STUDIES ON THE CORROSION INHIBITION BEHAVIOR OF SOME POLYMER SURFACTANTS ADDITIVES

ABSTRACT
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THESIS

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ABSTRACT

As a consequence of the industry’s motivation to achieve improved efficiency and enhanced performance, engineering components are required to operate in environments, which are becoming increasingly severe. The critical industrial components are, therefore, being degraded more aggressively due to surface environment interactions referred to as corrosion. Corrosion is an undesirable phenomenon which destroys the lustre and beauty of the metallic objects and shortens their life. Among the metals, mild steel is the most extensively investigated metals for corrosion studies due to its wide application in different corrosive environments. It is subjected to excessive corrosion attack when exposed to service in aqueous acidic environments. Acid solutions are widely used in various industries, the most important area being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. These processes are generally carried out at temperature up to 60°C. Since the acids solutions are quite aggressive and may lead to the corrosion of the contacting metals if used as such, inhibitors are often used in these processes to control the corrosion of metals. Most of the efficient pickling inhibitors are organic compounds containing hetero atoms such as sulphur, nitrogen, oxygen, phosphorus, and multiple bonds or aromatic rings in their structures. However, most of the organic compounds used as corrosion inhibitors are toxic and hazardous to both human beings and the environment and needs to be replaced by non-toxic, environment friendly compounds. As a result, the current research trend is towards the development of non-toxic, economical and more environmentally safe green chemicals as corrosion inhibitors. Naturally occurring substances of both plants and animal origin otherwise tagged ‘green inhibitors’ are known to meet these requirements. In the past two
decade, the research in the field of "green" or "eco-friendly" corrosion inhibitors has been directed towards the goal of using cheap, effective compounds at low or "zero" negative environmental impact. However, though the number of investigations on corrosion inhibitors has dramatically increased, only 5% of the literature published during the last decade concerns green inhibitors.

The use of polymers as corrosion inhibitors has gained wide acceptance in recent times. It has been shown by a number of investigators that some water soluble polymers and their derivatives can act as corrosion inhibitors, which has generated an increasing interest in these compounds. The polymers have been found to be attractive as corrosion inhibitors as they are cost effective, inherently stable, and non-toxic. They have been reported to exhibit superior corrosion inhibition properties in contrast to simple organic molecules. This is because of the fact that they possess long chain carbon linkage and multiple adsorption sites and thus block large surface area of the corroding metal, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution. The polymers provide two advantages namely (i) a single polymeric chain displaces many water molecules from the metal surface thus making the process entropically favorable and (ii) the presence of multiple bonding sites makes the desorption of polymers a slower process. The application of water-soluble polymers having functional groups (-OH, -COOH, -NH₂, etc.) have been reported as corrosion inhibitors in different aggressive media. The polymers through their functional groups form complexes with metal ions. On the metal surface these complexes occupy a large surface area thereby blanketing the surface and protecting the metal from corrosion. The inhibitive power of these polymers is related structurally to the cyclic rings, heteroatom (oxygen and nitrogen), which are the major
active centres of adsorption. Larger corrosion inhibition efficiencies that are observed using various polymers are due to the larger molecular size which ensures greater coverage of the metallic surface.

Surfactants, which have a remarkable ability of influencing the surfaces and interfaces, have shown a significant role in the inhibition of acid corrosion of mild steel. In aqueous solutions the inhibitory action of surfactant molecules may be due to the physiosorption (electrostatic) or chemisorption onto the metallic surface, depending on the charge of the solid surface. The degree of their adsorption on metal surfaces depend on the nature of the metal, the mode of adsorption, chemical structure of the surfactant, the metal surface condition, and the type of corrosion media. The corrosion inhibition by surfactant molecules is related to the surfactant’s ability to aggregate at interfaces and in solution. The effectiveness of surfactant as corrosion inhibitor can be studied on the basis of their micellar properties in a particular medium. The adsorbed molecules form monolayer or bilayer hemimicelles or admicelles, depending upon the surfactant concentration and prevent the acid to attack the surface, and thus reduce the corrosion attack. Surfactants have been used as corrosion inhibitors either alone or in combination with other compounds to improve their performance as inhibitors.

Synergism is an important effect in corrosion inhibition process and serves as basis for modern corrosion inhibiting formulations. Synergism of corrosion inhibitors is either due to interaction between constituents of the inhibitor or due to interaction between the inhibitor and one of the ions present in aqueous solution. A survey of literature indicates that the addition of halide ions to the polymers can synergistically improve their corrosion inhibition efficiency. However, corrosion inhibition effect of
polymers in presence of surfactants perhaps has yet not been reported. Polymers are likely to interact with the surfactants to form complex structure and help to adhere to mild surface and thus offer greater resistance to corrosion.

The work presented in this thesis deals with the corrosion inhibition behavior of different polymers (both natural and synthetic) separately and in combination with very low concentration of the anionic and cationic surfactants on mild steel in 0.1M H₂SO₄ solutions. The aim of the surfactants addition was to improve the corrosion inhibition behavior of environment friendly polymers as corrosion inhibitor for mild steel corrosion in acidic medium. The concentration of surfactants was intentionally kept low so that the green nature of polymers is least influenced. The natural polymers considered for the investigations are starch (polysaccharides) and gum acacia (GA) whereas synthetic polymers considered for investigation are polyvinyl alcohol (PVA) and polyethylene glycol (PEG). The surfactants subjected to investigation include both anionic and cationic surfactants. The anionic surfactants include: sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) whereas the cationic surfactants include: cetyltrimethyl ammonium bromide (CTAB) and cetyl pyridinium chloride (CPC). The techniques used are weight loss measurements, solution analysis of metal ions, potentiodynamic polarization measurements, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), atomic force microscopy (AFM) and thermodynamic/kinetic parameters. The break up of the work contained in various chapters is as follows:
Chapter I

This chapter deals with the general introduction. The general introduction briefly describes the fundamentals of corrosion which includes the definition of corrosion and its importance, cost of corrosion, corrosion reactions, corrosion measurement methods, types of corrosion and method of corrosion control. It presents an exhaustive literature survey exploiting green compounds including natural and synthetic polymers as corrosion inhibitor for mild steel in acid solutions. Except for some early pioneering research papers, the thesis include literature survey from the selected research papers, reviews and reports published on the subject during the last three decades. Special emphasis has been laid to the work which has direct or indirect bearing on the studies presented in this thesis. It might be possible that some results of the important studies have been left unquoted quite inadvertently, yet there was absolutely no intension to undermine those works.

Chapter II

This chapter deals with the experimental details which includes the materials and methods used during the experimental work. The details of corrosion tests which have been undertaken to investigate the inhibition behavior of polymers and surfactant additives have also been explained in this chapter.

Chapter III

The corrosion inhibition of mild steel in 0.1M H₂SO₄ in presence of starch (polysaccharide) was studied using weight loss and potentiodynamic polarization measurements in the temperature range of 30-60°C. Starch inhibits the corrosion rates
of mild steel to a considerable extent; the maximum inhibition efficiency (%IE) being 66.21% at 30°C in presence of starch concentration of 200 ppm. The IE increases with increasing inhibitor concentration but decreases with increasing temperature. The inhibition of mild steel corrosion in the presence of starch could be attributed to the adsorption of the compound on to mild steel surface, which blocks the metal and thus do not permit the corrosion process to take place. Starch can be adsorbed by the interaction between the lone pair of electrons of the oxygen atom and the steel surface. The presence of d π vacant orbital of low energy in the iron atom, as observed in transition group metals, facilitates the adsorption process. In acid medium starch may be partially hydrolyzed into simpler carbohydrates but the products with higher hydrophilicity than starch is likely to go into the bulk water. Since the hydrolysis is quite slow only negligible starch molecules are expected to hydrolyze and desorbs from the steel surface. Also, the starch in bulk water may occupy the steel surface as the molecules are in dynamic equilibrium. So, even after slow hydrolysis, inhibition by starch is effective. The increased IE with increasing starch concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film. A decrease in IE with increasing temperature suggests possible desorption of some of the adsorbed starch molecules from the metal surface at higher temperatures. This behavior shows that the starch was physically adsorbed on the metal surface.

The effect of the addition of very small concentration of sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) on the corrosion inhibition behavior of starch was also studied. The IE of starch significantly improved in presence of both the surfactants. The effect of surfactants on the corrosion
inhibition behavior of starch appears to be synergistic in nature. Starch alone and in combination with surfactants is found to obey Langmuir adsorption isotherm from the fit of the experimental data of all concentration and temperature studied. Phenomenon of physical adsorption is proposed from the trend of IE with temperature and also the values $E_a$, $\Delta G_{ads}$ and $Q_{ads}$ obtained. The results obtained by potentiodynamic polarization measurements are consistent with the results of the weight loss measurement.

The surface morphology of the mild steel before and after immersion in 0.1M $H_2SO_4$ solution was also examined using scanning electron microscopy (SEM). The results of SEM studies further confirmed the inhibitive character of the starch and starch-surfactant additives.

Chapter IV

The corrosion inhibition behavior of mild steel in 0.1M $H_2SO_4$ in presence of polyvinyl alcohol (PVA) was investigated using weight loss and potentiodynamic polarization measurements in the temperature range of 30-60°C. The inhibition efficiency (IE) increased with increasing PVA concentration showing a maximum IE of 81.41% at 30°C at 100 ppm and decreased with increasing temperature. The inhibition behavior of PVA on mild steel in 0.1M $H_2SO_4$ can be explained in terms of the adsorption of its molecules on the surface of steel. It may interact with the corroding steel and affect the corrosion reaction in more than one way. In the acidic medium the PVA can be easily protonated at the OH group and could interact with the corroding steel surface via protonated OH, which can be adsorbed at the cathodic sites and hinder the hydrogen evolution reaction. The oxygen atom carrying two lone pair
of electrons could also be adsorbed on the anodic sites of the steel surface and retard the iron electro dissolution. Therefore, PVA is expected to involve both physical and chemical adsorption. However, the variation in the values of %IE with temperature in presence of PVA compared to blank suggested dominant role of physisorption in the adsorption process. When the surface of steel is saturated with PVA molecules, the further increase in PVA concentration causes desorption from the steel surface and does not significantly affect the corrosion rate.

The inhibiting action of PVA is synergistically enhanced on addition of very small amount of surfactants sodium dodecyl sulphate (SDS) and cetyl pyridinium chloride (CPC). The adsorption of PVA alone or in combination with surfactants on the metal surface is found to obey Langmuir adsorption isotherm from the fit of the experimental data of all concentrations and temperatures studied. Synergism parameter evaluated is found to be greater than unity indicating that the enhanced IE of PVA caused by addition of surfactants is only due to synergism. Phenomenon of physical adsorption is proposed from the trend of the IE with temperature and also values of $E_{a}$, $\Delta H_{ads}$ and $\Delta G_{ads}$ obtained. Thermodynamic parameters reveal that the adsorption process is spontaneous. The results obtained by weight loss measurements are consistent with the results of the potentiodynamic polarization measurements.

