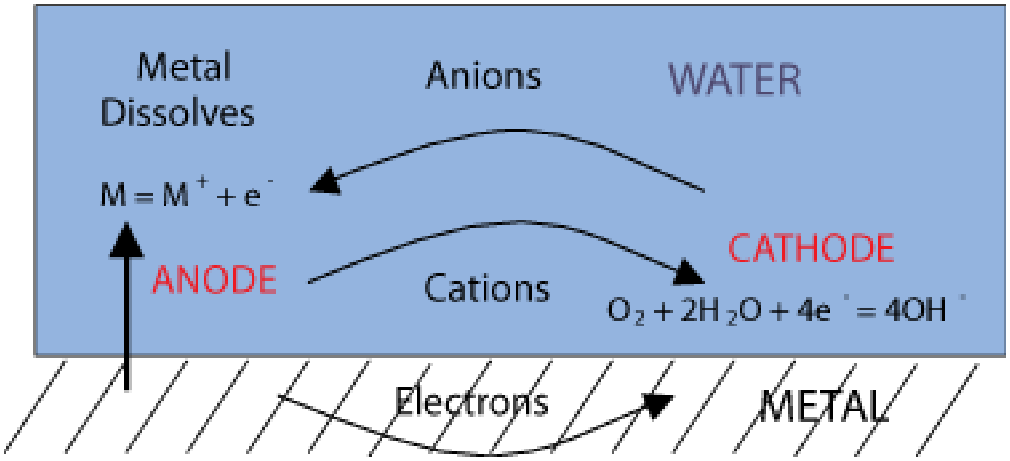


Figure 1. How aqueous corrosion occurs. Source: University of Cambridge. DoITPoMS, Aqueous Corrosion

The oxidation of a metal in aqueous environment is dependent on the potential *E* and the pH. When oxidation occurs, the metal is oxidized and loses electrons forming metal cations. Similarly, a reduction reaction occurs and consumes electrons at the cathode. In an aqueous environment, water is an ion conducting medium. This in essence allows oxidation and reduction sites to be spatially separate as opposed to a gaseous environment which cannot conduct ions. Metals oxidizing to form metal ions which may dissolve into water resulting in corrosion. In the case of a gas, the oxidized metal stays where it is produced as an oxide film on the metal (13).

2.3 Electrochemical Half Cell Reactions

A half cell is one of the two electrodes in a galvanic cell or simple battery (14). A half cell reaction is an electrochemical reaction that results in a net surplus or deficit of electrons. This reaction refers to the smallest complete reaction step. A reaction may be composed of many intermediate reactions which are not stable and as such only a complete reaction is considered.

n or a reduction reaction. An oxidation reaction occurs at trons. A reduction reaction results from gain of electrons and occurs at the cathode. Anions are negatively charged ions and are usually attracted to the anode. Similarly, cations are positively charged ions and are attracted to the cathode.

Reduction half cell reactions occur at the cathode and involve consumption of electrons. Reduction half cell reactions that involve corrosion cause reduction of oxygen or evolution of hydrogen gas. These reactions include the following:

$O_2 + H_2O + 4e^- = 4OH^-$

$O_2 + 4H + + 4e^- = 2H_2 0$

$2H_2 0 + 2e^- = H_2O + 20H^-$

$2H^+ + 2e^- = H_2$

Oxidation half cell reactions occur at the anode and result in production of electrons. These reactions include:

$Fe = Fe^{2+} + 2e-$

$Fe^{2+} = Fe^{3+} + e-$

$Fe + 2OH- = Fe(OH)_2 + 2e^-$

$2Fe + 3H_2O = Fe_2O_3 + 6e^-$

For corrosion of metals, the oxidation half cell reactions that take place correspond to metal dissolution or oxide formation (13). The oxide formed may sometimes be beneficial if it is a passive oxide. Passive oxides protect the metal beneath from further corrosion and this can result in a significant reduction in corrosion. In the case of aluminium when placed in water, an oxidized layer of Al_2O_3 protects the metal from further oxidation (15).

A reference electrode is an electrode that maintains a virtually invariant potential under the conditions prevailing in an electrochemical measurement and which permits observation, measurement or control of the potential of the indicator (or test) or working electrode (16).

A reference electrode acts as a benchmark against which all other electrode potentials can be measured. The particular reference electrode used must be stated as part of the units. A number of reference electrodes have been used in practice. They include standard hydrogen electrode (SHE), saturated calomel electrode (SCE), silver-silver chloride electrode and copper-copper II sulphate electrode

The most common reference electrode is the standard hydrogen electrode. It is relatively easy to build as it requires hydrogen gas of known pressure to be bubbled through an acid solution of known pH so that the acid solution is saturated with hydrogen. A noble metal electrode is placed into the solution. Platinized platinum is generally used to ensure large electrochemical surface area and rapid equilibrium condition (17).

The electrode reaction is as follows:

$2H^{+} + 2e^{-} = H_2$

This reaction yields an electrode potential E_{H+}/H_2 of 0.00 volts when all reactants and products are in standard state. The standard potential of H+ at 1 molar concentration is equal to zero. The standard conditions are 298K (25^{O}C), hydrogen gas at 1 bar pressure and 1M concentration of ions in aqueous solution. When SHE is coupled with an electrode, potential difference measured is the electrode potential of that electrode as SHE establishes the zero point on the electrochemical scale.

The diagram below represents how the standard potential E^{o} of magnesium can be determined. The magnesium electrode contains Mg^{2+} ions in equilibrium with magnesium metal. The role of the salt bridge is to complete the electrical circuit. The salt bridge is a glass tube filled with electrolyte like potassium nitrate solution. The ends are stoppered by bits of cotton wool to ensure that the contents do not mix with those of the electrodes.

a much higher tendency to ionize than hydrogen gas. The with the voltmeter showing magnesium as the negative electrode and hydrogen as being the positive electrode. If replaced by copper metal in a solution of 1M copper II sulphate a voltage of 0.34 volts would be read. The reason for the difference is that copper is less likely to lose electrons as compared to magnesium and is therefore a more positive (less negative) electrode as compared to magnesium (18).

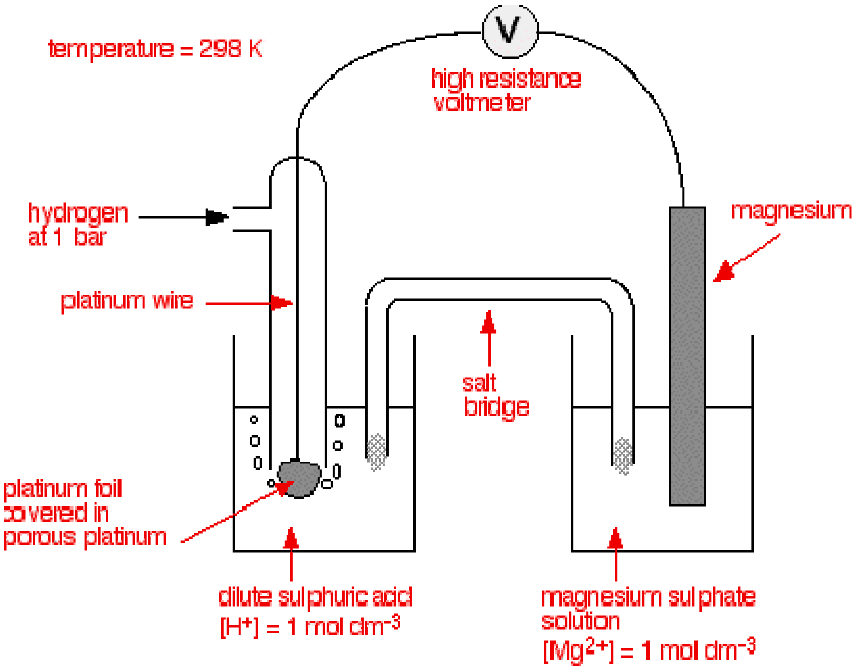


Figure 2. Determination of Standard Potential of Magnesium.

Source: www.chemiguide.co.ke/physical/redoxia/introduction.html

It is sometimes difficult or impossible to measure experimentally the standard electrode potential of an electrochemical system. The reason behind this is that many systems lie outside water stability zone or they exhibit passivity. An example of such a metal is zinc which undergoes oxidation when immersed in water. The approach used in the determination of standard equilibrium potential is based on the equation linking chemical driving force with electrical driving force as follows:

$\varphi G^o = -zFE^O$

can be expressed as

$\varphi G^{o\,-}\ \varepsilon^{o}$ (products) ï ε^{o} (reactants)

Where ε^{o} is the standard chemical potential. When these equations are combined

$E^{O} = \varphi G^{o}/zF = [\varepsilon^{o}$ (products) ï ε^{o} (reactants)]/zF

ε^{o} values are available in standard chemical potential tables (19).

It is sometimes impractical to use standard hydrogen electrodes (SHE) owing to the clumsy nature of hydrogen gas. This necessitates the use of other reference electrodes namely calomel reference electrode, silver/ silver chloride reference electrode and copper/copper II sulfate reference electrode.

Calomel reference electrodes are ruggedly constructed. They provide stable potential when used with an appropriate glass pH electrode, ion selective electrode or metallic electrode. It contains mercury/mercury I chloride reference element surrounded by saturated potassium chloride or gelled potassium chloride solution contained in an outer tube as shown below:

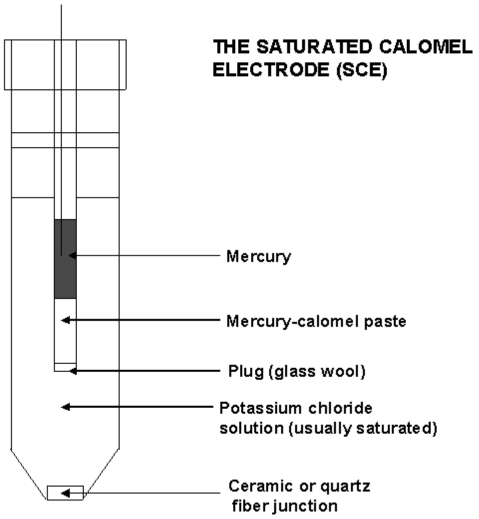


Figure 3. Saturated Calomel Reference Electrode. Source: www.chemwiki.ucdavis.edu

When immersed in a solution electrical contact is made between the sample and the electrolyte at an opening located at the end of electrode. An opening or junction forms a conductive bridge between the reference electrode, sample and indicating electrode. Calomel reference electrodes

r) and 4 junction types. Glass body liquid- filled types routine applications; cracked bead junctions for samples requiring fast electrolyte flow and/or o renewable junction. Polymer bodied types include liquid filled with ceramic junction and gel-filled with a porous polymer junction.

At 25°C saturated calomel electrode has a potential of 0.244V relative to Standard Hydrogen Electrode (SHE). This value is an average of 13 values reported in literature between 1916 and 1956. The difference in reading is probably due to junction potential error caused by the frit the electrode and environment. Calculations have been done to estimate the potential in the absence of the liquid junction with a resulting value of 0.241V ± 1 millivolt. This response is a fraction of the temperature. The potential is therefore given by the equation:

$V_T = 0.2442 - 0.00072(T-25)$ where T is the temperature in °C (19).

As a general rule, great care must be taken in the use of the calomel electrode as it contains mercury I chloride which is harmful if swallowed (20).

The silver/silver chloride electrode is increasingly being used in corrosion studies and is currently preferred over the calomel electrode. It is easy to prepare, readily available, very stable and robust to contamination. It can also withstand high temperatures. The electrode can have single or double junction. The diagram below shows a silver/silver chloride reference electrode.

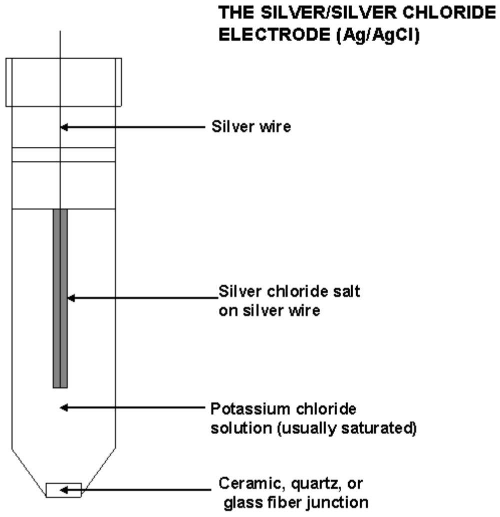


Figure 4. Silver/Silver Chloride Reference Electrode. Source: www.chemwiki.ucdavis.edu

de is related to the concentration of chloride through the

$E = E^{o}\ (Ag/Ag^{+}) + [RT/F * \ln\ (K_{sp}/a_{cr})]$

Or

$E = E^{o}\ (Ag/AgCl)\ \text{ï}\ [RT/F * \ln K_{sp}]$

When the above are combined

$E^{o}\ (Ag/AgCl) = E^{o}\ (Ag/Ag+) + RT/F * \ln K_{sp}$

Where K_{sp} refers to the solubility product (the product of solubilities of the ions in moles per litre)

The half cell potential shown in the equation above is constant as long as the chloride activity is constant. It is therefore important to keep concentration high so as to minimize the effect of contamination. In the above equations the electrode is a direct immersion reference electrode and for the electrode to serve as a true reference electrode in direct immersion application the chloride activity must be constant.

The silver/silver chloride reference electrode is very prone to interfering ions. Interfering ions can have a large effect on reference electrode potential if they can react with silver wire or replace the silver chloride covering the wire. Salts that are less soluble than silver chloride at room temperature like silver bromide, silver iodide, silver chromate or silver sulphide are more thermodynamically favoured over silver chloride and if present will interfere with potential of the electrode. Silver oxide is more stable under basic conditions at elevated temperatures. Sulfide ions are also a source of contamination (21).