The surface morphology of the corroded steel samples in presence and absence of inhibitors was also evaluated using scanning electron microscopy (SEM). In uninhibited acid solution a damaged and heterogeneous surface is observed. The surface heterogeneity is considerably decreased in the presence of PVA inhibited acid solution which is further decreased in presence of surfactant additives. SEM studies further confirm the inhibitive character of the additives.
Chapter V

The adsorption and corrosion inhibition effect of gum acacia (GA) alone and in presence of surfactants sodium dodecyl benzene sulphonate (SDBS) and cetyltrimethyl ammonium bromide (CTAB) on mild steel in 0.1M H$_2$SO$_4$ in temperature range of 30-60°C was investigated using weight loss method, chemical analysis of solution, scanning electron microscopy (SEM), atomic force microscopy (AFM) and determination of thermodynamic/kinetic parameters. The corrosion rates are reduced in presence of GA, and GA-surfactants mixture as compared to the free acid solution. Also the corrosion rate increased with increase in temperature at all concentrations studied. The inhibiting action of GA is synergistically enhanced on addition of small amount of surfactants. The corrosion rate and IE of mild steel was also investigated from determination of total iron ions (Fe$^{2+}$/Fe$^{3+}$) entered in the solution during time period for which reaction is carried. The %IE as obtained by chemical analysis of solution is highly consistent with %IE obtained by weight loss measurements.

The inhibition of mild steel corrosion by GA can be explained in terms of its adsorption on the steel surface. The adsorption of GA on mild steel surface makes a barrier for mass and charge transfer and consequently, mild steel is protected from aggressive anions of acid. GA is a complex mixture of arabinogalactan, oligosaccharides, polysaccharides and glycoproteins. This is suggestive of the fact that GA contains constituents which contain active adsorption sites in the form of hetero atoms such as oxygen and nitrogen. However, owing to the complex chemical composition of GA, it is quite difficult to assign the inhibitive effect to a particular constituent. Further, in acidic solution some of the constituents of GA (eg.
Glycoproteins) may exist in protonated form and could be electrostatically attracted to the cathodic sites on steel surface, thereby decreasing the hydrogen evolution reaction and indicating physical adsorption. The increased IE with increasing GA concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film. A decrease in IE with increasing temperature suggests possible desorption of some of the adsorbed GA molecules from the metal surface at higher temperatures. This behavior shows that the GA was physically adsorbed on the metal surface.

Surface photographs were obtained by means of SEM and AFM so as to determine if the mild steel corrosion inhibition is due to the formation of a protective film by adsorption of inhibitor. SEM and AFM results confirmed the existence of an adsorbed protective film on the mild steel surface. Thermodynamic parameters reveal that adsorption process is spontaneous and obey Freundlich adsorption isotherm.

Chapter VI

This chapter presents the results of the investigation concerning with the corrosion inhibition behavior of polyethylene glycol (PEG) and surfactants (SDBS and CTAB) additives on mild steel corrosion in 0.1M H₂SO₄ in the temperature range of 30-60°C. The corrosion performance of the additives was investigated by weight loss measurements, solution analysis of iron ions, scanning electron spectroscopy (SEM), energy dispersive X-ray analysis (EDAX) and atomic force microscopy (AFM) techniques.

PEG effectively inhibits the corrosion rate of mild steel in 0.1M H₂SO₄. The inhibition efficiency (IE) increased with increasing PEG concentration showing a
maximum IE of 86.91% at 30°C at 25 ppm and decreased with increasing temperature. The further increase in inhibitor concentration does not significantly affect the IE. The IE of mild steel was also investigated from determination of total iron ions (Fe$^{2+}$/Fe$^{3+}$) entered in the solution during time period for which reaction is carried. The %IE was also as obtained by determination of total iron ions (Fe$^{2+}$/Fe$^{3+}$) entered in the solution; the values are highly consistent with %IE obtained by weight loss measurements.

The corrosion inhibition by PEG is attributed to the presence of heteroatom oxygen in the inhibitor molecules and can be explained in terms of its adsorption on the steel surface through the lone pairs of electrons present on the oxygen atom. The hydroxyl group of polyethylene glycol could act as bridge between the polymer and the surface of metal and result in an inhibiting effect in acidic solution. The adsorption of PEG is assumed to be a quasi-substitution process between water molecules on the steel surface and the PEG molecules. The adsorption of PEG on mild steel surface makes a barrier for mass and charge transfer and consequently, mild steel is protected from aggressive anions of acid. Further, in acidic solution PEG may exist in protonated form and could be electrostatically attracted to the cathodic sites on steel surface, thereby decreasing the hydrogen evolution reaction and indicating physical adsorption. SEM, EDAX and AFM studies adequately confirmed the inhibitive character of the PEG and PEG-surfactant additives.
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2012
Dedicated To
My Beloved Parents
Certificate

This is to certify that the Ph.D. thesis entitled "Studies on the Corrosion Inhibition Behaviour of some Polymer Surfactants Additives" which has been submitted by Mr. Mohammad Alam Khan contains an original piece of research. The entire work has been carried out under my supervision and it has not been submitted elsewhere for the award of a degree or a diploma.

Professor Mohammad Mobin
(Supervisor)
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I dedicate this work to my beloved parents, my sister, my brothers and relatives whose sincere praying, encouragement for their invaluable help and great patience was my true support during my study.

Mohammad Alam Khan
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Chapter 1

General Introduction
1. GENERAL INTRODUCTION

1.1 Introduction

The word corrosion, commonly known as rust, refers to the destructive attack of a metal by chemical or electrochemical reactions with the environment. Corrosion is an undesirable phenomenon which destroys the luster and beauty of the metallic objects and shortens their life. Since ancient times corrosion has affected not only the quality of daily lives of people, but also their technical progress. Corrosion can be defined as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties. The European standard [1] defines the term corrosion as “physiochemical interaction between a metal and its environment that results in changes in the properties of the metal, and which may lead to significant impairment of the function of the metal, the environment, or the technical system, of which these form a part”. Up to the 1960s, the term corrosion was restricted only to metals and their alloys and it did not incorporate ceramics, polymers, composites and semiconductors in its regime. The term corrosion now encompasses all types of natural and man-made materials including biomaterials and nanomaterials and it is not confined to metals and alloys alone. This fact was taken into account and a broader and widely accepted definition of corrosion was suggested [2-4]. The general definition of corrosion refers corrosion as “an irreversible interfacial reaction of a material (metal, ceramic, and polymer) with its environment which results in consumption of the material or in 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.
Exclusively physical or mechanical processes such as melting or evaporation, abrasion or mechanical fracture are not included in the term corrosion. The scope of corrosion is consistent with the revolutionary changes in materials development witnessed in recent years.

Corrosion is a natural process. All natural processes tend to return toward the lowest possible energy states. For example, iron and steel have a natural tendency to combine with other chemical elements to return to their lowest energy states. Thus iron and steel frequently combine with oxygen and water to form hydrated iron oxides (rust), similar in chemical composition to the original iron ore. The energy required to convert iron ore to metallic iron is returned when the iron corrodes to form the same compound. Only the state of energy change is different. The driving force for all corrosion is the lowering of a system’s Gibbs free energy. The production of almost all metals involves adding energy to the system. As a result the metal has a strong driving force to return to its native, low energy oxide state. The return of the metals to the native oxide state is termed as corrosion.

The subject of corrosion has undergone an irreversible transformation from a state of isolated and obscurity to a recognized discipline of engineering. Corrosion is now considered as an essential component of design. Learned societies like National Association of Corrosion Engineers, European Federation of Corrosion, Japan Society of Corrosion Engineers and others are playing leading role in the development of corrosion engineering education.
1.2 Cost of Corrosion

The corrosion problems are quite costly and as a result each year industries are paying huge price for corrosion and that cost is continuously rising. In recent years many papers and documents have appeared about the cost of corrosion. The first comprehensive landmark study on losses due to metallic corrosion was carried out in USA in late seventies. According to the study the total cost of corrosion for the year 1975 was estimated to be 70 billion US dollars, which is approximately 5% of the Gross National Product for that year [5]. The cost of corrosion, 70 billion US dollars was divided into avoidable costs (costs which may be reduced by the application of available corrosion control practices) and unavoidable costs (costs which require advances in new materials and in corrosion technology and control). The total avoidable costs were estimated to be about 15% that of total cost of 70 billion dollars. In another study on the cost of corrosion conducted in the US the annual direct cost of corrosion was found to be staggering at $ 276 billion which is approximately 3.1% of the nation’s GDP [6]. The study was conducted jointly by C.C. Technologies Inc., USA [7], Federal Highway Agencies (FHWA), USA [8] and National Association of Corrosion Engineers [9]. According to the above study on the cost of corrosion, the indirect cost of corrosion was conservatively estimated to be equal to or greater than the direct cost. If the indirect cost is also 3.1% of DGP, then the total cost of corrosion is 936.2 billion US dollars. Thus the total cost of corrosion (6.2% of GDP) will be more than 1 Trillion dollars by the end of 2012.

The cost of corrosion differs from country to country. At 6.2% of GDP, corrosion is one of the largest single expenses in the US economy yet it rarely receives the attention it requires. Corrosion costs money and lives, resulting in
dangerous failures and increased charges for everything from utilities to transportation and more. In USA, the transportation sector is the largest sector contributing to corrosion after public utilities, whereas in the oil producing countries, such as the Arabian Gulf countries. petroleum and petrochemical industries are the largest contributor to corrosion expenditure. The storage of defense equipment is a serious matter for countries with corrosive environments, such as Saudi Arabia, Malaysia and South-East Asia. Humidity is the biggest destroyer of defense hardware. Storage of defense equipment demands minimum humidity, scanty rainfall, alkaline soil, no dust storms, no marine environment and minimal dust particles.

1.3 Corrosion Reactions

Most of the corrosion reaction is the sum of two complementary electrode processes or half reactions; anodic process (oxidation reaction) and cathodic process (reduction reaction). The anodic process involves the oxidation of the metallic material, making electrons available in the metallic phase. The positively charged metal atoms detach from the metal surface and enter into the solution or electrolyte as ions. The cathodic process consumes the electron made available by the anodic process, through a reduction reaction. When a metal corrodes in solution, the two halves of the reaction can be separated by large distances. This is unlike oxidation in air, where the reaction sites are always close to each other. In aqueous solution the reaction separation is large and there is both electronic and electrolytic contact between the anodic and cathodic sites.
1.3.1 Anodic reactions

The anodic reaction involves the oxidation of a metal to its ion because of the electric charge difference at the solid-liquid interface. The metal loss at anodic sites occurs as the metal atoms give up one or more electrons and move into the electrolytes as positively charged ions. The generic anodic process of a metal can be represented by the oxidation reaction of a metal to its ions which passes into solution:

\[ M \leftrightarrow M^{z+} + e^- \]  
(1.1)

where \( z \) is the valence of metal, \( e^- \) indicates the electron, \( M \) the generic metallic material and \( M^{z+} \) its ion which passes into the solution. In cases where the metallic material tends to form hydroxides, the anodic reaction is of the following type:

\[ M + zH_2O \leftrightarrow M(OH)_z + zH^+ + ze^- \]  
(1.2)

1.3.2 Cathodic reactions

The electrons that are produced at anodic sites are consumed at cathodic sites. The generic cathodic reaction can be represented by the following reaction:

\[ R^+ + e^- \rightarrow R_0 \]  
(1.3)

where \( R^+ \) is a positive ion in solution, \( e^- \) is an electron in the metal and \( R_0 \) is the reduced chemical species. Several different cathodic reactions are possible and the one that occurs is determined by the environment. The possible cathodic reactions are as follows:
1.3.2.1 Acidic environment

Hydrogen evolution or oxygen reduction with the formation of water is likely to occur in acid media. In the absence of oxygen, hydrogen ions are reduced by the excess of electrons and evolve as molecular hydrogen. However, in presence of oxygen, oxygen reduction forming water is the dominant reaction.

\[ 2H^+ + 2e^- \rightarrow H_2 \]  
(1.4)

\[ \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \]  
(1.5)

1.3.2.2 Neutral or alkaline environment

In presence of oxygen, reduction of oxygen with the formation of hydroxyl ions is more dominant reaction. In absence of oxygen water is reduced forming hydrogen gas.

\[ \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \]  
(1.6)

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  
(1.7)

1.3.2.3 Metal ion reduction

Metal ion reduction and metal deposition are less common reactions and are most frequently found in chemical process streams [14]

\[ M^{3+} + e^- \rightarrow M^{2+} \]  
(1.8)

\[ M^{+} + e^- \rightarrow M \]  
(1.9)
1.4 Forms of Corrosion

It is convenient to classify corrosion by the forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. Each form can be identified by mere visual observation with either the naked eye in most cases or magnification sometimes.

1.4.1 Uniform or general corrosion

It is the most common form of corrosion which proceeds uniformly over the entire exposed area by a chemical or electrochemical reaction. This type of corrosion though represents only a small fraction of industrial corrosion failures but the total tonnage wasted is generally regarded as the highest of all forms. Uniform corrosion is characterized by the lack of any significant non-uniform attack such as pitting or crevice corrosion. The rate of attack is measurable by relatively simple tests and the life of equipment can be accurately estimated with confidence. On a polished surface, this type of corrosion is first seen as a general dulling of the surface and, if it continues, the surface becomes rough and possibly frosted in appearance. Uniform corrosion occurs when there are local anodic and cathodic sites on the surface of the metal. Due to polarization effects, these locations shift from time to time and a given area on a metal will act both as an anode and a cathode over any extended period of time. Rusting of steel in the atmosphere and the corrosion of copper alloys in seawater are common examples where uniform corrosion is usually encountered. Uniform corrosion is usually controlled by selecting suitable materials, chemical-resistant protective coatings, cathodic and anodic protection, and corrosion inhibitors. In uniform corrosion, the metal loss occurs at essentially the same rate over the entire
metal surface. Weight loss is the most commonly used method of measuring the corrosion rate of metals when uniform corrosion occurs. In this method, a test sample is cleaned, weighed, and its surface area is measured. It is then exposed for specific period of time, re-cleaned and re-weighed. The amount of metal loss as measured by the weight loss is used to calculate the loss in thickness of the metal assuming that the corrosion was absolutely uniform. These results are commonly expressed in mils per year (mpy).

1.4.2 Galvanic or two-metal corrosion

Galvanic corrosion, also known as dissimilar metal corrosion, involves an electrochemical process in which one metal corrodes preferentially to another when both metals are in electrical contact and immersed in an electrolyte. Dissimilar metals and alloys have different electrode potentials and when two or more come into contact in an electrolyte a galvanic couple is set up. When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would all by itself, while the other becomes the cathode and corrodes slower than it would alone. The potential difference between the dissimilar metals is the driving force for the accelerated attack on the anode member of the galvanic couple. The anode metal dissolves into the electrolyte, and deposition is formed on the cathodic metal. There are three conditions that must exist for galvanic corrosion to occur. First there must be two electrochemically dissimilar metals present. Second, there must be an electrical contact between the two metals. And third, there must be a conductive path for the metal ions to move from the more anodic metal to the more cathodic metal. If any one of these three conditions does not exist, galvanic corrosion will not occur.
There are several ways of reducing or preventing this form of corrosion. One way is to electrically insulate the two metals from each other. Another way is to keep the metals dry or shielded from ionic compounds (salts, acids, bases). Coating the two metals or if it is not possible to coat both then coating the more noble one (metal with higher potential) is another option to prevent galvanic corrosion. It is also possible to choose metals that have similar potentials. Using the same metal for all construction is the most precise way of matching potentials. Electroplating or other plating can also help. This tends to use more noble metals that resist corrosion better. Chrome, niekel, silver and gold can all be used. Corrosion inhibitors such as sodium nitrite or sodium molybdate can be introduced to these systems to reduce the galvanic potential.

1.4.3 Crevice corrosion

Crevice or contact corrosion [10] is the corrosion produced at the region of contact of metals with metals or metals with nonmetals. It also refers to corrosion in occluded regions and is one of the most damaging forms of material degradation [11]. It may occur at washers, under barnacles, at sand grains, under applied protective films etc. This type of corrosion involves an electrochemical oxidation-reduction (redox) process. Crevice corrosion is considered much more dangerous than uniform corrosion since its rate is 10-100 times higher than uniform corrosion. Crevice corrosion is highly accelerated if chloride, sulfate or bromide ions are present in electrolytic solution. Stainless steels, aluminum alloys and other metals forming a passive oxide layers on their surface in electrolytes and atmosphere are sensitive to crevice corrosion. Cleanliness, the proper use of sealants, good fit-up and adhesion of non-metal joints or gaskets and protective coatings are effective means of controlling crevices being formed between the two metals. As a general rule stainless steels such
as the 6% molybdenum austenitic stainless steel and superduplex grades can be expected to give the best crevice corrosion attack resistance.

1.4.4 Pitting corrosion

Pitting is the most detrimental form of corrosion attack and is often responsible for failures of components in process plants [12]. In process plants, it accounts at least 90% of the metal damage by corrosion [13]. Pitting corrosion is a form of extremely localized attack that leads to the formation of small holes in the metal. The pits formed on the metallic surfaces are sometimes isolated or so close together that they look like a rough surface. It is one of the most destructive forms of corrosion. Sometimes pitting corrosion can be quite small on the surface and very large below the surface, which is common on stainless steels and other film-protected metals. The driving force for pitting corrosion is the depassivation of a small area, which becomes anodic while an unknown but potentially vast area becomes cathodic, leading to very localized galvanic corrosion. This kind of corrosion is extremely insidious, as it causes little loss of material with small effect on its surface, while it damages the deep structures of the metal. The pits on the surface are often obscured by corrosion products. Polished surface display higher resistance to pitting. Metals that are susceptible to uniform corrosion in turn do not tend to suffer from pitting. Thus regular carbon steel will corrode uniformly in seawater, while stainless steel will pit. There are many metal/environment combinations that can lead to pitting [14-16]. The pitting resistance of stainless steels can be improved by addition of about 2% of molybdenum. Pitting is most likely to occur in the presence of chloride ions, combined with such depolarizers as oxygen or oxidizing salts. Besides chlorides, other anions implicated in pitting include thiosulfates (S₂O₃²⁻), fluorides and iodides.
Stagnant water conditions favor pitting. Methods that can be used to control pitting include maintaining clean surfaces, application of a protective coating, and use of inhibitors or cathodic protection for immersion services.

### 1.4.5 Intergranular corrosion

Intergranular corrosion also called intercrystalline corrosion is localized attack along the grain boundaries, or immediately adjacent to grain boundaries, while the bulk of the grains remain largely unaffected. It is generally considered to be caused by the segregation of impurities at the grain boundaries or by enrichment or depletion of one of the alloying elements in the grain boundary areas. For example, in certain aluminium alloys small amounts of iron have been shown to segregate at the grain boundaries and cause intergranular corrosion. Also, it has been shown that if the zinc content of a brass is higher at the grain boundaries then it is subjected to such corrosion. In the case of the austenitic stainless steels, when these steels are sensitized by being heated in the temperature range of about 500 to 800°C, depletion of chromium in the grain boundary region occurs, resulting in susceptibility to intergranular corrosion.

The driving force of intergranular corrosion is the difference between the electrode potentials of the grain boundary and the grain itself, which form a galvanic cell in presence of an electrolyte. If the phases segregated at the grain boundaries have lower value of electrode potential, they will oxidize (anodic reaction) and the grain metal having higher value of electrode potential will reduce (cathodic reaction). Thus dissolution of anodic grain boundaries starts from the surface and advances along the grain interfaces; this results in deterioration of the bonding between the grains and
drop of mechanical properties. On the other hand if the precipitates at the grain boundaries have higher electrode potential then the grains will dissolve (anodic reaction) and the grain boundaries will not be attacked.

1.4.6 Selective leaching (Dealloying)

Selective leaching is the removal of an element from an alloy by corrosion. Many alloys are susceptible to selective leaching under certain conditions. The elements that are more resistant to the environment remain behind. The most common example is dezincification. In this case zinc is preferentially leached out of the copper-zinc alloy, leaving behind a copper-rich surface layer that is porous and brittle. The corrosive attack can take place in quite weakly aggressive solutions and is accelerated by increase in temperature and oxygen content. Selective corrosion may occur in a single-phase and in multi-phase alloys.