The copper/copper sulphate reference electrode contains water of hydration. The potential of this electrode arises from the redox reaction between a copper wire and a solution of saturated copper II sulphate as shown in the diagram below. The major application for this type of electrode is its use as a reference electrode for cathodic protection systems.

The potential of this reference electrode can be calculated as follows:

$SO_4^{2-})]$

Or

$E= E\text{o}\ (Cu^{2+/}CuSO_4^{2-})$ ï [RT/2F * lnaSO_4^{2-}]

When combined

$E^o\ (Cu/Cu\ SO_4^{2-}) = E^o\ (Cu/Cu^{2+}) + [RT/2F * \ln K_{sp}]$

Where K_{sp} is the solubility product of $CuS0_4$ forming Cu^{2+}, SO_4^{2-} and water.

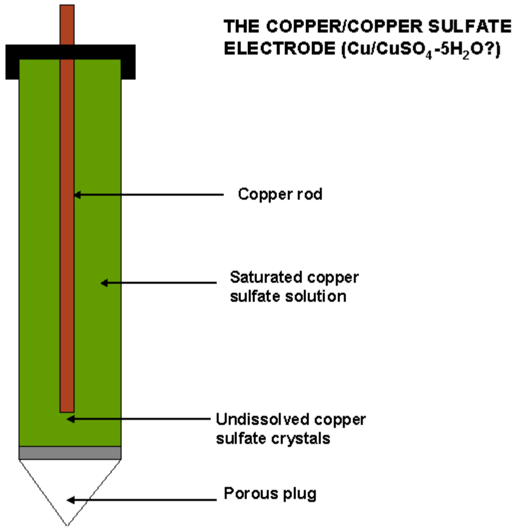


Figure 5. Copper/Copper Sulphate Reference Electrode. Source: www.chemwiki.ucdavis.edu

The potential of Cu/Cu^{2+} reference electrode is 0.338 V compared to the standard hydrogen electrode. Temperature has an effect of 9*10-4 V/°C. (22)

2.5 The Effect of pH on Corrosion

The chemical nature of the electrolyte is an external factor that governs the rate of corrosion. The pH is an important characteristic of the electrolyte. The influence of pH on the rate of corrosion of water containing oxygen is dependent on the metal being corroded (23)

The rate of corrosion in acid affected metals like Ni, Cu, Mn, Mg, Co, Cr, Cd decreases with increase in pH. In the case of amphoteric metals the rate decrease with increase in pH (decrease te again increases with increase in alkalinity. The rate of th increase in pH until in very strong alkalinity (about pH 13) when the rate increases sharply. Noble metals like Pt, Pd and Au do not show change in corrosion rate with change in pH (24).

The relationship between potential and pH is illustrated using Pourbaix diagrams. An electrochemical system contains several types of species such as dissolved ions, oxides and hydroxides. These diagrams show the stability areas of these species in the redox potential - pH coordinates. The redox potential axis is normally based on the standard hydrogen electrode scales but other scales can be used. The redox potential designated as Eh refers to the ability of a system to change electrons. When the potential is high (Eh is greater than 0) the system tends to remove electrons from the species.

In reducing conditions where (Eh is less than 0) the system is able to supply electrons to the species. The pH of the system determines the system ability to supply protons to the species. In acid conditions (pH less than 7) the concentration of protons is high while in basic conditions (pH greater than 7) the concentration of protons is low. In any system, there exist large amounts of different species in fixed Eh-pH conditions. Pourbaix diagrams are of great use as they show only the predominant species whose content is high in a stability area. The line in the diagram represents Eh-pH conditions whose content of adjacent species is the same in the equilibrium state. Horizontal lines represent reactions that involve electrons but are independent of pH. Neither H^+ nor OH^- participates in these reactions. Diagonal lines with either positive or negative slope represent reactions that involve both electrons, H^+ and OH^-. Vertical lines represent reactions that are involved with OH^-, H^+ but are independent of Eh essentially meaning that electrons do not participate in this reaction. The chemical stability of water is denoted by dotted lines. The upper stability of water represents potential where oxygen generation starts at the anode as given by the reaction:

$$2H_20 = 0_2 + 4H^+ + 4e^-$$

While the lower stability of water is based on hydrogen formation on the cathode as given by the reaction:

$$2H^+ + 2e^- = H_2$$

mentals of constructing a pourbaix diagram (25),

Pourbaix diagrams for Gold, Zinc and Aluminium are shown below. Gold is immune in all regions in which cathodic reactions take place and therefore Gold does not corrode in aqueous environments. The immunity of aluminium is at lower potentials and therefore unless it is under conditions that causes it to passivate it is much susceptible to corrosion than gold or zinc (26).

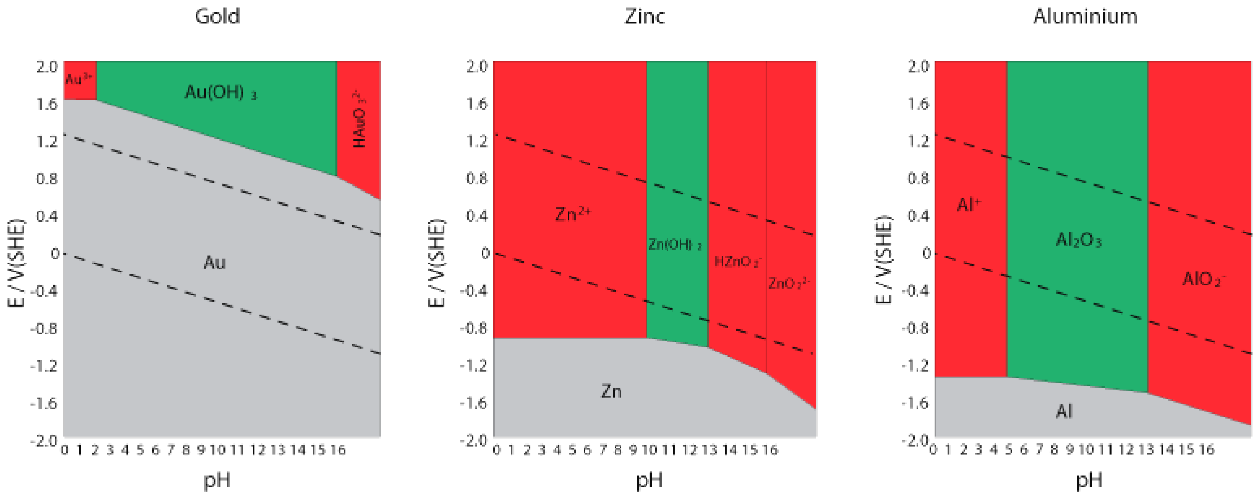


Figure 6. Pourbaix Diagrams for Gold, Zinc and Aluminium

Source: University of Cambridge. DoITPoMS

2.6 Effect of Temperature on Corrosion Rate

The rate of a chemical reaction depends on temperature as denoted by the Arrhenius equation $k = A.e^{-E/RT}$ where k is corrosion rate, R is gas constant and T is absolute temperature. In the case of a corroding system the reactants are the metal, water and oxygen. In a well aerated system, an increase in temperature results in a marked increase in corrosion rates due to increase in activation processes (27).

In a deaerated system, an increase in temperature causes a decrease in solubility of oxygen and a significant increase in water vapour tension. The two combined effects result in a significant concentration decrease of water and oxygen as reactants for the process of corrosion. The net result is a decrease in the rate of corrosion regardless of the acceleration effects of temperature as expressed by the Arrhenius law. An increase in temperature from 20-50 ^{o}C causes a decrease in oxygen solubility of about 60% and increase in vapour tension of about 330%. This process may ic conditions in the process of corrosion when ambient ce of a decrease in the concentration of oxygen and water in the corroding system. It is this principle that leads to a decrease in corrosion rate in a de aerated system even after temperature increase (28).

2.7 Effect of Chlorides on Corrosion

The effect of chloride ion is best explained in pitting corrosion. Pitting corrosion is an electrochemical oxidation- reduction process which occurs deep on the surface of metals coated with a passive film.

The anodic reactions inside the pit result in dissolution of metal

$Fe = Fe^{2+} + 2e^{-}$

The electrons given up flow to the cathode and are discharged in the cathodic reaction

$I/2\ O_2 + H_2O + 2e^{-} = 2OH^{-}$

The resulting effect is that electrolyte enclosed in the pit gains positive charge in contrast to the electrolyte surrounding the pit which becomes negatively charged. The positively charged pit attracts negative ions of chlorine increasing the acidity of electrolyte through the following reaction

$FeCl_2 + 2H_2O = Fe\ (OH)_2 + 2HCL$

The pH in the pit decreases from 6 to between 2 and 3 and this markedly increases the corrosion rate and there is a further growth in the size of the pit as illustrated by the diagram below (29),

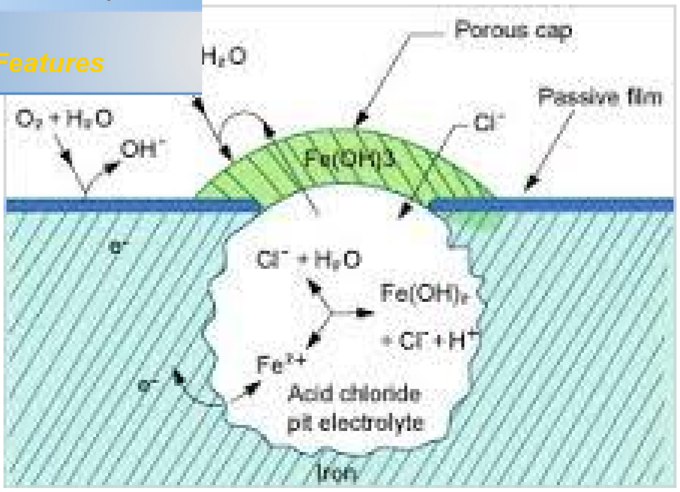


Figure 7. Effects of Chlorides on Corrosion. Source: www.substech.com

2.8 Effect of Micro Organisms on Corrosion

Microorganisms can influence the kinetics of corrosion of metals caused by microorganisms by adhering to interfaces. The requirements for microbially influenced corrosion are an energy source, carbon source, electron donator, electron acceptor and water. Corrosion is achieved by altering the pH and through redox reactions. Sulphate oxidizing bacteria cause the oxidation of sulphide (a weak acid) to sulphate (a strong acid) as shown below

$$S^{2-} +20_2 = SO_4^{2-}$$

Microorganisms also corrode metals in search of elements like iron, copper, aluminium for physiological gain. Sulphate reducing bacteria cause corrosion due to action of enzyme dehydrogenase, anodic depolarization, production of corrosive iron sulphide, release of exopolymers capable of binding Fe- ions, sulphide induced stress corrosion cracking and hydrogen induced cracking or blistering. Metal reducing bacteria like pseudomonas cause corrosion of iron and its alloys through reactions leading to dissolution of corrosion resistant oxide films on metal surfaces. Some bacteria are metal depositing. They participate in biotransformation of oxides of metals such as Iron and Manganese.

They include *Gallionella* which oxidizes Fe^{2+} to $Fe^{3+.}$ Other bacteria can produce significant quantities of inorganic and organic acids. Such acids include nitric acid, sulphurous acid, sulphuric acid, nitrous acid and carbonic acid. Sulphurous and sulphuric acids are mainly *hiobacillus*. Bacteria such as *Pseudomonas Aureginosa* ke alginic acid. Fermentation of organic compounds by bacteria results in organic acids such as acetic, formic and lactic acid which cause corrosion (30).

2.9 Electrochemical Polarization

Metallic surfaces can be polarized by the application of external voltage or by spontaneous production of a voltage away from equilibrium. This deviation from equilibrium potential is called polarization (31). There are 3 types of polarization namely activation, concentration and resistance polarization.

Activation polarization is the over potential caused by overcoming energy barrier of the slowest step of the electrochemical reaction. The commonest cause of cathode activation polarization is the reaction of hydrogen formation and evolution at the cathode. The first step is the reduction of hydrogen ions resulting in formation of atomic hydrogen on cathode surface, followed by formation of hydrogen gas molecules and finally evolution of gas as shown below.

$H^+ + e^- = H$

$2H = H_2$

$H_2 + H_2 + H_2 + H_2 +$ é é . $= nH_2$

The cathode is polarized by hydrogen atoms producing a film covering the cathode surface. This film slows down the reaction between electrons and hydrogen ions dissolved in the electrolyte thereby altering the process kinetics. At equilibrium state, the rates of oxidation and reduction proceeding at any electrode are equal. They produce two equal electric currents in opposite directions. The activation polarization over potential is calculated as follows:

˝$\Omega_{act} = -\ (RT/anF) \ln (i/i_o) = 2.3(RT/anF) \log (i/i_o)$ for cathodic activation polarization

˝$\Omega_{act} = (RT/anF) \ln (i/i_o) = 2.3(RT/anF) \log (i/i_o)$ for anodic activation polarization

Where;

R is gas constant

n is number of moles transferred by one ion

a is electron transfer coefficient (0’ a’ 1)

i is current density

i_o is current exchange density

the factor ϐ = 2.3 (RT/anF) is called tafels slope

and as such activation potential ˝Ƞ$_{act}$ = ϐ log (i/i_o)

Concentration polarization is caused by formation of a diffusion layer adjacent to the electrode surface where there is an ion concentration gradient. Diffusion of ions through the layers controls the electrochemical reaction. This electrode potential can be calculated using Nernst equation

$E = E^o$ ï (RT/nF) lnC_{ion}

Where;

E^o is standard electrode potential

R is gas constant

T is absolute temperature

n is the number of electrons transferred by one ion

F is faradays constant

C_{ion} is molar activity (concentration) of ions.