The potential difference between the alloying elements is the driving force for the preferential attack on the more active element in the alloy. The component having lower value of electrode potential get oxidized and dissolved in the electrolyte whereas the component having higher value of electrode potential get reduced. The common dealloying examples are dezincification as in brasses, desiliconification as in silicon bronze, dealuminification as in aluminium bronze, destannification as in tin bronze, deniclelification as in copper-nickels and graphitic corrosion (leaching of iron) as in grey cast irons.
1.4.7 Erosion-corrosion

Erosion-corrosion is a material’s surface degradation process due to mechanical action initiated by impinging liquid, abrasion by slurry, particles suspended in fast flowing liquid or gas, bubbles or cavitations, etc. This type of corrosion occurs due to the continuous flow of liquid over the metal surface, which removes any protective film or metal oxide from the metal surface. It can occur both in the presence and in the absence of suspended matter in the flow stream. Erosion-corrosion takes the form of grooves, waves, gullies, rounded holes, horseshoe-shaped undercutting in the surface. Undercutting may occur in either upstream or the downstream direction. Some materials are more resistant than other to erosion-corrosion under the same fluid conditions. Erosion-corrosion is most prevalent in soft alloys, such as copper, aluminium and lead alloys. Alloys which form a surface film in a corrosive environment commonly show a limiting velocity above which corrosion rapidly accelerates. Other factors such as turbulence, cavitation, impingement or galvanic effects can add to the severity of attack. Increasing the flow rate of the fluid in cooling application may increase its performance but at the same time it may also increase erosion-corrosion. The rate of corrosion depends upon the flow rate of the fluid. Turbulent flow results in much higher corrosion rates than Laminar flow. The initial stage involves the mechanical removal of a metal’s protective film and then corrosion of bare metal by a flowing corrosive occurs. The process is cyclic until perforation of the component occurs. Erosion-corrosion is usually found at high flow rates around tube blockages, tube inlet ends, or in pump impellers.

Cavitation corrosion is a special form of erosion-corrosion. It is caused by water bubbles produced by a high-speed impeller, which then collapse and cause pits
on the metal surface. Erosion-corrosion can be prevented through streamline the piping to reduce turbulence, control fluid velocity, using more resistant materials and using corrosion inhibitors or cathodic protection.

1.4.8 Stress corrosion cracking (SCC)

Stress corrosion cracking is the growth of cracks induced into the metal from the combined influence of tensile stress and a corrosive environment [17]. The stress may be due to applied loads, residual stresses from the manufacturing process, or a combination of both. Welding, heat treatment, machining and grinding can introduce residual stresses. One of the most important forms of stress corrosion is chloride stress corrosion. This is a type of intergranular corrosion and occurs in austenitic stainless steel under tensile stress in the presence of oxygen, chloride ions, and high temperature. This form of corrosion is controlled by maintaining low chloride ion and oxygen content in the environment and use of low carbon steels. Most common media where stress corrosion cracking occurs are chloride containing solutions, but in other environments, such as caustics and polythionic acid, problems with SCC may also appear.

The mechanism of stress corrosion cracking is not well understood. It has been found that cracks often initiate in trenches or pits on the surface, which can act as stress raisers. It has been shown experimentally that stress corrosion cracking can be stopped by applying cathodic protection, i.e. when corrosion is stopped but the stress conditions remain unchanged. Standard austenitic stainless steels, like AISI 304 and AISI 316, are generally prone to SCC in chloride containing environments at temperatures above 60°C [18, 19].
Hydrogen embrittlement (HE) is sometimes stated to be a kind of SCC. Perhaps most important is that HE cannot be reduced by cathodic protection, but might instead increase under such circumstances. The risk for HE is increased for harder metals, but the tendency to hydrogen cracking decreases with increasing temperature. Cracks may propagate in a transgranular or intergranular fashion or in a combination of the two. Temperature is a significant environmental factor affecting crack formation. In addition, catastrophic failure can occur without significant deformation or obvious (surface) deterioration of the component.

1.5 Corrosion Measurement Methods

Corrosion measurement methods are usually quantitative method of evaluating the performance and effectiveness of corrosion control and prevention techniques. After evaluation is completed, the result obtained is used to improve and enhance the techniques. A corrosion measurement method involves the application of various techniques to determine the corrosiveness of the environment and the rate of metal loss. The methods for corrosion measurement can be broadly divided into five categories [20].

1.5.1 Non-destructive testing methods

- Intelligent pigging
- Ultrasonic testing
- Radiography testing
- Thermography
- Eddy current
- Magnetic flux
1.5.2 **Analytical methods**

- pH measurement
- Dissolved gas (such as carbon dioxide, hydrogen sulfide, oxygen)
- Metal ion analysis (such as Fe$^{2+}$, Fe$^{3+}$)
- Microbiological analysis

1.5.3 **Fluid electrochemistry**

- AC impedance
- Potential measurement
- Potentiostatic measurement
- Potentiodynamic measurement

1.5.4 **Operational data**

- pH
- Pressure
- Temperature
- Velocity or flow rate

1.5.5 **Corrosion monitoring methods**

- Weight loss coupons
- Hydrogen penetration
- Galvanic current
- Electrical resistance
- Linear polarization

1.6 **Laboratory Corrosion Measurements Methods**

The corrosion measurements methods which are widely used in laboratory
can be broadly classified into two categories namely, non-electrochemical measurements and electrochemical measurements methods.

1.6.1 Non-electrochemical measurements

The following non-electrochemical measurement techniques can be used to assess corrosion rate.

1.6.1.1 Weight loss method

The weight loss measurement, considered to be the “gold standard,” of corrosion testing is certainly the most widely used and simplest of all corrosion monitoring techniques. In this method a weighed coupon of the material is exposed to the corrosive solution or process environment and later removed after a reasonable time interval. The coupon is then cleaned to remove corrosion products and is reweighed. The corrosion rate is expressed by measuring the weight loss taking place over the period of exposure. However, there are important issues to consider even for weight loss measurements. First, since mass can be measured easily only to about 0.1 mg, the sensitivity of weight loss measurements is limited. Other issues include end-grain attack leading to different corrosion rates on different exposed faces, crevice corrosion associated with hanging or supporting the sample and waterline attack if the sample extends beyond the surface. Finally, weight loss measurements are usually performed after long exposure times so they provide an average rate over time as well as over the exposed surface.
1.6.1.2 Metal ion analysis of solution

When a metal is subjected to corrosion in an electrolytic solution of a fixed volume, cations of the corroding metal will enter into the solution. Chemical analysis of withdrawn aliquots of the solution as a function of time allows determination of the corrosion rate. UV-visible (colorimetric) and atomic absorption spectrophotometry are the two important and useful techniques, used for chemical analysis of metal ions in the electrolyte. The first technique depends on the formation of a colored complex, the intensity of which is proportional to the concentration of the complex formed and correspondingly to the concentration of the dissolved metal ions in solution. In the second method of chemical analysis, sample is accurately weighed and then sprayed into the flame of the instrument and atomized. Light of a suitable wavelength for a particular element is directed through the flame, and some of this light is absorbed by the atoms of the sample. The amount of light absorbed is proportional to the concentration of the element in the solution.

This approach also has sensitivity limitations similar to weight loss method. However, solution analysis can be particularly powerful for studying the corrosion of alloys because of the ability for chemical differentiation, which is only possible using electrochemistry by rotating ring-disk measurements.

1.6.1.3 Gasometric techniques

When corrosion is taking place in acidic environment hydrogen gas is evolved as a by-product of the corrosion reaction. The progress of the corrosion reaction can be monitored by careful measurement of the volume of the evolved hydrogen gas at fixed time intervals. The corrosion rate is determined from the volume of hydrogen evolved during the corrosion reaction.
1.6.1.4 Electrical resistance (ER) probe technique

This technique involves a change in electrical resistance, ER of a probe sample. The reduction of the cross-sectional area of a probe by corrosion is accompanied by a proportionate increase in the electrical resistance, which can be tracked easily. A major advantage of the ER technique is its applicability to a wide range of corrosive conditions including environments having poor conductivity or non-continuous electrolytes such as vapors and gases. However, ER monitoring typically requires a relatively long exposure period for a detectible difference in probe resistance and electrically conductive deposits can affect the measurements.

1.6.2 Electrochemical techniques

The corrosion of metals occurs primarily by electrochemical processes involving metal oxidation and simultaneous reduction of some other species. The fundamental understanding of these processes has allowed the development of a number of electrochemical techniques for the study of the corrosion phenomena and assessment of the corrosion rate. A number of excellent reviews have appeared describing the existing electrochemical techniques in detail and providing instructions on their proper use [21-25]. Electrochemical techniques, which are based on the electrode kinetics taking place as a result of the corrosion processes, are used to study both the corrosion rates and qualitative behavior of corrosion mechanisms. The electrochemical techniques require the use of working electrode, counter electrode and reference electrode. Working electrode refers to the specimen being studied whereas the counter electrode serves to provide current path into solution. Reference electrode is the reference connection for potential measurement. The advantage of the electrochemical technique is that the measurement of corrosion rate
is made instantaneously. The disadvantage of these techniques is that these can only be successfully performed in relatively clean aqueous electrolytic environments, and will not work in gases or water/oil emulsions where fouling of the electrodes will prevent measurements being made. Some of the common electrochemical techniques and their significance are given below:

1.6.2.1 Potentiodynamic polarization (PDP)

The potentiodynamic polarization (PDP) over a potential range about ± 200-250 mV from the open circuit potential (OCP) results in a polarization curve that can be analyzed for corrosion rate, provided that the rates of other anodic reactions such as those associated with redox reactions are small in comparison which is a requirement of all electrochemical assessments of corrosion rate. Typically presented in a semi-logarithmic plot, polarization curves provide corrosion rate by extrapolation of the linear cathodic and/or anodic regions to the corrosion potential. PDP over a wide range of potential generates more information about the system than just the corrosion rate. For instance, information can be obtained about the proximity of the OCP to regions of passivity or localized corrosion susceptibility. It is often possible to view more of the anodic polarization curve by de-aerating the solution, which can reduce the corrosion potential. PDP is a tool for laboratory investigations, not corrosion rate monitoring, as it involves perturbation of the potential relatively far from the steady-state corrosion potential.

1.6.2.2 Linear polarization resistance (LPR)

The corrosion rate can also be determined from the polarization resistance (RP) using the Stearn-Geary equation provided that the polarization resistance is
similar to the charge transfer resistance and if the Tafel slopes are known. The most common way to determine RP is by the linear polarization resistance, LPR method, in which the potential is scanned about ± 5-10 mV relative to the corrosion potential. The LPR method has been put to considerable use in corrosion monitoring as it involves relatively little potential perturbation. However, accurate assessment of corrosion rate requires knowledge of the Tafel slopes, which must be determined separately or assumed. On the other hand, calculated corrosion rates are usually not wrong by more than a factor of 2-3 if the Tafel slopes are both assumed to be 100 mV / dec.

1.6.2.3 Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) technique involves the application of a time-varying voltage and measurement of the current response. The ratio of two gives the frequency-dependent impedance. A number of books and papers have been written on EIS and its application to corrosion [26-32]. The low frequency limit of the impedance magnitude can be related to RP and thus the corrosion rate using the Stearn-Geary equation. Again, the Tafel slopes are required to do so. Constant phase elements CPEs are used widely in the analysis of EIS corrosion data. EIS is a particularly useful technique for low conductivity electrolytes as the ohmic resistance is determined explicitly. It also provides a good description of the response of paint-coated samples and is sensitive to early stages of coating failure. One main difficulty with the technique is the proper selection of an equivalent circuit. An equivalent circuit should always be based on a physical model of the corroding system; addition of circuit elements simply to improve the fit is
unacceptable. However, a number of complex circuits could be rationalized as the
detailed nature of the physical system often is not known.

1.6.2.4 Electrochemical noise (EN)

The electrochemical noise (EN) technique involves the measurement of
electrochemical events i.e., current or potential transients or both simultaneously
produced by the corrosion process. EN has been reviewed by several investigators
[32-40]. The most common approach is to measure current noise utilizing a zero
resistance ammeter of two identical electrodes shorted together and the potential noise
between the pair and a reference electrode (RE) or a third identical electrode. The
ratio of the root mean squared deviation of the potential and current fluctuations is
one measure of the noise resistance. Alternatively, the data can be transformed into
the frequency domain to generate a power density spectrum or evaluated using
wavelet analysis. One problem with EN is the proper approach for accounting for the
exposed area of the sample. EN is particularly appealing for in situ monitoring as no
applied perturbation is required. Even though the absolute corrosion rate cannot be
obtained, the EN character is quite different for passive conditions low noise,
metastable pitting random events of short duration, and stable pitting individualized
events of longer duration so it can be useful for assessing the onset of localized
corrosion or stress corrosion cracking for a stressed sample. Changes in conditions
can be detected, triggering closer inspection or sampling of passive probes immersed
in the environment.
1.7 Factors Affecting Corrosion Rates

1.7.1 Temperature

Temperature is a complex external variable and can affect corrosion in a number of ways. As a general rule, increasing temperature increases corrosion rates. The corrosion rate increases exponentially with an increase in temperature if it is completely governed by metal oxidation (called activation control) process. Occasionally, because of certain solubility considerations, the corrosion rates in a system may decrease with increasing temperature. Many gases have lower solubility in open systems at higher temperatures. As temperature increases, the solubility of the gas decreases, which causes corrosion rates to go down. Temperature also alters the form of corrosion. Pits and tubercles tend to form in cold water while hot water promotes uniform corrosion. Uniform corrosion spreading across the entire surface of a pipe is far less problematic than tuberculation, so high temperatures can slow the corrosive process.

If a corrosive component has limited solubility in the solution, a temperature change can increase the solubility of that component and this increased solubility can have a profound effect on corrosion. The corrosion rate of iron in a system closed to atmosphere increases almost linearly with temperature from 40 to 160°C but in open system, the corrosion rate increases up to approximately 80°C and then decreases [41]. An increase in temperature could affect corrosion by moving a pH from a neutral to an acidic value. The solution temperature can also be affecting the onset of localized attack of passive alloys such as type 304 and 316 stainless steel. The solution usually contains the chloride ion that aids in the initiation process [42].
1.7.2 pH

pH is a measure of acidic/basic character of water. The range goes from 0-14, with 7 being neutral. pH, less than 7 indicate acidity, whereas pH, greater than 7 indicate a base. In general, corrosion rates almost always increase with decreasing pH (increasing acidity). This is a direct result of increasing the concentration of an aggressive ion (H+) and increasing the solubility of most potentially corrosive products. Iron or steel shows a complex dependence of corrosion rate on pH. At low pH, the corrosion mechanism is dependent not only on the hydrogen ion concentration but also on the anions present. The corrosion rate in hydrochloride acid is rapid at all acidic concentrations of pH<3, establishing the fact that the chloride ion seems to participate in corrosion reaction and accelerate the corrosion [43]. The corrosion rate of iron in sulfuric acid between a pH of less than 0 and about 4 tends to be limited by diffusion of and saturation concentration of iron sulfate [44, 45]. The presence of chloride ions raise the possibility of localized attack such as crevice corrosion, pitting and stress corrosion cracking (SCC) [46]. In near neutral range, pH no longer plays a direct role in corrosion process. Iron corrosion persists even at high pH because of soluble species [Fe(OH)3]⁺ or at elevated potentials [Fe(OH)₄]⁻ being the most thermodynamically stable corrosion products [47, 48]. Even though a number of iron hydroxide species can be found that can create a porous barrier [49], corrosion still persists, although usually at a fairly low rate, until very high pH is reached.

A number of other metals also show a very strong dependence of corrosion on pH. For example, aluminum, the rate increases exponentially as pH decreases in the acidic region [50]. A similar effect of a sharp decrease in corrosion rate with
increasing pH for pH<4 has been noted for both lead in nitric acid (HNO₃) and zinc in HCl [41].

1.7.3 Oxygen concentration

Oxygen’s role in corrosion is as an aggressive gas or oxidizing agent. Oxygen reacts with hydrogen gas at the cathode, causing depolarization and speeding up the corrosion. As a result, water with high dissolved oxygen will tend to be corrosive. As its concentration increases, corrosion rates increase until the rates of diffusion to the surfaces reach maximum. Other oxidizing agents can perform the same function, although they are less common. Nitrates and chlorine are two other oxidizing agents found in water.

1.7.4 Fluid velocity

The fluid velocity is a complex variable [51] and is influenced by a number of factors e.g., fluid constituents, fluid physical properties, corrosion mechanism, geometry in which the fluid is contained and the alloy type. Carbon steel corrosion in water in near neutral pH range is governed by the rate of mass transfer of dissolved oxygen from the bulk fluid to surface even in presence of a porous oxidized layer on the surface [52]. The presence of fluid flow can sometime be beneficial in preventing or decreasing localized attacks such as pitting or crevice corrosion as the mass transfer rate of oxygen is high enough to maintain a completely passive surface. However, in absence of flow, mass transfer of oxygen is too slow and surface cannot remain passive [53, 54].

In general, higher the fluid velocity, higher is the corrosion rate. The moderate flow rates are most beneficial since they promote the formation of scale without
breaking loose tubercles. At very low flow velocities, even zero, there are diffusion effects that can cause corrosion and tends to be in the form of tuberculation due to the prevalence of oxygen concentration cell corrosion. As fluid velocities increase from stagnant to moderate values, the corrosion rates increase. Then, as the limit of diffusion at a particular temperature is reached, further increases in velocity have little effect on the corrosion rate. High flow velocities also remove protective scale and tubercles and increase the content of the pipe with oxygen, all of which will increase the rate of corrosion.

1.7.5 Suspended solids

An increase in suspended solids levels will accelerate corrosion rates. These solids include any inorganic or organic contaminants present in the water. These contaminants include clay, sand, silt or biomass.

1.7.6 Corrosion inhibitors

Small amount of corrosion inhibitors can be added to water system and process streams to inhibit corrosion. Generally, the corrosion inhibitors incorporate themselves into corrosion product films in such a way as to increase the film’s capacity to prevent corrosion. The polar nature of some molecules promotes adsorption and the adsorption of these molecules is accompanied by the companion process of desorption. An inhibitor molecule is being adsorbed and desorbed between the fluid and the corrosion product film. The rate of adsorption onto the surface is dependent on the nature of the molecule, as well as the concentration of the inhibitor in the fluid. The same is true for the process of desorption.
1.7.7 Biological effect

There are biological organisms (microbes) which directly or indirectly affect the integrity of many materials used in industrial systems. Most metals including iron, copper, nickel, aluminium, and their alloys, are more or less susceptible to damage. Only titanium and its alloys appear to be generally resistant. In a general sense, the biological organisms fall into either of the two groups based upon their oxygen requirements; one being aerobic (requires oxygen) such as sulfur oxidizing bacteria, and the other being anaerobic (requires little or no oxygen), such as sulfate reducing bacteria (SRB). General corrosion affects the entire surface or at least the wetted surface whereas microbiologically induced corrosion (MIC), on the other hand is much localized. It creates a nodule and a pit beneath the nodule. There can be only a few nodules or there can be many. The different microbes perform different functions within the community. For example, in an aerobic environment, anaerobic bacteria are generally inhibited or killed. Layers of anaerobic bacteria can exist in the inner parts of the corrosion deposits, while the outer parts are inhibited by aerobic bacteria.

The first line of defense against MIC is cleanliness of the metallic surfaces. General corrosion prevention techniques are a good starting point since once corrosion begins the introduction of MIC producing bacteria will greatly accelerate the process. Once bacteria are established, both anaerobic bacteria which “tunnel” into metal, and other forms which adhere under biofilms, are extremely difficult to completely remove from the affected system. Water and other fluids should be monitored for solids and debris content. These contaminants provide nutrients to bacteria, accelerating their proliferation. Filtering of fluids is useful in this respect.
1.8 Methods of Corrosion Prevention and Control

Corrosion control and prevention are both issues used to describe the procedures necessary to provide effective corrosion maintenance. In effect they must be considered as complementary because corrosion and prevention can have a synergistic effect when each one explicates its specific action. There are many different methods of corrosion prevention and control. Each offers its own complexities and purposes. In general, the approach to control most corrosion is to understand the corrosion mechanism involved and remove one or more of the element of the corrosion cell; for example, by electrically separating the anode and cathode from each other or from the electrolytic environment by reducing the driving potential. The most commonly used corrosion control methods include materials selection and design using corrosion-resistant alloys, plastics, and polymers; organic and metallic protective coatings; cathodic protection; and corrosion inhibitors. All of these methods are appropriate for controlling corrosion in certain situations and not for others.

1.8.1 Materials selection and design

There are no materials which are resistant to all corrosive situations, however, materials selection is critical to preventing many types of corrosion failures. When selecting a material, the required characteristics need to be defined in advance. If no material has every characteristic that a specific project requires, a corrosion control system will be needed to meet the characteristics of the candidate material. Factors that influence materials selection are corrosion resistance in the environment, availability of design, cost, availability, reliability, maintainability, compatibility with
other system components and life expectancy. Appropriate system design also is highly important for effective corrosion control. Design includes the consideration of many factors, such as material selection, process and construction parameters, geometry for drainage, electrical separation of dissimilar metals, sealing of crevices, and corrosion allowance.

1.8.2 Protective coatings

Putting a barrier between a corrosive environment and the material to be protected is a fundamental method to control corrosion. Coating system selection is similar to materials selection in that many factors need to be considered, including types of exposure, operating conditions, substrate, ambient condition during application, environmental regulations, cost, application during operation, new construction or maintenance and field application. Common coating application methods include brush or roller, spray, and dipping. In addition to proper coating selection and application methods, substrate preparation is critical to the success of the coating. The majority of coating failures are caused either completely or partially by faulty surface preparation, such as leaving contaminants on the surface or having an inadequate anchor (sand blast) pattern.