The concentration within the diffusion layer changes from C_b (bulk concentration) to Cs (concentration at electrode space). The corresponding potential changes are as follows

$E_b = E^O$ ï (RT/nf) ln C_b

$E_s = E^O$ ï (RT/nF) ln C_s

E_s ï E_b

The equation can also be rewritten as

˝Ω_c= E_s ï E_b = (RT/nF) ln (C_s/ C_b)

Or in terms electric current and limiting electric current passing through diffusion layer as

˝Ω_c= E_s ï E_b = (RT/nF) ln (1- i/i_L)

Concentration over potential can be corrected by raising the electrolyte temperature or agitation of the electrolyte to eradicate the ion concentration gradient.

Resistance polarization refers to potential drop due to either high resistivity of the electrolyte surrounding electrode or an insulation effect of film on the electrode surface formed by the reaction products. It is expressed by ohms law as follows:

˝Ωres =i R

Where i is electric current and R is resistivity.

Polarization curves and tafel plots can be used to demonstrate the above types of polarization (32).

2.10 Passivity and Breakdown of Passivity in Corrosion

A metal is referred to as passive when its corrosion in course of chemical or electrochemical reaction is lower at higher affinity of reaction than at lower affinity of chemical or electrochemical process. It can be demonstrated using the following diagram (33).

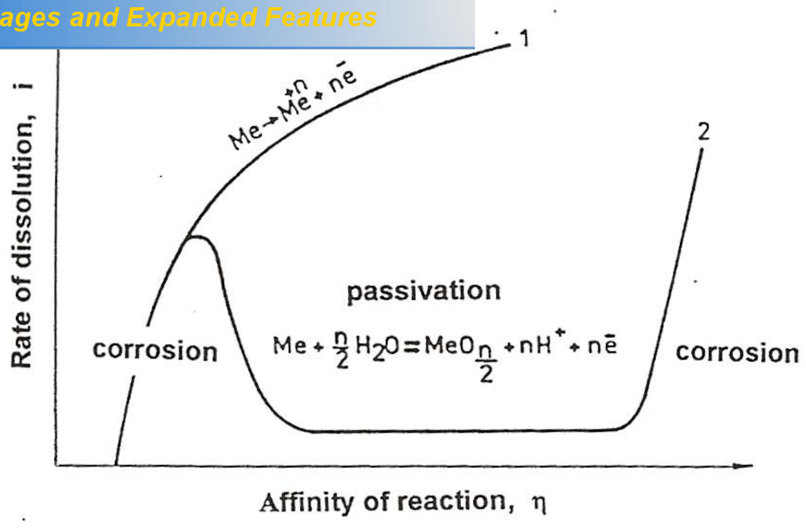


Figure 8. Passivation of Metals and Corrosion Rate. Source: C. Wagner 1965. Corrosion Science 5th edition. p751

Passivation occurs due to formation of a solid film of the product of the chemical reaction at the anode and polarization of the anode with a simultaneous shift of electrode potential to the positive side. The above phenomenon is basically due to formation of oxides that protect it from corrosion. The oxide layer prevents water and oxygen from penetrating the metal surface and thereby improves its resistance to electrochemical corrosion. The oxide film also alters the structure of the double electric layer changing the rate of electrochemical reactions (34).

Figure 8 attempts to illustrate how passivity of metal occurs (35).

Passivity is usually broken under certain conditions. An increase in cathodic currents and anodic polarization results in breakdown of passivity. Exposure to acidic conditions leads to dissolution of the oxide thus loss of passivity. The main mechanism of corrosion that occurs after passivity

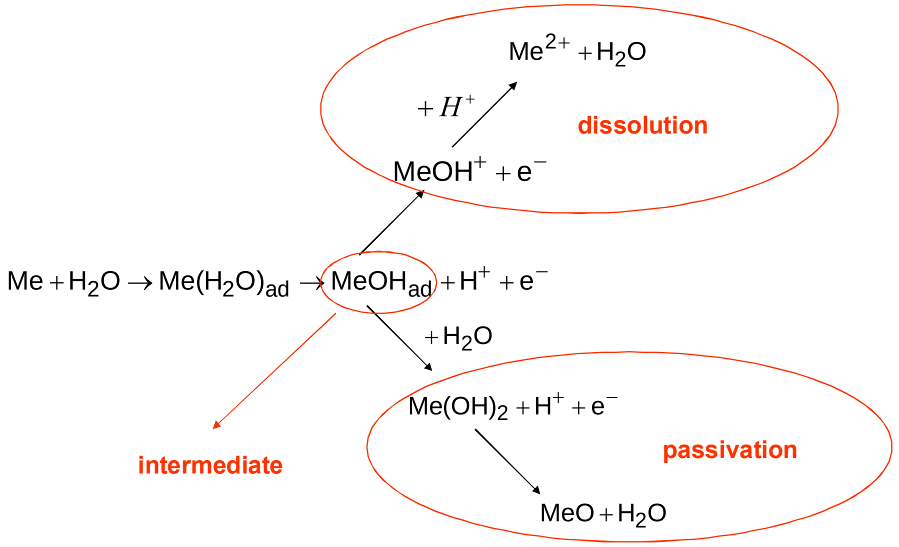


Figure 9. Mechanism of Passivation of Metals. Source: Nikon D. & Galina P. 1967. Passivity and Protection of Metals against Corrosion.

2.11 Types of Corrosion

There are several types of corrosion. They include: general attack corrosion, localized corrosion, galvanic corrosion, environmental cracking, flow assisted corrosion, inter granular corrosion, de-alloying, fretting corrosion and high temperature corrosion.

General attack corrosion is also known as uniform corrosion. It is the most common type of corrosion and is caused by a chemical or electrochemical reaction. It results in deterioration of the whole exposed surface of a metal. The final result is deterioration to a point of failure. It accounts for the bulk of the proportion of metal destruction by corrosion. However, it is easy to deal with as it is predictable, manageable and preventable.

Localized corrosion targets one area of the metal structure. It can be classified into pitting, crevice and film forming corrosion. Pitting corrosion results when a small hole or cavity forms in a metal usually as a result of loss of passivity. The net effect is that the pitted area becomes dic thereby producing a localized galvanic reaction which sion is difficult to detect. Crevice corrosion also occurs at specific locations and is associated with stagnant microenvironment like those found under gaskets, clamps and washers. Depletion of oxygen and acidic conditions can also lead to crevice corrosion.

Film forming corrosion occurs under painted or plated surfaces where water breaches the integrity of paint or seal. It begins with small defects and can spread to form structural weakness.

Galvanic corrosion is also referred to as dissimilar metal corrosion. It occurs when 2 different metals are located together in a corrosive electrolyte. One metal becomes the anode, the other the cathode and hence corrosion. Three conditions must be met for galvanic corrosion to occur: the metals must be electrochemically dissimilar, metals must be in electrical contact and the metals must be exposed to an electrolyte.

Environmental cracking refers to a corrosion process that result from a combination of environmental conditions affecting the metal. It is a result of chemical, temperature and stress related conditions. The following are types of environmental corrosion: Stress Corrosion Cracking (SCC), corrosion fatigue, hydrogen induced cracking and liquid metal embrittlement.

Flow assisted corrosion results when the protective oxide layer on metal surface is dissolved or removed by wind or water thereby exposing the underlying metal to corrosion through erosion assisted corrosion, impingement and cavitations.

Intergranular corrosion refers to electrochemical attack on the grain boundaries of a metal. This is mostly as a result of impurities in the metal which are usually higher in quantity near grain boundaries.

Dealloying is also called selective leaching. It occurs when there is selective corrosion of a specific element in an alloy. This has been observed in de-zincification of unstabilized brass resulting in deteriorated and porous copper.

Fretting corrosion results from repeated wearing, weight application, vibration or uneven rough surface of metals. It occurs on surface and is characterized by pits or groves. This type of mpact machinery, bolted assemblies as well as surfaces on.

High temperature corrosion is the type of corrosion that occurs to metal alloys normally resistant to high temperatures and corrosion. Fuel used in gas turbines, diesel engines may contain vanadium or sulphates which during combustion for compounds with low melting points. These combustion products attack the alloy leading to high temperature corrosion. High temperature oxidation, sulfidation and carbonization can also cause this type of corrosion (37).

2.12 Corrosion Inhibitors

Corrosion inhibitors are chemicals that react with a metallic surface or the environment the surface is exposed to giving the surface a certain level of protection (38).

Corrosion inhibitors have also been defined as chemical substances which when added in small concentration to an environment effectively decrease the corrosion rate (39).The efficiency of a corrosion inhibitor is therefore expressed as a measure of this improvement.

Inhibitor efficiency (%) = $100\,(CR_{\text{uninhibited}} - CR_{\text{inhibited}})/CR_{\text{uninhibited}}$

Where $CR_{\text{uninhibited}}$ is the corrosion rate of the uninhibited system

$CR_{\text{inhibited}}$ is the corrosion rate of inhibited system

In general, efficiency of an inhibitor increases with increase in inhibitor concentration. A good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at concentration of 0.004% (39).

Large numbers of compounds have corrosion inhibition activity. However, very few are ever used in practice. The reason is that the desirable properties of an inhibitor extend beyond metal protection. Factors such as cost, toxicity, availability and environmental friendliness are also of great importance.

2.13 Classification of Corrosion Inhibitors

Inhibitors can be classified into environmental and interface inhibitors as shown in figure 10. Environmental inhibitors are also called scavengers. They decrease the corrosivity of the substances. When the media is near neutral and alkaline, dic reaction and which can be controlled by decreasing oxygen content using scavengers like hydrazine. Interface inhibitors control corrosion by forming a film at the metal/environment interface. Interface inhibitors can be classified into liquid and vapour phase inhibitors.

Liquid phase inhibitors are classified as anodic, cathodic or mixed inhibitors depending on whether they inhibit anodic, cathodic or both electrochemical reactions. Anodic inhibitors are used in near neutral solutions where soluble corrosion products such as oxides, hydroxides and salts are formed. They form or facilitate formation of passivating films that inhibit the anodic metal dissolution reaction. They are commonly referred to as passivating inhibitors. If the concentration of anodic inhibitors is insufficient, corrosion may be accelerated rather than inhibited. Cathodic inhibitors act by either decreasing reduction rate (cathode poisons) or by precipitating selectively on the cathodic areas (cathode precipitation). Cathodic poisons such as serenades and sulfides are adsorbed on to the metal surface whereas others like arsenic, bismuth and antimony are reduced at the cathode to form a metal layer. When the pH is near neutral or alkaline, inorganic anions such as phosphates, silicates and borates form protective films that decrease cathodic reactions by limiting diffusion of oxygen to metal surface. Cathode poisons are associated with hydrogen blisters and hydrogen embrittlement caused by absorption of hydrogen into steel. Cathodic precipitators cause an increase in alkalinity at the cathode causing precipitation of insoluble compounds on metal surface. The commonly used cathodic precipitators are carbonates of calcium and magnesium.

Mixed Inhibitors refers to the great number of organic inhibitors that can neither be designated as anodic or cathodic. The effectiveness of organic inhibitors is related to the extent to which they adsorb and cover the metal surface. The extent of adsorption is related to the structure of the inhibitor, surface charge of the metal and type of electrolyte in solution. Mixed inhibitors act by physical adsorption, chemisorption and film formation. Physical adsorption results from electrostatic attraction between inhibitor and metal surface. If metal is negatively charged, adsorption of positively charged ions is facilitated. Positively charged molecules acting in combination with negatively charged intermediates can inhibit a positively charged metal. This can be demonstrated when anions, such as halide ions, in solution adsorb on the positively ns subsequently adsorb on the dipole. The diagram below

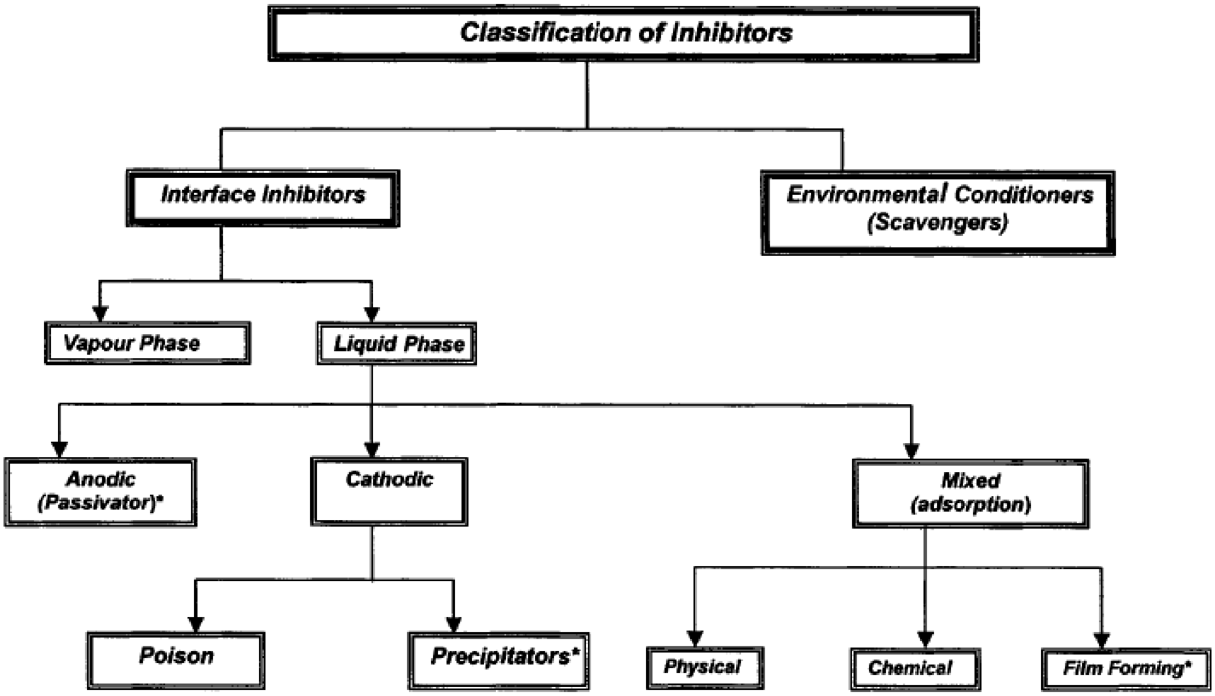


Figure 10. Classification of Corrosion Inhibitors. Source: R. Winston Revie 2000. Uhligôs Corrosion Handbook 2nd Edition p1090, John Wiley and Sons Inc.

This has been seen in the corrosion of iron in sulphuric acid containing chloride ions which is inhibited by quaternary ammonium cations through this synergistic effect. Physically adsorbed inhibitors interact rapidly but can also be removed from the metal surface. Temperature rise greatly facilitates desorption of physically adsorbed molecules. Inhibitors that chemically adsorb (chemisorb) are most effective. Chemisorption involves sharing or charge transfer between the inhibitor molecule and metal surface. It is slower compared to physical adsorption. It is specific and not completely reversible. The adsorbed inhibitor molecules undergo surface reactions which lead to production of polymeric films. The films grow from 2 dimension adsorbed layers to 3 dimension films with a remarkable increase in corrosion protection. For inhibition to occur, films must be adherent to metal surface, insoluble and must prevent access of the solution to the metal. Protective films result from film formation. They can be conducting or non-conducting. Non inhibitors as they increase resistance of the circuit hence

Vapour Phase Inhibitors give temporary protection against atmospheric corrosion. Wrapping papers are impregnated with vapour phase inhibitors thus protecting the metal from air and moisture. They are more effective in ferrous than non ferrous metals (40).

2.14 Corrosion Inhibition Mechanism

There are 4 main types of environment that are interest for corrosion inhibitors.

a. Aqueous solutions of acids for metal cleaning for processes such as pickling for removal of rust or mill scale during production, fabrication of metal or cleaning of metal surfaces during servicing.

b. Natural water, supply water and industrial cooling water in near neutral pH (5-9)

c. Primary and secondary production of oil, refinement and transportation of the same

d. Atmospheric or gaseous corrosion in confined environment during transportation and storage

Inhibitors of acid solutions include halides, carbon monoxide and organic compounds. Organic compounds that have multiple bonds especially triple bonds are very effective as corrosion inhibitors. The primary mechanism of action is adsorption onto the metal surface which is usually oxide free in acid solutions. The adsorbed inhibitor acts to retard the cathodic and/or anodic electrochemical corrosion processes. The adsorption of corrosion inhibitors onto metals is influenced by the surface charge on the metal, functional group and structure of the inhibitor, interaction of the inhibitor with water molecules, interaction of adsorbed inhibitors. Corrosion inhibitors in acidic solutions have been shown to affect the corrosion reaction by formation of a diffusion layer, blocking of reaction sites, precipitation on the electrode and alteration of the electrical double layer.

e anions of weak acids like chromate, nitrite, benzoate, ists a difference between how corrosion occurs in neutral and near neutral solution as opposed to acid solutions in 2 important respects. In air saturated solutions, the main cathodic reaction in neutral solutions is the reduction of dissolved oxygen whereas in acid solutions it is hydrogen evolution. The corroding metal surfaces in neutral solutions have films of oxide while those in acid are oxide free. The distinction is that compounds that inhibit corrosion in acid by adsorption on oxide free surfaces do not inhibit corrosion in neutral solutions. The passivating oxide layer gives high resistance to diffusion of metal ions and as such the anodic reaction of metal dissolution is inhibited. These anions of weak acids used for this purpose are also referred to as anodic inhibitors and are more commonly used as opposed to cathodic inhibitors in the inhibition of corrosion of Iron, Zinc, Aluminium and their alloys in neutral or near solution. The mechanism of inhibition occurs through the following mechanisms: reduction of dissolution rate of passivating oxide film, repair of the oxide film by promotion of the formation of oxide, repair of the oxide film by plugging pores with insoluble compounds and the prevention of adsorption of aggressive ions.

The corrosion of Iron/Steel in neutral or near neutral solutions can be inhibited effectively by most weak acids. Anions of strong acids tend to prevent the action of inhibitive anions and stimulate breakdown of the protective oxide film. Halides, sulphates, and nitrates are examples of aggressive ions and can destroy protective oxide films. A number of factors can affect the balance between inhibitive and aggressive properties of a specific anion. They include:

a. Concentration- In distilled water, inhibition of Iron corrosion occurs when anion concentration exceeds a critical value. If concentration is below critical value, inhibitive anions may act aggressively and cause breakdown of the oxide layer. A good inhibitive anion has low critical concentration for inhibition. The order for decreasing inhibitive efficiency is azide, cyanide, nitrite, carbonate, chlorate, O-chlorobenzoate, bicarbonates, fluorides, nitrate and formate.

b. pH- Inhibitive anions can only prevent corrosion at pH values more alkaline than a critical value. The critical pH depends on the anion type.

nd supply- the inhibition of corrosion of Iron by anions of oxidizing power in solution.

d. Aggressive anion concentration- when aggressive anions are present in solution, the critical concentration of inhibitive anions for protection of iron is increased. A mathematical relationship has been demonstrated.

$$\text{Log } C_{inh} = n \log C_{agg} + K$$

where K is a constant dependent on nature of inhibitive and aggressive anions, n is an exponent approximately equal to the ratio of valency of inhibiting ions to the valency of aggressive anions, C_{agg} is the maximum concentration of aggressive anions permitting full protection, C_{inh} is the concentration where full inhibition is achieved in presence of aggressive anions.

e. Nature of metal surface- the critical concentration required to inhibit corrosion may increase with increase in surface roughness.

f. Temperature- as a general rule the critical concentration of anions required to protect iron /steel for example benzoate, chromate and nitrate increases with an increase in temperature.

Inhibitors for Oil and Gas Systems that are currently being used are organic nitrogenous compounds with long chain hydrocarbons. They include amides, imidazolines, salts of nitrogenous molecules with carboxylic acids, nitrogen quaternaries, polyoxyalkylated amides and amines, nitrogen heterocyclic and organic compounds containing Phosphorous, Sulphur and Oxygen. Various hypotheses have been put forward as regards to the mechanism of protection. The most plausible is the sand witch theory. Under this theory, the bottom part of the sandwich is the bond between the polar end of the molecule and metal surface. The strength of protective action depends on the bond. The centre portion of the sand witch is non polar end and its contribution towards protection is the degree to which this portion of the molecule can cover or wet the surface. The top portion is the hydrophobic layer of oil attached to the long carbon tail of the inhibitor. Oil layer acts as external protective film covering the inhibitor film and creating a barrier to both outward diffusion of ferrous ion and inward diffusion of corrosive species. Water and water solutions cannot cause damage to this system unless they contain specific corrodents phide. Corrosion in oil can be sweet corrosion that is due ich arises due to effect of hydrogen sulphide. Other forms of corrosion in oil systems include acidizing corrosion which occurs due to the effect of acids that are used to stimulate oil and gas well or oxygen influenced corrosion that results from air contamination during mining oil.

Atmospheric and Gaseous Corrosion Inhibitors that are commonly used are referred to as Volatile Corrosion Inhibitors (VCIs). Volatile corrosion inhibition is based on conditioning of the environment with trace amounts of inhibitive material to give protection. VCIs are volatile and promote electrochemical effects such as change in potential in the diffuse part of the double layer that controls migration of components of the electrode reactions. A good vapour phase inhibitor must reach the metallic surface to be protected and its rate of transfer should be quick enough to prevent an initial attack of metal surface to be protected.

Only compounds with an appreciable value under atmospheric conditions and can act as electrolyte layer inhibitors by electrochemically changing the kinetics of electrodes should be classified as VCIs. Example include: morpholine, benzylamine, cyclohexylamine carbonate, and diisopropylamine and morpholine nitrite (41).

2.15 How to Measure Corrosion

Techniques that are used to determine corrosion rates can be broadly classified to destructive and non destructive techniques. A measurement technique is referred to a destructive if it alters the corrosion process during measuring process like potentiodynamic polarization or if material is physically removed from environment like in the case of weight loss measurement. Non destructive techniques like linear polarization (LPR), electrochemical impedance spectroscopy (EIS) and electrochemical noise can be used to make repeated measurements at different time intervals. The following techniques are the most commonly used to measure corrosion.

Weight loss determination method is the commonest method used to calculate corrosion rates. The metal to be tested is cleaned and weighed before and after the experiment to remove surface and corrosion product. The corrosion rate is determined as follows:

Corrosion rate (mm/year) = (w * 10^4/a) (0.365/ɟ) ensity in g/cm^3 and a is surface area in cm^2

Electrochemical methods like linear polarization, EIS, electrochemical noise (non destructive methods) and potentiodynamic polarization (dynamic) are all used to assess the efficiency of inhibitors.

Solution analysis involves determination of changes of content of metal ions arising from corrosion products over time. This method is of great application when the corrosion products are soluble (42).

2.16 Selection of Corrosion Inhibitors

The following factors should be kept in mind when selecting a corrosion inhibitor system. The type of material to be protected, the required timeframe of protection, type and thickness of coating required, potential interaction of the inhibitor with contents and removal methods of the inhibitor if need be. The method of application be it by dipping, spraying or brush application is also important. The type of protection required whether in- process, storage or shipping, storage condition in particular temperature and humidity and environmental, health and safety requirements should also be considered. Finally, the type of the product whether oil or water based also has an impact on the choice of corrosion inhibitor (43).

2.17 The use of Pharmaceuticals and Pharmaceutical Excipients to Inhibit Corrosion

Most organic molecules containing heteroatoms such as sulphur, phosphorous, nitrogen and oxygen show appreciable corrosion inhibition efficiency. Despite many of them having promising results, their use as corrosion inhibitors is limited by them being expensive, non biodegradable and toxic. This in turn means that they cannot be incorporated in formulations intended for human consumption. A lot of plant extracts and naturally occurring substances have been tested based on the principle that most plant extracts are environmentally acceptable, cost effective and readily available. Plant extracts and naturally occurring compounds used for corrosion inhibition are commonly referred to as green inhibitors (44). Tannins and their derivatives can be used to protect corrosion of steel in acid media (45). Extracts of tobacco from twigs, stems and leaves can protect steel and aluminium against corrosion in saline and acidic media. Tobacco extracts contain alcohols, polyphenols, nitrogen containing compounds and

ht to be responsible for corrosion inhibition activity (44,
e corrosion inhibition properties are: *Hibiscus sabdariffa* extracts for mild steel in acidic media (46) and acidic extract of leaves of *Citrus aurantiifolia* for mild steel in acidic media (47). Black pepper, Acacia gum, Castor seeds and lignin also have good anticorrosion properties for steel in acidic media (48).

Aminopolycarboxylic acids are compounds which when included in formulations are substances which have been shown to have good corrosion inhibition properties. Aminopolycarboxylic acids are compounds which contain one or more nitrogen atoms connected through carbon atoms to two or more carboxyl groups. Their ionized forms form strong complexes (chelates) with metal ions. This property is very important and is the basis of their role as chelating agents in chemical, medical and environmental applications. Examples of aminopolycarboxylic acids include the amino acid glycine, iminodiacetic acid, nitriloacetic acid, aspartic acid and EDTA (49, 50).

Surfactants are organic compounds that are amphiphilic, meaning they contain both hydrophobic and hydrophilic groups. Surfactants act by lowering surface tension between two liquids or between a liquid and a solid. Surfactants also act as detergents, wetting agents, emulsifiers and foaming agents. Surfactants have been widely used as corrosion inhibitors. Surfactant inhibitors can be classified into inorganic inhibitors, organic inhibitors, surfactant inhibitors and mixed material inhibitors. Organic surfactants are widely used as corrosion inhibitors in acid media. The organic components have multiple bonds in their molecules that contain the heteroatoms N, S and O which get adsorbed onto metal surfaces thereby delivering corrosion inhibition properties. Surfactant inhibitors are considered to have great advantages because they have high inhibition efficiencies, are cheap to buy and produce and the fact that they have low toxicity profile. The ability of a surfactant to adsorb is generally related to its ability to form micelles. The degree of adsorption depends on the nature of metal, metal surface condition, chemical structure of inhibitor and the type of corrosion media. Upon adsorption onto the metal surface, a protective film is formed that prevents the metal from corrosion (51).

Surfactants can further be classified into anionic, nonionic, cationic and zwitterionic surfactants. Anionics are greatly used and they comprise about 60% of total worldwide surfactant production because of their ease and low cost of manufacture. Anionics are mostly used for detergent formulations and generally alkyl chains in the C_{12}-C_{18} range obtain best detergency. Nonionic y mostly contain polyether or polyhydroxyl groups as the contain a cation as the surface active species. Quaternary ammonium salts and amines are the main groups responsible for the positive charge. Zwitterionic surfactants have two charged groups (positive and negative). The predominant charge depends on the prevailing pH (51).

Sodium dodecylsulphate, when studied through polarization technique, has been found to be an efficient corrosion inhibitor for copper in acidic media (52). For weight loss measurements, sodium dodecylsulphate has been found to be an effective inhibitor for nickel (53).

The corrosion inhibition activity of penicillins has been studied and demonstrated. Ampicillin, cloxacillin, flucloxacillin and amoxicillin have shown corrosion inhibition effects. Cephalosporins are closely related to penicillins in terms of their fundamental structure and antibactericidal mechanism of action. Cefatrexyl, cefazolin and cephalexin can be used as corrosion inhibitors of iron in acidic media. The inhibition action is thought to result from blocking the surface through formation of insoluble complexes on the metal (54).