1.8.3 Cathodic protection

Cathodic protection (CP) is an electrochemical technique used to control the corrosion of a metal surface by making it the cathode. The application of cathodic protection was first reported by Sir Humphrey Davy in a series of papers to the Royal Society in London in 1824. The first application of cathodic protection was to the HMS Semarang in 1824. Sacrificial anodes made from iron were attached to the
copper sheath of the hull below the waterline to reduce the corrosion rate of the copper. However, this led to a side effect as there was an increase in the marine growth on the ship hull. Since excess marine growth affected the performance of the ship, the Royal Navy decided not to use CP further. It was about 100 years after Sir Davy’s experiment that cathodic protection was widely used to protect oil pipelines in the United States. Cathodic protection was for the first time applied to steel gas pipelines in 1928 and more widely in the 1930s. The principle of cathodic protection is to connect an external anode to the metal to be protected and the passing of an electric dc current so that all areas of the metal surface become cathodic and therefore do not corrode. The external anode may be a galvanic anode, where the current is a result of the potential difference between the two metals, or it may be an impress current anode, where the current is impressed from an external dc power source. Cathodic protection systems are used to protect a wide range of metallic structure in various environments. Common applications are; steel water or fuel pipelines and storage tanks; ships and boats; offshore oil platforms and onshore oil well casings and metal reinforcement bars in concrete buildings and structures. Cathodic protection is widely used in several environments, including water and soil. It is often used in combination with coating that reduces the exposed surface area to receive protective current. Cathodic protection can be achieved either by the use of (i) galvanic (sacrificial) anodes, or (ii) by impressed current.

1.8.3.1 Galvanic or sacrificial anode

Galvanic anodes are selected to have a more negative electrochemical potential than the metal of the target structure (typically steel). The galvanic anode continues to corrode consuming the anode material until eventually it must be
The polarization of the target structure is caused by the electron flow from the anode to the cathode. The metals commonly used as sacrificial anodes are aluminium, zinc and magnesium.

1.8.3.2 Impressed current

For larger structures, galvanic anodes cannot economically deliver enough current to provide complete protection. Impressed current cathodic protection (ICCP) system use anode connected to a DC power source. Usually this will be a cathodic protection rectifier, which converts an AC power supply to a DC output. The materials that are used as anode in rectifier type systems almost universally today are graphite, high silicon cast iron and precious metal oxide coated titanium. In underground water, special coke breeze backfills are usually used for the purpose of providing a uniform environment around the anode and for lowering the anode-to-earth resistance.

1.8.4 Anodic protection

Anodic protection is another method used to prevent corrosion. In contrast to cathodic protection, anodic protection is relatively new. Edeleanu first demonstrated the feasibility of anodic protection in 1954 and tested it on small-scale stainless steel boilers used for sulfuric acid solutions. This was probably the first industrial application of anodic protection. Anodic protection possesses unique advantages, for example, the applied current is usually equal to the corrosion rate of the protected system. Thus, anodic protection not only protects but also offers a direct means for monitoring the corrosion rate of a system. The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low 31
current requirements. For example, anodic protection used for carbon steel storage tanks containing extreme pH environments including concentrated sulfuric acid and 50% caustic soda where cathodic protection is not suitable due to very high current requirements. Another major application of this technique is the protection of carbon steel or 304 or 316 stainless steel in concentrated (>93wt%) sulfuric acid. Anodic protection has been most extensively applied to protect equipment used to store and handle sulfuric acid. Anodic protection has more limited, but important applications in chemical environments. It is achieved by maintaining an active-passive metal or alloy in the passive region by an externally applied anodic current. In anodic protection, electric current is used to create a protective oxidized layer on the base protected material, often known as the substrate. This technique can usually be found in factories that work with high or low pH solutions, particularly sulfuric acid, phosphoric acid, or chromic acid. Other lesser-used substrate materials that can benefit from anodic protection include magnesium, titanium and zinc.

1.8.5 Corrosion inhibitors

The use of inhibitors is one of the most effective, practical and economic methods to protect metallic surfaces against corrosion in aggressive acidic media [55-57]. Corrosion inhibitors are the chemical substances that, when added in small concentration to an environment, effectively decrease the corrosion rate. Inhibitors are commonly added to acids, cooling waters and steam, either continuously or intermittently. They generally control corrosion by forming thin film that modifies the environment at the metal surface. Some retard corrosion by adsorption to form a thin, invisible film. Others form bulky precipitates that coat the metal and protect from attack. Inhibitors are often easy to apply and offer the advantage of in-situ
application without causing any significant disruption to the process. However, there are several considerations when choosing an inhibitor for corrosion control:

- Cost of the inhibitor can be sometimes very high when the material involved is expensive or when the amount needed is huge.
- Toxicity of the inhibitor can cause jeopardizing effects on human beings, and other living species.
- Availability of the inhibitor will determine its selection, if the availability is low, the material is often expensive.
- Environmental compatibility.

There are several classes of inhibitors which are available in the industries for corrosion prevention. They are as follows:

1.8.5.1 *Vapor phase (volatile) inhibitors*

As corrosion can also occur in vapor environment, it is useful to carry corrosion inhibitors into the system, which then need to be, themselves, volatile. Vapor phase corrosion inhibitors or volatile corrosion inhibitors (VCIs) are similar to organic adsorption-type inhibitors. These inhibitors possess moderately high vapor pressure and consequently can be used to inhibit atmospheric corrosion of metals without applying VCIs directly on the metal surface. Volatile corrosion inhibitors are secondary-electrolyte layer inhibitors that possess appreciable saturated vapor pressure under atmospheric conditions, thus allowing vapor-phase transport of the inhibitive substance [58]. They are usually effective if used in enclosed spaces such as closed packages or the interior of machinery during shipment [59]. Vapor phase inhibitor function by forming a bond on the metal surface or by forming a barrier.
layer to aggressive ions. These include species like amines and nitrites for inhibition of ferrous metal.

1.8.5.2 Passivating (anodic) inhibitors

Passivating inhibitors or passivators are usually inorganic oxidizing substances that cause a large anodic shift of the corrosion potential several tenths volt, forcing the metallic surface into the passivation range. There are two types of passivating inhibitors: (a) Oxidizing anions, such as chromate, nitrite and nitrate, which can passivate steel in the absence of oxygen and (b) Non oxidizing ions such as phosphate, tungstate and molybdate that require the presence of oxygen to passivate steel. These kinds of inhibitors are the most effective inhibitors and consequently the most widely used and possesses higher efficiency than others. Chromate based inhibitors are the least expensive inhibitors and were used until recently in a variety of applications, e.g. recirculation-cooling systems of internal combustion engines, rectifiers, refrigeration units, and cooling towers. However, one major drawback of passivating type inhibitors is that in order to maintain sufficient passivation of the metal and thus providing sufficient inhibition, the concentration of the inhibitor must be kept well above a critical or minimum concentration. If the concentration is below the minimum value, it is likely that the metal, which is to be protected in to the first place, will suffer from localized corrosion such as pitting.

1.8.5.3 Precipitation inhibitors

Precipitation inhibitors, for example, silicates and phosphates are often film-forming in nature. They are effective at blocking both anodic and cathodic sites. They precipitate on the metal surface, forming a protective barrier. Hard water
is rich in magnesium and calcium. When these salts precipitate on the metal surface, for example at the cathode where the pH is higher, they establish a protection layer on the metal. Film-forming types of inhibitors are often distinguished by two classes. The first one works by slowing down the corrosion without stopping it completely whereas the second type ceases the attack completely. The efficiency of this type of inhibitors depends on the pH value and saturation index. The saturation index is then in turn determined by the water composition and temperature.

1.8.5.4 Cathodic inhibitors

Cathodic inhibitors reduce the rate of cathodic reaction namely oxygen reduction in near neutral environments and hydrogen evolution in acid solutions, respectively. These types of inhibitors form species that precipitate on cathodic sites and thus increase the surface impedance and lower the diffusion rate. The inhibiting action of cathodic inhibitors work by three mechanisms:

Cathodic poisons: In this case, the cathodic reduction process is suppressed, for example, by impeding the hydrogen recombination and discharge. But it may increase the susceptibility of metal to hydrogen induced cracking. Hydrogen may absorb into the metal during this process. Therefore, it is essential to keep hydrogen in atomic form. Typical types of cathodic poisons are arsenic and antimony.

Cathodic precipitates: Compounds such as calcium, magnesium will precipitate as oxides to form a protective layer which acts as a barrier on the metal surface.
Oxygen scavenger: This type of inhibitors functions by the removing the oxygen from the system to reduce corrosion.

1.8.5.5 *Organic inhibitors*

These types of inhibitors are also film-forming in nature. They form a hydrophobic layer on the surface of the metal to prevent corrosion. The inhibition efficiency depends upon the chemical composition and molecular structure of the inhibitor as well as their affinity with the metal. They are classified into organic anions and cations. Inhibitors like sulphonates and phosphonates fall into the anions category whereas chemicals with active groups such as aliphatic and aromatic and positively charged amine groups falls into organic cations category.

1.8.5.6 *Inorganic inhibitors*

The common inorganic inhibitors used are crystalline salts, for instance, sodium chromate and molybdate. The only active groups of these compounds that functions to reduce corrosion are the negative anions they carry.

1.8.5.7 *Mixed inhibitors*

Corrosion inhibitors as such are rarely used as a single compound. The formulation can be composed of two or more inhibitors with different characters due to following factors:

(i) A single inhibitor can only inhibit a few numbers of metals. When the environments involve multi-metal system, the inhibitive action may sometimes cause jeopardizing effects to other metals.
(ii) Advantages from anodic and cathodic inhibitors can be combined and optimized for best performance.

(iii) Addition of halide ions synergistically improved the inhibiting action of organic inhibitors in acid solutions.

1.9 Actual Corrosion Inhibitors Used in Corrosive Environments

1.9.1 Chromates

Chromates are one of the most widely used corrosion inhibitors. However, their application as corrosion inhibitor has been reduced greatly in recent years due to disposal and environmental issues. Chromates were once used in one through type cooling system and are still occasionally used on open recirculating systems with the concentration between 300-500 ppm. However, the inhibitive effect is restricted because there is a possibility of localized attack if chloride and sulphate concentrations in the system rise to a significant value. Thus, it is often combined with cathodic type of inhibitors such as zinc for economical and pollution reasons. This combination operates between pH 6-7 and the performance can be further improved by adding organic compounds and phosphates. In high-chloride system such as refrigerating brines, chromates are employed at pH 8-8.5 with a concentration of 2000-3000 ppm. It is also used as volatile inhibitor to control atmospheric corrosion for copper and its alloys. As far as pollution issues are concerned, even low concentrations of chromate are toxic and it is now replaced with more environmental friendly organic inhibitors.

1.9.2 Nitrites

Nitrite is used in inhibition for engine coolant for road vehicles and marine
diesels. It has been found that nitrite is able to reduce corrosion in diluted seawater. In the oil and gas industry, nitrites in oil-soluble form have been applied to inhibit corrosion induced by the water settled at the bottom of the tank. Nitrites can be used in a volatile form. In an open recirculation system, sodium nitrite may induce chloride and sulfate induced localized attack. It is also susceptible to bacterial decomposition, causing stress corrosion cracking in copper-base alloys if it is reduced to ammonia. Nitrite loses its inhibitive effect when the pH is below 5.5-6.0.