The use of antioxidants as corrosion inhibitors is a common practice in the petroleum industry. Antioxidants prevent oxidation reaction which may cause a series of reactions that can trigger corrosion. Studies have shown that an increase in antioxidant activity of compounds results in an increase in corrosion inhibition activity (55). The proposed use of reducing agents/ antioxidants ascorbic acid and sodium metabisulphite is informed by the above studies.

CHAPTER 3: METHODOLOGY

3.1 Study Design

This research was designed as an experimental study.

3.2 Study Location

The study was carried out at the laboratories of the Department of Pharmaceutics and Pharmacy Practice and the Department of Pharmacology at the School of Pharmacy, University of Nairobi.

3.3 Materials

Pharmaceutical excipients and other laboratory materials that were used in the study were purchased from CHEMOQUIP LTD, a reputable supplier in Nairobi.

The Pharmaceutical excipients used were: Sodium Lauryl Sulphate (0.5 and 2%), Ascorbic Acid (0.1% and 0.5%), Sodium Metabisulphite (0.1% and 0.5%), EDTA (0.5% and 2%), Gelatin (2% and 5%), Avicel (2% and 5%), Ethanol (20% and 50%), Isopropyl Alcohol (20% and 50%).

The test solutions for the experiment were H_2SO_4 (0.01, 0.1 and 1M), NaOH (0.01, 0.1 and 1N), NaCl (0.01, 0.1 and 1N) and Distilled water.

3.4 Equipment

Shimadzu weighing balance (0.0001g balance), 100ml beakers, Filter papers, Pipettes and 100ml volumetric flasks.

3.5 Method

Commercially available lacquered tin plated steel sheets obtained from a container ready for packing pharmaceuticals were cut into 30*30*0.2 mm pieces. The external side of the tin plated sheet contained clear vanish lacquer rendering it waterproof. The internal part of the sheet contained an epoxy phenolic lacquer. The amount of tin was 2.8 mg per square metre of steel. The pieces were mechanically polished using filter paper, washed with distilled water, dried between clean filter papers and finally weighed. The tin plated pieces were immersed in 100 mL inhibitor for 72 hours. After the test, the pieces were ried as before and weighed again.

To test for the effect of substitution of distilled water with ethanol (20% and 50%) and isopropyl alcohol (20% and 50%) the procedure was as above but the duration was 14 days.

For every concentration of test solution, only one concentration of pharmaceutical excipient was investigated.

The weight loss of the metal was calculated as follows:

$\varphi W = W_1 - W_2$

where W_1 and W_2 are the weights of the metal before and after exposure to corrosive solution respectively.

The Inhibition Efficiency (%IE) was calculated from the equation below:

$\%IE = [1-(\varphi W_{inh}/\varphi W_{free})]*100$

where φW_{free} and φW_{inh} are weight losses of a single 30*30*0.2mm tin plated steel in grams per nine square centimeters in the absence and presence of inhibitor at a given time, period and temperature respectively.

3.6 Data Management

All raw data collected was recorded on a laboratory manual book at the point when the weight measurements were taken. The data was backed up on Microsoft Excel.

3.7 Data Analysis

Data analysis was done using the program Microsoft Excel. Percentage Inhibitor Efficiency was calculated using the formulae shown below:

$\%IE = [1-(\varphi W_{inh}/\varphi W_{free})]*100$

Where φW_{free} and φW_{inh} are weight losses of metal in grams per nine square centimeters in the absence and presence of inhibitor at a given time, period and temperature respectively.

ON AND CONCLUSION

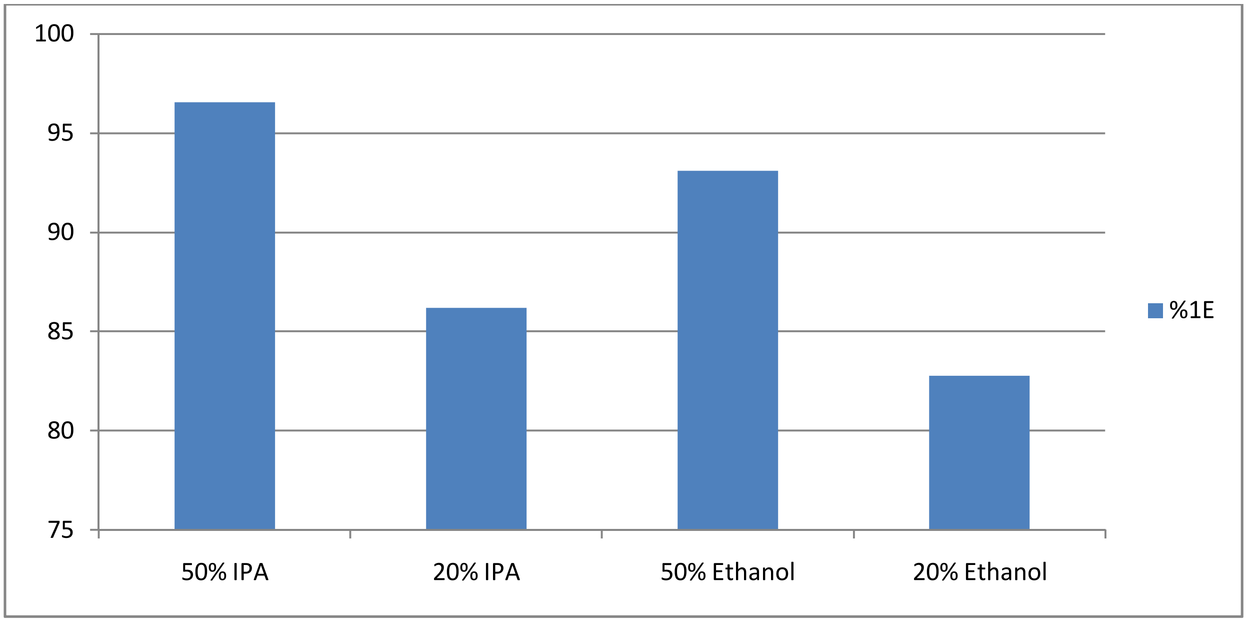
4.1 Solvents as Corrosion Inhibitors

Table 1 and Figure 11 show the inhibition efficiencies of various concentrations of ethanol and isopropyl alcohol obtained from weight loss measurements and a graphical representation of inhibition efficiencies of the same respectively.

Table 1. Table of Solvents as Corrosion Inhibitors

Solvent	$\varphi W_{inh}(g/9cm^2)$	$\varphi W_{free}(g/9cm^2)$	%IE
50% IPA	0.0001	0.0029	96.5
20% IPA	0.0004	0.0029	86.2
50% Ethanol	0.0002	0.0029	93.1
20% Ethanol	0.0005	0.0029	82.7

Figure 11. Graph of %IE for Solvents



In this experiment, ethanol and isopropyl alcohol showed good corrosion inhibition properties when compared to distilled water. Isopropyl alcohol 50% demonstrated the best corrosion

l 50%. Isopropyl alcohol demonstrated better corrosion
ations of 50% and 20%.

4.2Pharmaceutical excipients as corrosion inhibitors in 0.01N NaOH

Table 2 and figure 12 show inhibition efficiencies of various concentrations of pharmaceutical excipients obtained from weight loss measurements in 0.01N NaOH and a graphical representation of inhibition efficiencies of the same respectively.

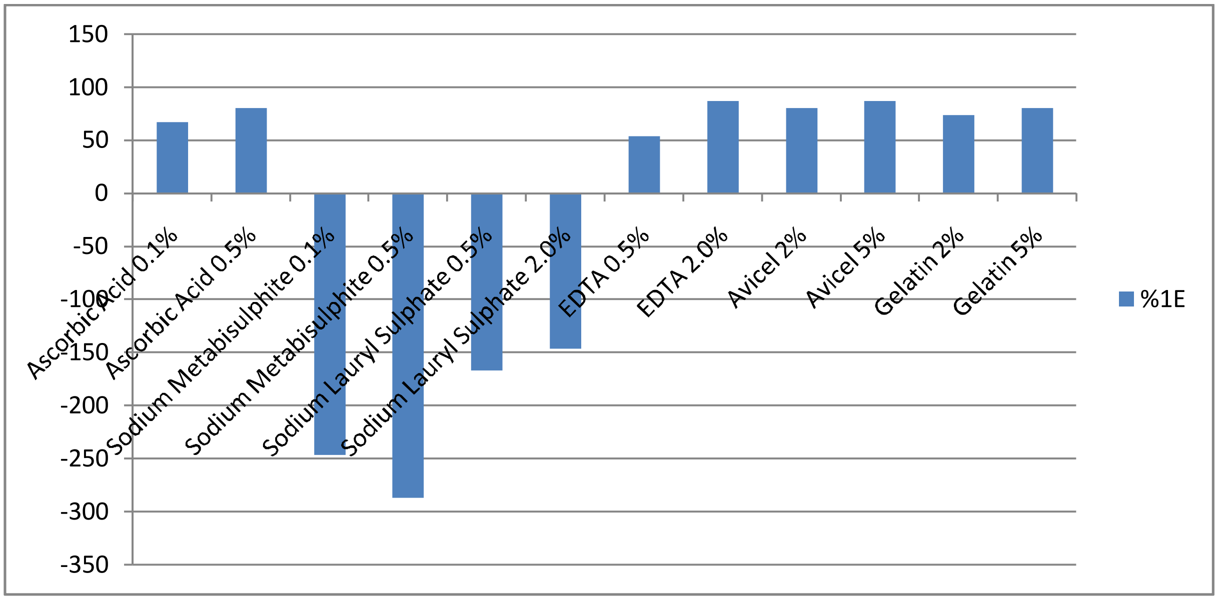
Table 2. Table of Inhibitors in 0.01N NaOH

Excipient	φW_{inh}(g/9cm^2)	φW_{free}(g/9cm^2)	%IE
Ascorbic Acid 0.1%	0.0005	0.0015	66.6
Ascorbic Acid 0.5%	0.0003	0.0015	80
Sodium Metabisulphite 0.1%	0.0052	0.0015	-246.6
Sodium Metabisulphite 0.5%	0.0058	0.0015	-286.7
Sodium Lauryl Sulphate 0.5%	0.004	0.0015	-166.6
Sodium Lauryl Sulphate 2.0%	0.0037	0.0015	-146.6
EDTA 0.5%	0.0007	0.0015	53.3
EDTA 2.0%	0.0002	0.0015	86.6
Avicel 2%	0.0003	0.0015	80
Avicel 5%	0.0002	0.0015	86.6
Gelatin 2%	0.0004	0.0015	73.3
Gelatin 5%	0.0003	0.0015	80

In this experiment, Avicel 5%, EDTA 2%, Gelatin 5%, Ascorbic Acid 0.5%, Avicel 2%, Gelatin 2%, Ascorbic acid 0.1% and EDTA 0.5% (in order of decreasing percentage corrosion inhibition efficiency) showed varying degrees of corrosion inhibition of tin plated steel in alkaline media of 0.01N NaOH.

above excipients was accompanied by an increase in cy.

Figure 12: Graph of % IE of Pharmaceutical Excipients in 0.01N NaOH



Sodium Metabisulphite (0.1% and 0.5%) and Sodium Lauryl Sulphate (0.5% and 2%) enhanced corrosion of tin plated steel. Sodium Metabisulphite promoted corrosion to a greater extent as compared to Sodium Lauryl Sulphate in alkaline media of 0.01N NaOH.

4.3 Pharmaceutical excipients as corrosion inhibitors in 0.1N NaOH

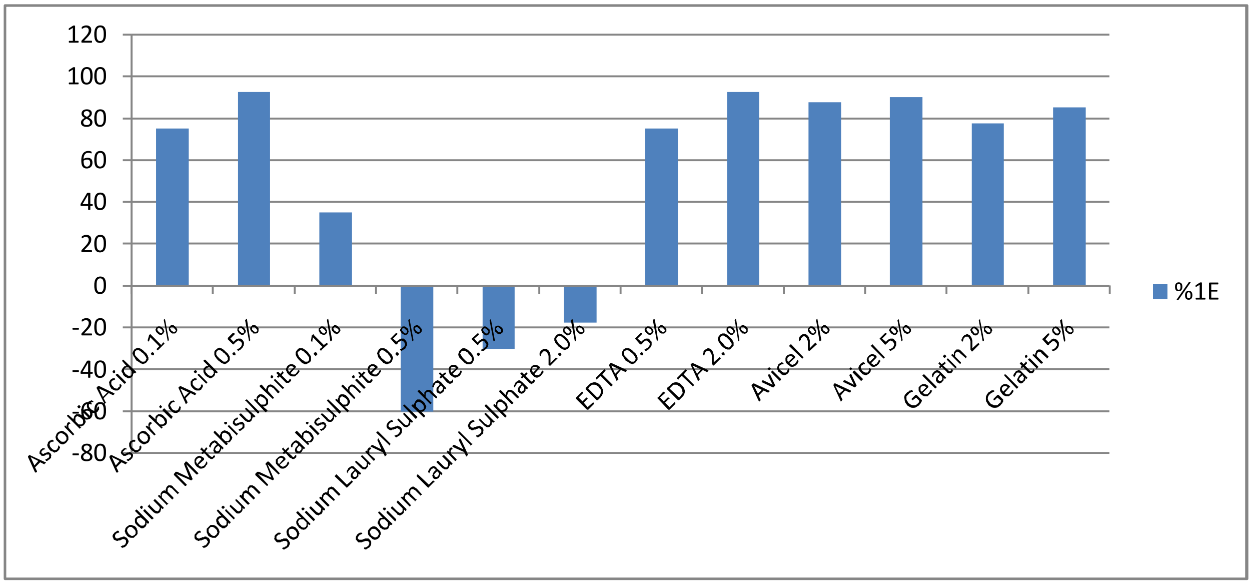
Table 3 and figure 13 show inhibition efficiencies of various concentrations of pharmaceutical excipients obtained from weight loss measurements in 0.1N NaOH and a graphical representation of inhibition efficiencies of the same respectively.