1.9.3 Bezoates

Bezoates are used as anodic type inhibitor for mild steels. One major drawback of benzoates is that they may induce localized attack if added in insufficient concentration. When the system to be protected involves dissimilar metals, benzoate is often mixed with nitrite. However the effectiveness of this inhibitor is greatly affected by the nature of metal surface.

1.9.4 Phosphates

Phosphates, which are generally classified as cathodic inhibitors, find their application in near neutral solution. Phosphates are precipitated as a thin adherent film at the cathodic sites on the corroding metal surfaces and thus block oxygen from accessing the cathodic sites. Phosphates are added in water system in the concentration range of 5 to 10 ppm to mitigate the corrosion of Fe, Zn, Cu and Al. In some boiler systems, 10 ppm of phosphate inhibitor is added to prevent the corrosion of Fe, Zn and Cu.
1.9.5 Amines

Amines, a cationic type of inhibitors, are often added to HCl-rich environments in the concentration of 0.2% in the form of mixture in polyhydric alcohols (glycol). When the system involved is ferrous metal, neutralizing amines work by the mechanism that modifies the pH of the electrolyte and thus inhibiting rust formation. Amines can be applied in volatile environment to prevent atmospheric corrosion. The corrosion inhibition for steam-condensate lines is effective when long chain aliphatic amines with alkyl groups containing 8-22 carbon atoms are used. When protecting storage tanks, a mixture of amines and imidazolines are added.

1.9.6 Ammonia

The steam-condensate systems are often subjected to carbon dioxide and oxygen induced corrosion. Such type of corrosion can be prevented by using ammonia which act as a neutralizing agent and maintain the pH value between 8.5-8.8. Unlike amines, ammonia does not have the same condensation rate as steam, thus it should not be used for a copper-based alloy system. The same principle applies to boiler as well. In refining processes, corrosion arises due to the attack by water, hydrogen sulphide, carbon dioxide, oxygen and other aggressive agents. These species bring together fouling and scaling of the metal at lower pH, which may be remedied by modifying the pH to a range between 7.0-7.5 by adding a mixture of ammonia, sodium hydroxide and sodium carbonate. At higher pH, ammonia does not offer this advantage as copper-based alloys become susceptible to stress corrosion cracking induced by ammonia. Another major drawback of this
inhibitor is that when it neutralizes hydrochloric acid, it produces ammonium chloride which when deposited on the surface of the metal become very corrosive.

1.10 Toxicity of Corrosion Inhibitors

Toxicity is defined as the ability of a chemical to damage an organ system, such as the liver or kidneys, or to disrupt a biochemical process, such as blood-forming mechanism, or to disturb an enzyme system at some site in the body [60, 61]. Most of the corrosion inhibitors used is toxic substances. Considering the case of chromates, unlike other corrosion inhibitors their inhibiting action is very stable in most system. They are used in the pretreatments of aluminium alloys [62, 63]. However, they are classified as substances known to be both toxic and carcinogenic [64]. They may cause chronic ulceration and perforation of the nasal septum. They also induce chronic ulceration of skin surfaces. Living organisms can be exposed to chromium through contaminated air, water, soils, and food. Chromate-zinc blend inhibitors are highly toxic to marine life. Despite the remarkable inhibitive effect of nitrites their application has decreased due to their toxic nature.

1.11 Environment Friendly or Green Corrosion Inhibitors

When selecting an inhibitor for corrosion control, in addition to its availability and economic viability environmentally acceptability is another major requirement. There are growing concerns about the use of certain compounds like chromates as inhibitors for corrosion processes, mainly due to the issue of toxicity as the compounds are toxic and hazardous to both human beings and the environment [65] and needs to be replaced by nontoxic, environment friendly compounds. As a result, the current research trends is towards the development of nontoxic, economical and more environmentally safe green chemicals as corrosion inhibitors [66-70].
Naturally occurring substances of both plants and animal origin otherwise tagged ‘green inhibitors’ are known to meet these requirements. In the past two decades, the research in the field of ‘green’ or “eco-friendly” corrosion inhibitors has been directed towards the goal of using cheap, effective compounds at low or ‘zero’ negative environmental impact [71-75]. In a very recent review on green corrosion inhibitors the authors performed a survey on the literature published on corrosion inhibitors during 1950-2010 [76]. It was shown that the number of articles published has been doubled during the last decade (2001-2010) compared to 1991-2000. The increasing number of publications clearly indicates the interest in exploring the new inhibitors for a variety of corrosive environments in order to control the corrosion of various metals. However, though the number of investigations on corrosion inhibitors has dramatically increased, only 5% of the literature published during the last decade concerns green inhibitors. The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that have biocompatibility in nature. The inhibitors like plant extracts presumably possess biocompatibility due to their biological origin. The green inhibitors can be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors.

1.11.1 Organic green inhibitors

The organic green inhibitors are the flavonoids, alkaloids and other natural products obtained from natural sources like plants [77]. It also includes synthetic compounds with negligible toxicity. Some of the notable developments on organic green inhibitors are discussed below.
1.11.1.1 *Plant extracts as green corrosion inhibitors*

Plant extracts, in addition to being environmentally friendly and ecologically acceptable, are inexpensive, readily available and renewable. The extracts of *Azaricta indica*, *Fenugreek* leaves, *Zenthoxylum alatum*, *Opuntia*, *lawsonia*, *khillah*, *Musa sapientum*, *Stevia rebaudiana*, *Nypa fruticans*, *Ocimum viridis*, *Phyllanthus amarus*, *Chamomile*, *Halfabar*, and *Murraya koenigii* were studied as corrosion inhibitors in sulphuric and/or hydrochloric acid medium [78-90]. The inhibition performance of plant extract is normally ascribed to the presence of complex organic species including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products in their composition. These organic compounds usually contain polar functions with nitrogen, sulfur, or oxygen atoms as well as triple or conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers.

1.11.1.2 *Amino acids as green corrosion inhibitors*

A number of investigators have reported that some amino acids can act as potential corrosion inhibitors, which has generated an increasing interest in these compounds [91-133]. Amino acids are attractive as corrosion inhibitors because they are relatively easy to produce with high purities greater than 99% at low cost and are nontoxic, biodegradable and completely soluble in aqueous media. Amino acids contain both amino and carboxyl functionalities bonded to the same carbon atom and hence can adsorb strongly on the metallic surfaces providing good protection. In acidic medium amino acids exist as protonated species and both molecular and protonated species can adsorb on the corroding steel surface.
1.11.1.3 Polymers as green corrosion inhibitors

The use of polymers as corrosion inhibitors has gained wide acceptance in recent times. The polymers have been found to be attractive as corrosion inhibitors as they are cost effective, inherently stable, and non-toxic [134]. They have been reported to exhibit superior corrosion inhibition properties in contrast to simple organic molecules [135]. This is because of the fact that they possess long chain carbon linkage and multiple adsorption sites and thus block large surface area of the corroding metal, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution. Polymers are adsorbed stronger than their monomer analogs [136] and hence are better corrosion inhibitors than the corresponding monomers. The polymers provide two advantages namely (i) a single polymeric chain displaces many water molecules from the metal surface thus making the process entropically favorable and (ii) the presence of multiple bonding sites makes the desorption of polymers a slower process [137]. The application of water-soluble polymers having functional groups (-OH, -COOH, -NH2, etc.) have been reported as corrosion inhibitors in different aggressive media [138-146]. The polymers through their functional groups form complexes with metal ions. On the metal surface these complexes occupy a large surface area thereby blanketing the surface and protecting the metal from corrosion. The inhibitive power of these polymers is related structurally to the cyclic rings, heteroatom (oxygen and nitrogen), which are the major active centers of adsorption. Larger corrosion inhibition efficiencies that are observed using various polymers are due to the larger molecular size which ensures greater coverage of the metallic surface. Polymers such as polyvinyl alcohol, polyethylene glycol, polyvinyl pyridine, polyvinylbipyridine,
polyvinylpyrrolidone, polyvinylpyrrolidone (PVP), polyethylenimine, polyacrylic acid, polyaniline, polyacrylamide and polyvinylimidazoles have been reported [147-161].