In this experiment, EDTA 2%, Ascorbic Acid 0.5%, Avicel 5%, Avicel 2%, Gelatin 5%, Gelatin 2%, Ascorbic Acid 0.5%, EDTA 0.5% and Sodium Metabisulphite 0.1% (In order of decreasing percentage corrosion inhibition efficiency) showed varying degrees of corrosion inhibition activity of tin plated steel in alkaline media 0.1N NaOH.

OH

Excipient	$\varphi W_{inh}(g/9cm^2)$	$\varphi W_{free}(g/9cm^2)$	%IE
Ascorbic Acid 0.1%	0.001	0.004	75
Ascorbic Acid 0.5%	0.0003	0.004	92.5
Sodium Metabisulphite 0.1%	0.0026	0.004	35
Sodium Metabisulphite 0.5%	0.0064	0.004	-60
Sodium Lauryl Sulphate 0.5%	0.0052	0.004	-30
Sodium Lauryl Sulphate 2.0%	0.0047	0.004	-17.5
EDTA 0.5%	0.001	0.004	75
EDTA 2.0%	0.0003	0.004	92.5
Avicel 2%	0.0005	0.004	87.5
Avicel 5%	0.0004	0.004	90
Gelatin 2%	0.0009	0.004	77.5
Gelatin 5%	0.0006	0.004	85

Figure 13. Graph of % IE of Pharmaceutical Excipients in 0.1N NaOH



An increase in concentration of the above excipients with the exception of Sodium Metabisulphite was accompanied by an increase in percentage corrosion inhibition efficiency.

um Lauryl Sulphate (0.1% and 0.5%) enhanced corrosion .1N NaOH.

4.4 Pharmaceutical excipients as corrosion inhibitors in 1 N NaOH

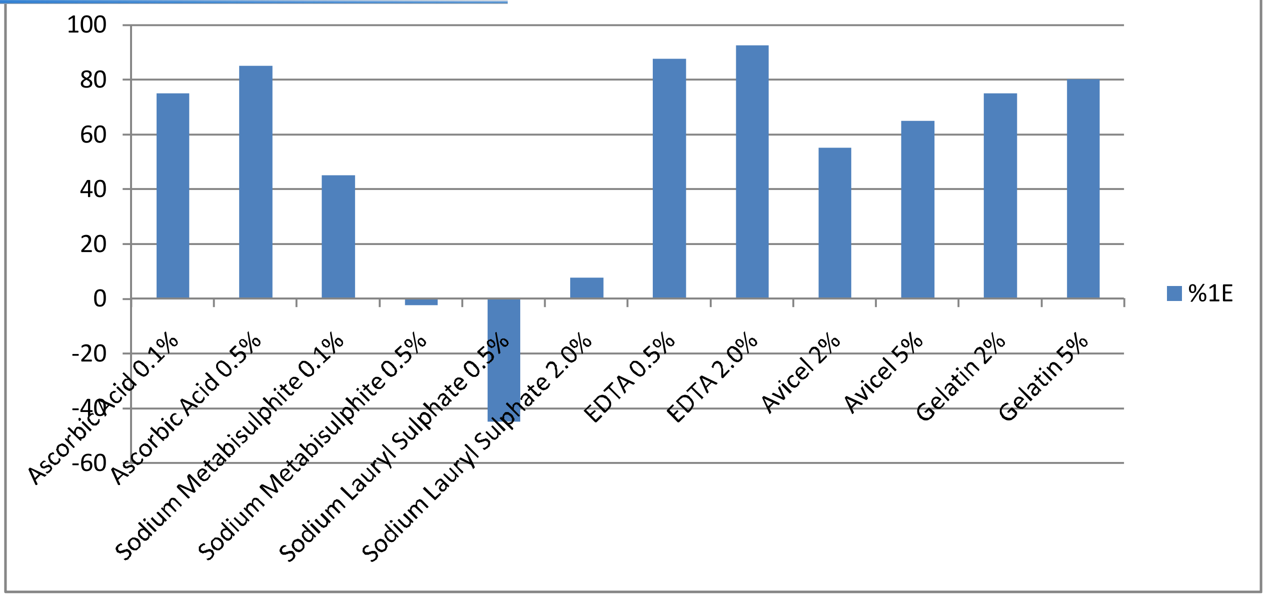
Table 4 and figure 14 show inhibition efficiencies of various concentrations of pharmaceutical excipients obtained from weight loss measurements in 1N NaOH and a graphical representation of inhibition efficiencies of the same respectively.

Table 4. Table of Inhibitors in 1N NaOH

Excipient	$\varphi W_{inh}(g/9cm^2)$	$\varphi W_{free}(g/9cm^2)$	%IE
Ascorbic Acid 0.1%	0.001	0.004	75
Ascorbic Acid 0.5%	0.0006	0.004	85
Sodium Metabisulphite 0.1%	0.0022	0.004	45
Sodium Metabisulphite 0.5%	0.0041	0.004	-2.5
Sodium Lauryl Sulphate 0.5%	0.0058	0.004	-45
Sodium Lauryl Sulphate 2.0%	0.0037	0.004	7.5
EDTA 0.5%	0.0005	0.004	87.5
EDTA 2.0%	0.0003	0.004	92.5
Avicel 2%	0.0018	0.004	55
Avicel 5%	0.0014	0.004	65
Gelatin 2%	0.001	0.004	75
Gelatin 5%	0.0008	0.004	80

In this experiment, EDTA 2%, EDTA 0.5%, Ascorbic Acid 0.5%, Gelatin 5%, Gelatin 2%, Ascorbic Acid 0.1%, Avicel 5%, Avicel 2%, Sodium Metabisulphite 0.1% and Sodium Lauryl Sulphate 2% (in order of decreasing percentage corrosion inhibition efficiency) showed varying degrees of corrosion inhibition activity of tin plated steel in alkaline media of 1N NaOH.

tical Excipients in 1NaOH



An increase in concentration of the above excipients with the exception of Sodium Lauryl Sulphate and Sodium Metabisulphite was accompanied by an increase in percentage corrosion inhibition efficiency.

Sodium Metabisulphite 0.5% and Sodium Lauryl Sulphate 0.5% enhanced corrosion of tin plated steel in alkaline media of 1N NaOH.

4.5 Pharmaceutical excipients as corrosion inhibitors in 0.01M H_2SO_4

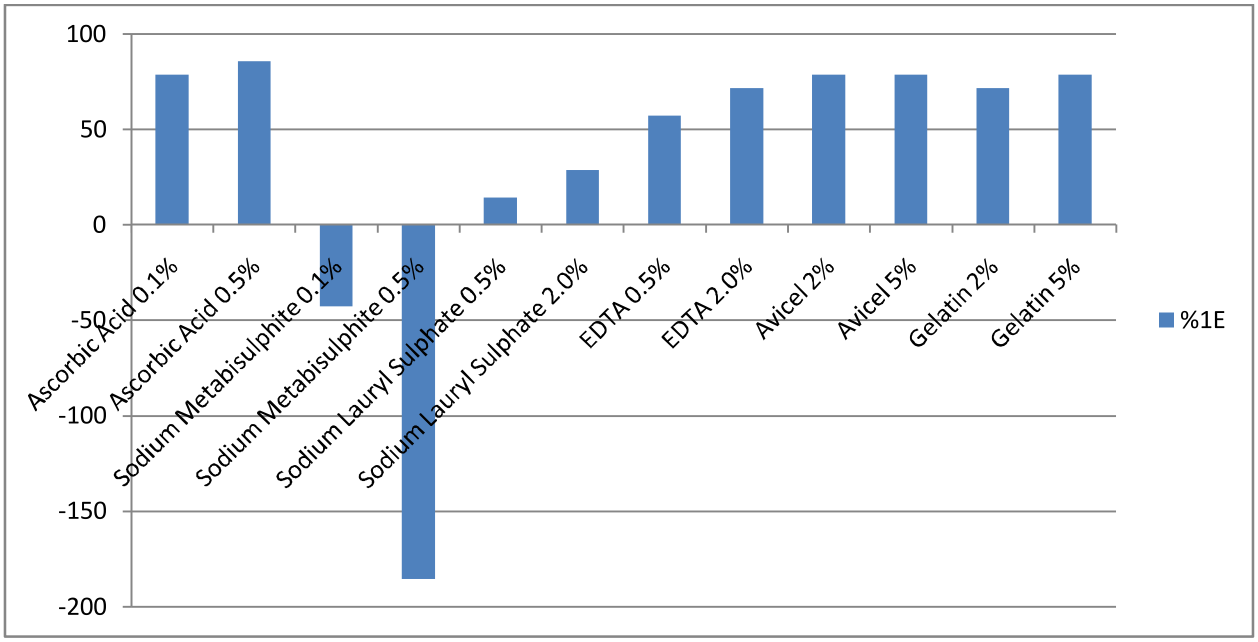
Table 5 and figure 15 show inhibition efficiencies of various concentrations of pharmaceutical excipients obtained from weight loss measurements in 0.01M H_2SO_4 and a graphical representation of inhibition efficiencies of the same respectively.

In this experiment, Ascorbic acid 0.5%, Ascorbic acid 0.1%, Avicel 5%, Avicel 2%, Gelatin 5%, Gelatin 2%, EDTA 2%, EDTA 0.5%, Sodium Lauryl Sulphate 2% and Sodium Lauryl Sulphate 0.5% (In order of decreasing percentage corrosion inhibitor efficiency) showed varying degrees of corrosion inhibition activity of tin plated steel in acidic media of 0.01M H_2SO_4.

$_2SO_4$

Excipient	$\varphi W_{inh}(g/9cm^2)$	$\varphi W_{free}(g/9cm^2)$	%IE
Ascorbic Acid 0.1%	0.0003	0.0014	78.5
Ascorbic Acid 0.5%	0.0002	0.0014	85.7
Sodium Metabisulphite 0.1%	0.002	0.0014	-42.8
Sodium Metabisulphite 0.5%	0.004	0.0014	-185.7
Sodium Lauryl Sulphate 0.5%	0.0012	0.0014	14.2
Sodium Lauryl Sulphate 2.0%	0.001	0.0014	28.5
EDTA 0.5%	0.0006	0.0014	57.1
EDTA 2.0%	0.0004	0.0014	71.4
Avicel 2%	0.0003	0.0014	78.5
Avicel 5%	0.0003	0.0014	78.5
Gelatin 2%	0.0004	0.0014	71.4
Gelatin 5%	0.0003	0.0014	78.5

Figure 15. Graph of % IE of Pharmaceutical Excipients in 0.01M H_2S0_4



above excipients was accompanied by an increase in

cy.

Sodium Metabisulphite (0.1% and 0.5%) enhanced corrosion of tin plated steel in acidic media of 0.01M H_2SO_4.

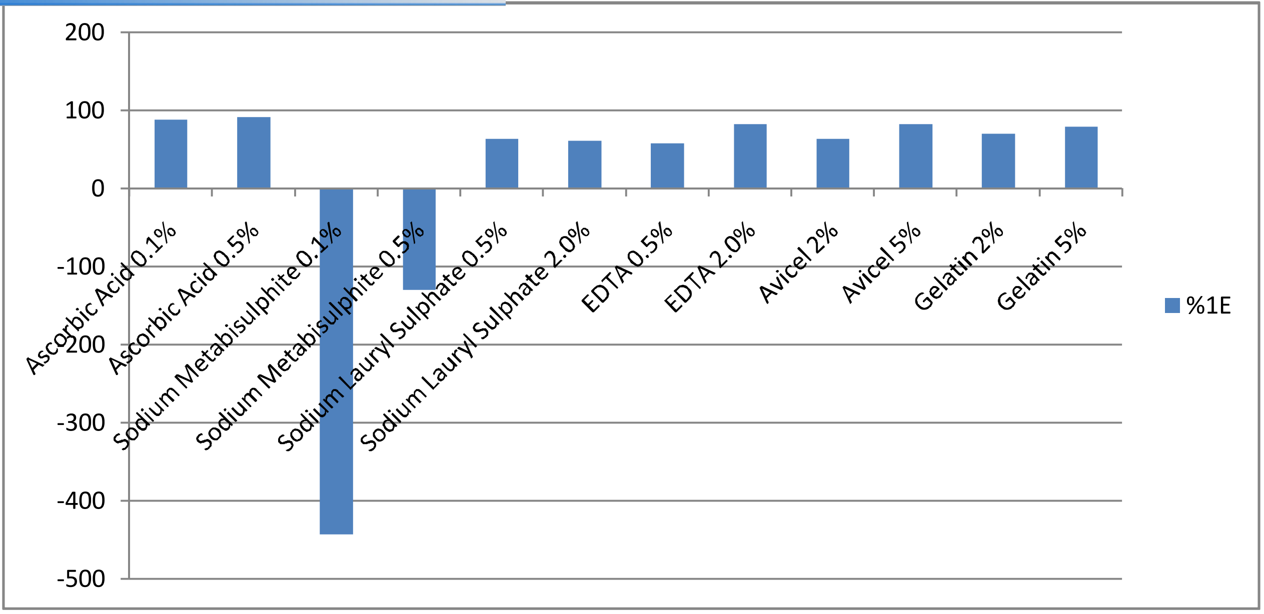
4.6 Pharmaceutical excipients as corrosion inhibitors in 0.1M H_2SO_4

Table 6 and figure 16 show inhibition efficiencies of various concentrations of pharmaceutical excipients obtained from weight loss measurements in 0.1M H_2SO_4 and a graphical representation of inhibition efficiencies of the same respectively. In this experiment, Ascorbic Acid 0.5%, Ascorbic Acid 0.1%, EDTA 2%, Avicel 5%, Gelatin 5%, Gelatin 2%, Sodium lauryl Sulphate 2%, Avicel 2%, Sodium Lauryl Sulphate 0.5% and EDTA 0.5% (In order of decreasing percentage corrosion inhibitor efficiency) showed varying degrees of corrosion inhibition activity of tin plated steel in acidic media of 0.1M H_2SO_4.

Table 6. Table of Inhibitors in 0.1M H_2S0_4

Excipient	$\varphi W_{inh}(g/9cm^2)$	$\varphi W_{free}(g/9cm^2)$	%IE
Ascorbic Acid 0.1%	0.0004	0.0033	87.8
Ascorbic Acid 0.5%	0.0003	0.0033	90.9
Sodium Metabisulphite 0.1%	0.0179	0.0033	-442.4
Sodium Metabisulphite 0.5%	0.0076	0.0033	-130.3
Sodium Lauryl Sulphate 0.5%	0.0012	0.0033	63.6
Sodium Lauryl Sulphate 2.0%	0.0011	0.0033	66.6
EDTA 0.5%	0.0014	0.0033	57.5
EDTA 2.0%	0.0006	0.0033	81.8
Avicel 2%	0.0012	0.0033	63.6
Avicel 5%	0.0006	0.0033	81.8
Gelatin 2%	0.001	0.0033	69.6
Gelatin 5%	0.0007	0.0033	78.7

tical Excipients in 0.1M H_2SO_4



An increase in concentration of the above excipients was accompanied by an increase in percentage corrosion inhibition efficiency. Sodium Metabisulphite (0.1% and 0.5%) enhanced corrosion of tin plated steel in acidic media of 0.1M H_2SO_4.

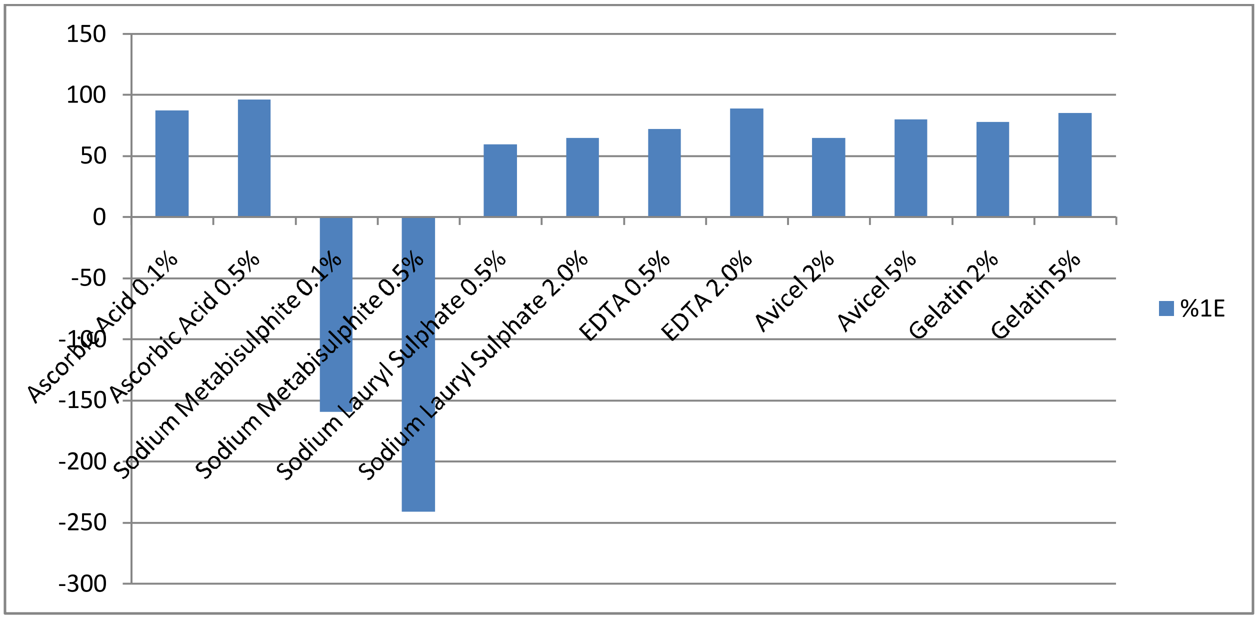
4.7 Pharmaceutical excipients as corrosion inhibitors in 1M H_2SO_4

Table 7 and figure 17 show inhibition efficiencies of various concentrations of pharmaceutical excipients obtained from weight loss measurements in 1M H_2SO_4 and a graphical representation of inhibition efficiencies of the same respectively.

In this experiment, Ascorbic acid 0.5%, EDTA 2%, Ascorbic Acid 0.1%, Gelatin 5%, Avicel 5%, Gelatin 2%, EDTA 0.5%, SLS 2%, Avicel 2% and SLS 0.5% (In order of decreasing percentage corrosion inhibitor efficiency) showed varying degrees of corrosion inhibition activity of tin plated steel in acidic media of 1M H_2SO_4.

Excipient	$\varphi W_{inh}(g/9cm^2)$	$\varphi W_{free}(g/9cm^2)$	%IE
Ascorbic Acid 0.1%	0.0007	0.0054	87
Ascorbic Acid 0.5%	0.0002	0.0054	96.2
Sodium Metabisulphite 0.1%	0.014	0.0054	-159.2
Sodium Metabisulphite 0.5%	0.0184	0.0054	-240.7
Sodium Lauryl Sulphate 0.5%	0.0022	0.0054	59.2
Sodium Lauryl Sulphate 2.0%	0.0019	0.0054	64.8
EDTA 0.5%	0.0015	0.0054	72.2
EDTA 2.0%	0.0006	0.0054	88.8
Avicel 2%	0.0019	0.0054	64.8
Avicel 5%	0.0011	0.0054	79.6
Gelatin 2%	0.0012	0.0054	77.7
Gelatin 5%	0.0008	0.0054	85.1

Figure 17. Graph of % IE of Pharmaceutical Excipients in 1M H_2S0_4



above excipients was accompanied by an increase in cy.

Sodium Metabisulphite (0.1% and 0.5%) enhanced corrosion of tin plated steel in acidic media of 1M H_2SO_4.

4.8 Pharmaceutical excipients as corrosion inhibitors in 0.01N NaCl

Table 8 and figure 18 show inhibition efficiencies of various concentrations of pharmaceutical excipients obtained from weight loss measurements in 0.01N NaCl and a graphical representation of inhibition efficiencies of the same respectively.

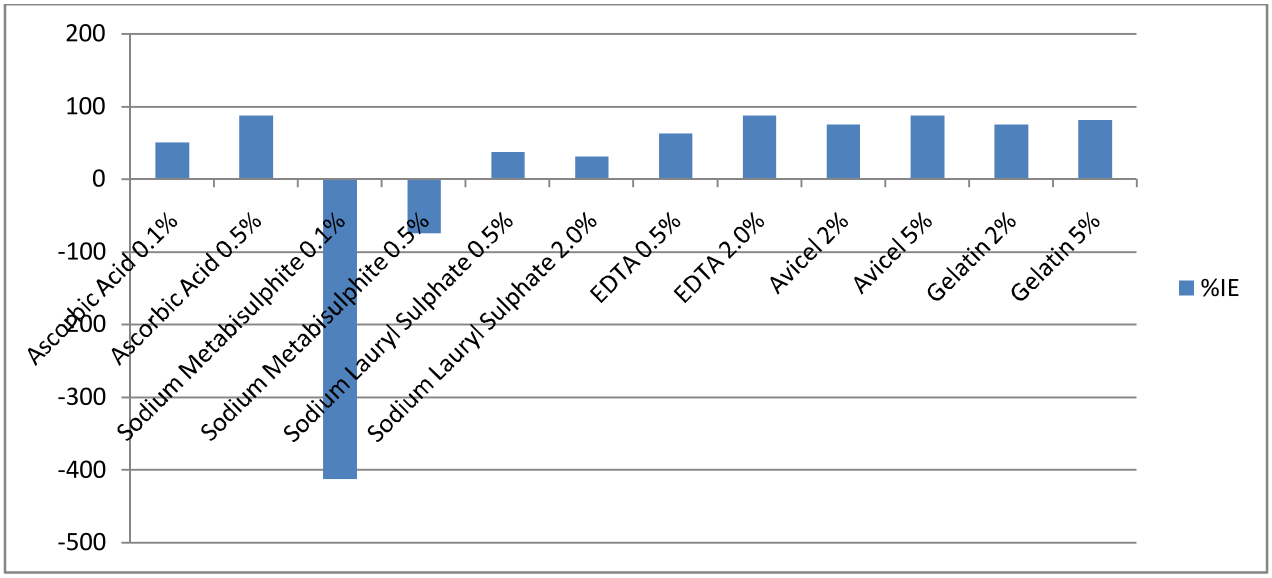
Table 8. Table of Inhibitors in 0.01N NaCl

Excipient	$\varphi W_{inh}(g/9cm^2)$	$\varphi W_{free}(g/9cm^2)$	%IE
Ascorbic Acid 0.1%	0.0007	0.0054	87
Ascorbic Acid 0.5%	0.0002	0.0054	96.2
Sodium Metabisulphite 0.1%	0.014	0.0054	-159.2
Sodium Metabisulphite 0.5%	0.0184	0.0054	-240.7
Sodium Lauryl Sulphate 0.5%	0.0022	0.0054	59.2
Sodium Lauryl Sulphate 2.0%	0.0019	0.0054	64.8
EDTA 0.5%	0.0015	0.0054	72.2
EDTA 2.0%	0.0006	0.0054	88.8
Avicel 2%	0.0019	0.0054	64.8
Avicel 5%	0.0011	0.0054	79.6
Gelatin 2%	0.0012	0.0054	77.7
Gelatin 5%	0.0008	0.0054	85.1

In this experiment, Ascorbic Acid 0.5%, EDTA 2%, Ascorbic Acid 0.1%, Gelatin 5%, Avicel 5%, Gelatin 2%, EDTA 0.5%, Sodium Lauryl Sulphate 2%, Avicel 2% and Sodium Lauryl Sulphate 0.2% % (In order of decreasing percentage corrosion inhibitor efficiency) showed varying degrees of corrosion inhibition activity of tin plated steel in chloride media of 0.01 NaCl.

above excipients was accompanied by an increase in
cy.

Figure 18. Graph of % IE of Pharmaceutical Excipients in 0.01N NaCl



Sodium Metabisulphite (0.1% and 0.5%) enhanced corrosion of tin plated steel in chloride ion media of 0.01N NaCl.

4.9 Pharmaceutical excipients as corrosion inhibitors in 0.1N NaCl

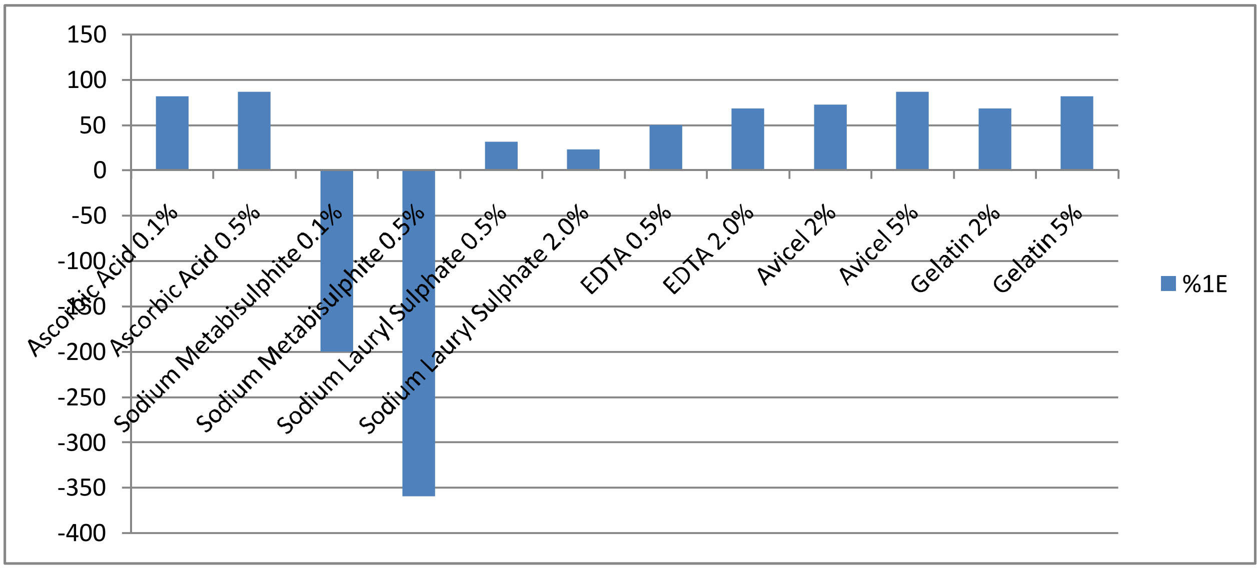
Table 9 and figure 19 show inhibition efficiencies of various concentrations of pharmaceutical excipients obtained from weight loss measurements in 0.1N NaCl and a graphical representation of inhibition efficiencies of the same respectively.

In this experiment, Avicel 5%, Ascorbic Acid 0.5%, Gelatin 5%, Ascorbic Acid 0.1%, Avicel 2%, Gelatin 2%, EDTA 2%, EDTA 0.5%, Sodium Lauryl Sulphate 0.5% and Sodium Lauryl Sulphate 2% (In order of decreasing percentage corrosion inhibitor efficiency) showed varying degrees of corrosion inhibition activity of tin plated steel in chloride media of 0.1 NaCl.

Cl

Excipient	φW_{inh}(g/9cm^2)	φW_{free}(g/9cm^2)	%IE
Ascorbic Acid 0.1%	0.0004	0.0022	81.8
Ascorbic Acid 0.5%	0.0003	0.0022	86.3
Sodium Metabisulphite 0.1%	0.0066	0.0022	-200
Sodium Metabisulphite 0.5%	0.0101	0.0022	-359
Sodium Lauryl Sulphate 0.5%	0.0015	0.0022	31.8
Sodium Lauryl Sulphate 2.0%	0.0017	0.0022	22.7
EDTA 0.5%	0.0011	0.0022	50
EDTA 2.0%	0.0007	0.0022	68.1
Avicel 2%	0.0006	0.0022	72.7
Avicel 5%	0.0003	0.0022	86.3
Gelatin 2%	0.0007	0.0022	68.1
Gelatin 5%	0.0004	0.0022	81.8

Figure 19. Graph of % IE of Pharmaceutical Excipients in 0.1N NaCl



An increase in concentration of the above excipients, with the exception of Sodium Lauryl Sulphate, was accompanied by an increase in percentage corrosion inhibition efficiency.

%) enhanced corrosion of tin plated steel in chloride ion

4.10 Pharmaceutical excipients as corrosion inhibitors in 1N NaCl

Table 10 and figure 20 show inhibition efficiencies of various concentrations of pharmaceutical excipients obtained from weight loss measurements in 1N NaCl and a graphical representation of inhibition efficiencies of the same respectively.

Table 10. Table of Inhibitors in 1N NaCl

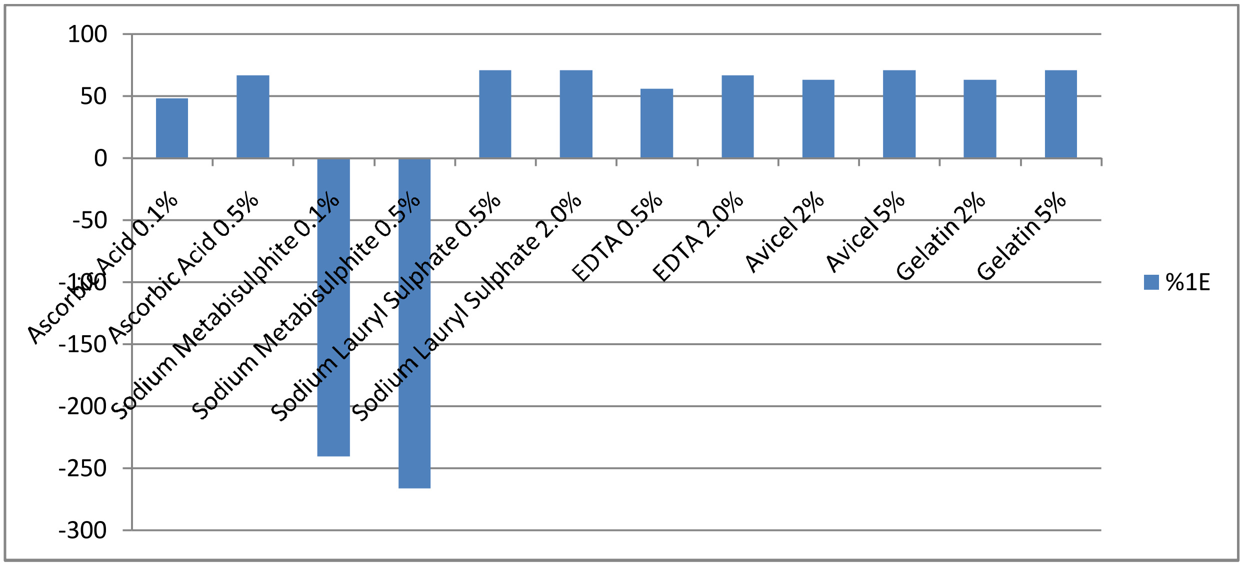
Excipient	$\varphi W_{inh}(g/9cm^2)$	$\varphi W_{free}(g/9cm^2)$	%IE
Ascorbic Acid 0.1%	0.0014	0.0027	48.1
Ascorbic Acid 0.5%	0.0009	0.0027	66.6
Sodium Metabisulphite 0.1%	0.0092	0.0027	-240.7
Sodium Metabisulphite 0.5%	0.0099	0.0027	-266.6
Sodium Lauryl Sulphate 0.5%	0.0008	0.0027	70.3
Sodium Lauryl Sulphate 2.0%	0.0008	0.0027	70.3
EDTA 0.5%	0.0012	0.0027	55.5
EDTA 2.0%	0.0009	0.0027	66.6
Avicel 2%	0.001	0.0027	62.9
Avicel 5%	0.0008	0.0027	70.3
Gelatin 2%	0.001	0.0027	62.9
Gelatin 5%	0.0008	0.0027	70.3

In this experiment, Gelatin 5%, Avicel 5%, Sodium Lauryl Sulphate 2%, Sodium Lauryl Sulphate 0.5%, EDTA 2%, Ascorbic Acid 0.5%, Gelatin 2%, Avicel 2%, EDTA 0.5% and Ascorbic Acid 0.1% (In order of decreasing percentage corrosion inhibitor efficiency) showed varying degrees of corrosion inhibition activity of tin plated steel in chloride media of 1 NaCl.

ve excipients was accompanied by an increase in

cy.

Figure 20. Graph of % IE of Pharmaceutical Excipients in 1N NaCl



Sodium Metabisulphite (0.1% and 0.5%) enhanced corrosion of tin plated steel in chloride ion media of 1N NaCl.

4.11 Discussion

Substitution of distilled water as the vehicle of formulation with Isopropyl alcohol (IPA) and Ethanol at concentrations of 20% and 50% for each resulted in substantial corrosion inhibition. The results obtained indicate that IPA is slightly more effective at both 20% and 50% concentrations as compared to ethanol at the same concentrations.

Ethanol and isopropyl alcohol are organic solvents that are soluble in water. These alcohols contain R-0H group. The presence of this group causes an increase in electron density of the metal at the point of attachment. This retards anodic and cathodic reactions because electrons are consumed at the cathode and furnished at the anode. The probable mechanism of action of e: adsorption of molecules or ions to anodic or cathodic ic overvoltage and formation of a protective barrier film (56). The use of solvents as corrosion inhibitors is popular in petroleum and automobile industries. Most formulations are however patented. Examples of such formulations include: Rustilo 4135HF, Rustilo DW4130 (both from Exxon Mobil), Cimguard 9C and Cimguard 10 (both from Cimcool Fluid Technology Company).

In alkaline media (0.01N NaOH, 0.1N NaOH and 1N NaOH), the inclusion of ascorbic acid (0.1% and 0.5%), EDTA (0.5% and 2%) Avicel (2% and 5%) and gelatin (2% and 5%) in test media resulted in corrosion inhibition at varying degrees with the best corrosion inhibitor being EDTA 2%. An increase in the concentration of these excipients resulted in increased corrosion inhibition efficiency. Sodium Lauryl Sulphate (0.5% and 2%) and sodium Metabisulphite (0.1% and 0.5%) showed little inhibitor efficiency and mostly facilitated corrosion.

Ascorbic acid and Sodium Metabisulphite are reducing agents. When incorporated into a formulation they are more readily oxidized than the contents of the formulation. They offer protection until they are used up. They act by blocking auto-oxidation which can result in many reactions amongst them corrosion. The typical pharmaceutical concentration for use as antioxidants is 0.01% - 0.5% (57). The use of ascorbic acid (0.1% and 0.5%) resulted in good corrosion inhibition efficiencies in alkaline media (0.01N NaOH, 0.1N NaOH and 1N NaOH). Sodium Metabisulphite (0.1% and 0.5%) despite being an antioxidant resulted in an increase in the rate of corrosion when compared with plain alkaline media at concentrations of 0.01N NaOH, 0.1N NaOH and 1N NaOH. The use of antioxidants as corrosion inhibitors is an approach studied to great detail in the automobile and petroleum industry. An increase in antioxidant activity has been associated with an increase in corrosion inhibition activity in various studies within petroleum industry (55).

EDTA is an aminopolycarboxylic acid. Aminopolycarboxylic acids are compounds which contain one or more nitrogen atoms connected through carbon atoms to two or more carboxyl groups. Their ionized forms form strong complexes (chelates) with metal ions. This property is very important and is the basis of their role as chelating agents in chemical, medical and environmental applications. The typical pharmaceutical concentration for use for EDTA is 0.01% to 2%. The use EDTA in alkaline media (0.01N NaOH, 0.1N NaOH and 1N NaOH) tion of tin plated steel in alkaline media. An increase in d in an increase in inhibition efficiency. Previous studies indicate that compounds containing COOH group have been found to contain corrosion inhibition properties. Other studies have also revealed that aminopolycarboxylic acids such as diethylenetriaminepentaacetic acid, polyacrylic acid and polymethacrylic acid have been found to be good inhibitors for metal corrosion (56).

Avicel, gelatin and other semi synthetic celluloses have been used as thickeners and or suspending agents in formulation of suspension. The concentration to be used depends on the type of suspension under formulation and the desired final viscosity profile of the suspension. The use of Avicel (2% and 5%) and Gelatin (2% and 5%) in alkaline media (0.01N NaOH, 0.1N NaOH and 1N NaOH) resulted in corrosion inhibition activity. An increase in concentration from 2% to 5% for both Avicel and Gelatin resulted in an increase in inhibition efficiencies. The mode of action of polysaccharides as corrosion inhibitors has been studied to some detail. Most polysaccharides are adsorbed onto the metal surface by displacing water molecules on the surface and forming a compact barrier. If lone pairs and π electrons are available in the inhibitor molecules, electron transfer from the inhibitor to the metal is facilitated. The presence of functional groups such as COOH, R-OH, NH_2 and NO_2 leads to increased electron density in metal at the point of attachment to the metal thereby retarding cathodic or anodic reactions. Corrosion inhibition is thought to be due to the following reasons: adsorption of molecules or ions to anodic or cathodic sites, increase in cathodic and/or anodic over voltages and the formation of a protective barrier film. Naturally occurring polymers are also thought to form complexes with metal ions and on metal surfaces. These complexes occupy large surface are thereby blanketing the metal surface and protecting the metal from corrosive agents in solution. The inhibitive power of natural polymers is related structurally to cyclic rings and presence of heteroatoms (oxygen and nitrogen) which are major active centres of adsorption. Many naturally occurring polymers have been studied for corrosion inhibition activity. Gum Arabic is a potential corrosion inhibitor for aluminium in alkaline solutions. Exudates from *D. edulis* are corrosion inhibitors for aluminium in acidic solutions. Guar gum has also been shown to be a mixed type corrosion inhibitor for steel.

surfactant. Its use in alkaline media (0.01N NaOH, 0.1N mal corrosion inhibition activity. Anionic surfactants are thought to act as corrosion inhibitors through adsorption of surfactant functional group onto the metal surface. The ability of an anionic surfactant to adsorb is generally related to its ability to aggregate and form micelles. Upon adsorption onto the metal surface, a protective layer is formed. This layer prevents or reduces corrosion of the metal (51). Anionic surfactants as corrosion inhibitors for metals have been studied to some detail. Sodium octylsulphate, sodium decylsulphate, sodium dodecylsulphate, sodium hexadecylsulphate and dodecyl benzene sulphonate have been shown to be effective as corrosion inhibitors for aluminium in acidic media (59).

In acidic media (0.01M H_2SO_4, 0.1M H_2SO_4 and 1M H_2SO_4), inclusion of ascorbic acid (0.1% and 0.5%), EDTA (0.5% and 2%) Avicel (2% and 5%) and gelatin (2% and 5%) in test media resulted in corrosion inhibition at varying degrees. An increase in concentration of the above excipients resulted in an increase in inhibition efficiency. Sodium Lauryl Sulphate showed little activity (below 50% IE) while sodium Metabisulphite facilitated corrosion in acidic media.

In chloride solution (0.01N NaCl, 0.1N NaCl and 1N NaCl), inclusion of ascorbic acid (0.1% and 0.5%), EDTA (0.5% and 2%) Avicel (2% and 5%) and gelatin (2% and 5%) in test media resulted in corrosion inhibition at varying degrees. Sodium Lauryl Sulphate showed lower inhibition efficiency as compared to the above four excipients. The use of sodium Metabisulphite resulted in an increase in corrosion rate.

4.12 Conclusion

EDTA, Avicel, Gelatin and Ascorbic acid can be incorporated in acidic formulations, alkaline formulations or formulations containing chloride ions packed in tin plated steel. The experiments done in this study show that these pharmaceutical excipients have good corrosion inhibition use were found to be EDTA 0.5%, Avicel 5%, Gelatin

Substitution of distilled water with ethanol or Isopropyl alcohol as vehicle for formulation, where possible, is also a good strategy in inhibition of corrosion of tin plated steel. A concentration of 50% isopropyl alcohol provides the best corrosion inhibition activity. In cases where Isopropyl alcohol cannot be used, 50% ethanol is also a good alternative.

Sodium Metabisulphite should be avoided in formulations containing acid, basic or chloride ions that are to be packed in tin plated steel. The experiments done reveal that its incorporation in acidic basic or chloride containing formulations at concentrations of 0.1% and 0.5% results in an increase in corrosion rate of tin plated steel.

Sodium Lauryl Sulphate is of minimal value as a corrosion inhibitor for tin plated steel. The value of inhibition efficiencies obtained from concentrations of 0.5% and 2% did not reveal any significant corrosion inhibition activity.

4.13 Recommendation

Combinations of EDTA, Avicel, Gelatin and Ascorbic acid should be tested for synergistic corrosion inhibition activity of tin plated steel in acidic, basic and chloride systems .These combinations may also be tested in systems containing mixtures of acidic, basic and chloride ions.

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