The inhibition of mild steel corrosion in H₂SO₄ using synthetic (polyethylene glycol) and naturally occurring (gum arabic) polymer was studied in the temperature range of 30-60°C. Both the polymers were found to act as inhibitors but synthetic polymer was more effective than natural polymer [91]. The inhibiting action of some polyethylene glycols on carbon steel corrosion, using 3N sulphuric acid as corroding solution, was evaluated by the weight loss method and polarization and impedance spectroscopy techniques. In order to study the effect of polyethylene glycol structure on the inhibition efficiency, different molar weights (200-10,000 gmol⁻¹) were selected. This work has demonstrated that the polyethylene glycols have an inhibition effect on the corrosion process and the inhibition efficiency is more than 90%. It was shown that polyethylene glycol is adsorbed physically on carbon steel in acid medium [162]. The corrosion inhibition of aluminum in H₂SO₄ in the presence of polyvinyl alcohol (PVA) and polyethylene glycol (PEG) and the effect of addition of halides (KCl, KBr, KI) were studied using the hydrogen evolution technique at 30 and 40°C. Inhibition efficiency (%IE) increases with concentration of PVA and PEG but with PEG having higher %IE. The %IE decreases with increase in temperature from 30 to 40°C in the absence and presence of inhibitor and halides. PVA and PEG were found to obey Freundlich adsorption isotherm. The synergism parameters (S₁) obtained was found to be greater than unity for both PVA and PEG, which indicates that the enhanced inhibition efficiency caused by the addition of halides is only due to synergism [163]. Studies were carried out to determine the inhibition efficiency and
adsorption characteristics of two water soluble polymers namely polyvinyl alcohol (PVA) and polyethylene glycol (PEG) as corrosion inhibitors for mild steel in H₂SO₄ using weight loss and hydrogen evolution techniques at 30-60°C. PEG was found to be a better inhibitor than PVA [154]. Umoren et al [164] studied the effect of halide ions on the corrosion inhibition of mild steel in H₂SO₄ at 30-60°C by polyvinyl alcohol using weight loss and gravimetric techniques. Results obtained showed that inhibition efficiency (%IE) increased with the increase in concentration of PVA, on the addition of halides and with the increase in temperature. The synergism parameter, S₁, evaluated was found to be greater than unity. The corrosion inhibition of aluminum in H₂SO₄ in the presence of PEG and PVA as inhibitors at 30-60°C was studied using gravimetric, gasometric, and thermometric techniques [153]. The inhibition efficiency (%IE) increased with increase in concentration of the inhibitors. Increase in temperature increased the corrosion rate in the absence and presence of inhibitors but decreased the inhibition efficiency. Again, PEG was found to be a better inhibitor than PVA. The inhibition effect of some PEGs on carbon steel corrosion at 25°C in 0.5N hydrochloric acid as corroding solution was evaluated by weight loss method and polarization and electrochemical impedance spectroscopy (EIS) techniques. In order to study the effect of polyethylene glycols’ structure on the inhibition efficiency, different molecular weights (400, 1000, 4000, and 10,000 g mol⁻¹) were selected. This work has demonstrated that polyethylene glycols have inhibition effect on corrosion process and their inhibition efficiencies are between 50 and 90%. The inhibition efficiencies are increased by increase of the inhibitors’ concentration and molecular weight [165].
The corrosion inhibition of aluminum in NaOH in the presence of PVA at 30 and 40°C and the effect of addition of halides (KCl, KBr, KI) were studied using weight loss and hydrogen evolution methods [166]. Results obtained showed that PVA acts as a corrosion inhibitor in the alkaline environment. The inhibition efficiency increased with increase in concentration of PVA and synergistically increased on the addition of the halides but however decreased with rise in temperature. The increase in inhibition efficiency (%IE), surface coverage values as well as synergistic parameter, $S_1$, were found to be in the order $I > Br > Cl$, which clearly indicates that the radii and electronegativity of the halides play a significant role in the adsorption process. The corrosion inhibition of aluminum in alkaline medium was studied at 30 and 40°C in the presence of PEG using gravimetric (weight loss) and thermometric techniques. The effect of halides (KCl, KBr, and KI) on the inhibitory action of PEG was also studied [167]. It was found that PEG acted as inhibitor for aluminum corrosion in the alkaline medium. Inhibition efficiency increased with increasing inhibitor concentration. An increase in temperature led to increase in both the corrosion rate and inhibition efficiency in the absence and presence of inhibitor and halides. The adsorption of PEG on the surface of aluminum was found to obey Flory-Huggins and Temkin adsorption isotherms. The synergism parameter, $S_1$, evaluated was found to be greater than unity indicating that the enhanced inhibition efficiency caused by the addition of halides is synergistic in nature. The inhibition efficiency, surface coverage and synergism parameter increased in the order; $I > Br > Cl$, showing that a joint adsorption of PEG and halide ions on aluminum plays a significant role in the adsorption process. The corrosion inhibition of mild steel in sulphuric acid solution in the presence of PEG, polyvinyl pyrrolidone (PVP), and their blends was investigated using weight loss and hydrogen evolution
techniques at temperature range of 30-60°C [168]. It was found that inhibition efficiency increases with increase in concentration of the homopolymers and decreases with increase in temperature. Inhibition efficiency was found to be synergistically enhanced on blending the two polymers with highest inhibition efficiency obtained for (PEG: PVP) blending ratio of 1: 3. The experimental data obtained fitted well into Temkin adsorption isotherm model. Physical adsorption mechanism is proposed from the trend of inhibition efficiency with temperature. The proposed mechanism is also corroborated by kinetic and thermodynamic parameters obtained.

The corrosion inhibition of mild steel in 1N sulphuric acid solution by Polyethylene Glycol Methyl Ether (PEGME) has been studied in relation to the concentration of the inhibitor as well as the temperature using electrochemical polarization (galvanostatic and potentiostatic) techniques [169]. The results were supplemented with scanning electron microscopy and infra-red spectroscopy. Adsorption of PEGME was found to follow the Langmuir’s adsorption isotherm. PEGME is a mixed type of inhibitor. There is no particular relationship of inhibition with concentration and temperatures. All the methods employed were in reasonable agreement.

The inhibitive effect of p-toluidine and poly(p-toluidine) on corrosion of iron in 1M HCl has been studied by the electrochemical methods such as impedance, linear polarization and Tafel polarization techniques. The effectiveness of poly(p-toluidine) was found to be high in comparison with that of monomer. The results showed that p-toluidine and poly(p-toluidine) suppressed both cathodic and anodic
processes of iron dissolution in 1M HCl. The inhibition efficiency of both p-toluidine and poly(p-toluidine) were found to increase with the inhibitor concentrations [170].

The corrosion inhibition of mild steel in 1M H₂SO₄ in the presence of polyvinylpyrrolidone (PVP) and polyacrylamide (PA) as inhibitors at 30-60°C was studied using gravimetric and gasometric techniques. The inhibition efficiency (%IE) increased with increase in concentration of the inhibitors. Increase in temperature increased the corrosion rate in the absence and presence of inhibitors but decreased the (%IE). Phenomenon of physical adsorption is proposed from the activation parameters obtained. Thermodynamic parameters reveal that the adsorption process is spontaneous. PVP was found to be a better inhibitor than PA [171]. The corrosion inhibition of mild steel in 1M H₂SO₄ by PVP and the synergistic effect of iodide ions were investigated using weight loss and hydrogen evolution methods in the temperature range of 30-60°C [172]. The corrosion rates of mild steel decreased with the increasing concentration of PVP, while the inhibition efficiency (%IE) increased. The inhibition efficiency of PVP decreased with rise in temperature, suggesting a physical adsorption mechanism, which was found to follow Freundlich and Temkin adsorption isotherms. The inhibition mechanism was further collaborated by the values of kinetics/thermodynamic parameters obtained from the experimental data.

The inhibiting action of PVP was considerably enhanced in the presence of iodide ions and values of the synergism parameter (S₁) obtained point to synergistic interactions between PVP and iodide ions. Water soluble poly(p-phenylene diamine) was chemically synthesized. Its corrosion inhibition performance was evaluated for iron corrosion in 1M HCl at various concentrations, and the results were compared with that of the monomer. The corrosion inhibition properties were evaluated by
polarization techniques and electrochemical impedance spectroscopy. The results showed that poly(p-phenylene diamine) was a more efficient corrosion inhibitor than the monomer and gave an 85% inhibition efficiency at a concentration of 50 ppm, whereas the monomer gave an efficiency of 73% at 5000 ppm [173]. The effect of polyethyleneimine (PEI) as a corrosion inhibitor for ASTM 420 and AISI 430 stainless steel in 3% aqueous NaCl solution was studied [174, 175]. PEI probably acts as a diffusion barrier by preventing an attack by the chloride of the salt solution PEI showed remarkable corrosion protection against uniform and pitting corrosion.

In recent years, polyanilines have emerged as efficient class of corrosion inhibitors for mild steel in acidic media. The corrosion inhibition of poly(aniline-formaldehyde) on mild steel in 1N HCl has been evaluated by potentiodynamic polarization, linear polarization, electrochemical impedance spectroscopy and weight loss measurements. Results obtained show that poly(aniline-formaldehyde) is a mixed inhibitor and it inhibits mild steel corrosion through adsorption mechanism. It showed >90% inhibition efficiency at 10 ppm. AFM clearly reveals that surface roughness of inhibited mild steel sample is less than uninhibited mild steel [176]. The corrosion inhibition performance of water soluble polyacrylamide (PA) in HCl/H2SO4 solution and the effect of halide additives on the performance of PA have been investigated. Corrosion inhibition was afforded by adsorption of PA onto the metal; the inhibition efficiency (%IE) of PA was found to be more pronounced in presence of halide ions [177-179]. Corrosion inhibition of iron in H2SO4 by polyacrylic acid (PAA) was investigated using electrochemical techniques at 30°C. Results obtained indicate that PAA inhibited the corrosion of iron in the acid medium. Inhibition efficiency increases with increase in PAA concentration and synergistically enhanced on
addition of iodide ions. Potentiodynamic polarization results suggest that PAA functions as a modest cathodic inhibitor. The adsorption of PAA onto the iron surface followed Temkin adsorption isotherm. FTIR analysis revealed that the synergistic effect due to co-adsorption of iodide ions and PAA is cooperative in nature [180]. Umoren et al studied the inhibition effect of PAA on the corrosion behavior of aluminium in sulphuric acid solution [181]. Electrochemical techniques using ac and dc as well as surface analyses approach were used to investigate the corrosion inhibition characteristics. The effect of iodide ion additives was also studied. The results obtained indicate that PAA inhibited the corrosion of pure cast aluminium in the acid medium by adsorption onto the metal surface following Frumkin adsorption isotherm model. Inhibition efficiency increases with an increase in PAA concentration and synergistically enhanced by the addition of iodide ions. A mixed inhibition mechanism is proposed for the inhibitive effects of PAA as revealed by potentiodynamic polarization technique. In a very recent paper, Poly(vinyl alcohol-aniline)(PVAA) water soluble composite was tested for its performance in protecting mild steel against corrosion in 1M HCl [182]. The inhibitive parameters were evaluated by means of weight loss, electrochemical polarization and impedance methods. Results indicated that the addition of PVAA to the acid reduces the corrosion of the metal. Inhibition efficiency increases with increase in inhibitor concentration. The results further revealed that PVAA at a concentration of 2000 ppm furnishes a maximum of 92% inhibition efficiency. Polarization curves revealed that PVAA is a mixed inhibitor.
1.11.2 Inorganic green inhibitors

Chromates have been widely used as potential corrosion inhibitors in aqueous systems due to their high efficiency. However, chromates exhibit high toxicity and consequently prohibited to be used for industrial applications. In search of alternatives for chromate inhibitors, lanthanide salts have been found to show excellent inhibition properties [183, 184]. Lanthanide salts like lanthanide chlorides were reported to possess toxicity that is comparable with sodium chloride [64]. Hence lanthanide salts can also be considered as green inhibitor or eco-friendly inhibitor. A few research studies have been reported on the corrosion inhibition properties of lanthanides during the last decade. For example, Arenas et al [185] reported the application of CeCl₃ as an inhibitor for an aluminium alloy (AA 5083) and galvanized steel in aerated NaCl solutions. The study has provided evidence for the formation of an inhibitor layer on the surface of alloy as well on galvanized steel. In another attempt by Arenas et al CeCl₃.7H₂O was employed as corrosion inhibitor for tinned iron or tin plate in NaCl solutions [186]. The coulometric studies revealed the cathodic nature of the inhibitor, which was similar to their previous report [185]. Similarly, Bernal et al [187] reported the inhibitive effects of lanthanum nitrate (La(NO₃)₃), samarium nitrate (Sm(NO₃)₃), lanthanum chloride (LaCl₃), and samarium chloride (SmCl₃) for corrosion of AISI 434 SS in sodium chloride solutions. Even though the nitrate ion is considered as an anodic inhibitor, the studied rare earth nitrates (La(NO₃)₃), (Sm(NO₃)₃) were demonstrated as mixed-type inhibitors, which was attributed to the presence of lanthanide ions in the solutions. Interestingly, for rare earth chlorides decrease in inhibition efficiency was observed on increasing the
inhibitor concentration. This negative effect was interpreted as due to the increase in the concentration of the chloride ions.

1.12 Surfactants as Corrosion Inhibitors

Surfactants, which have a remarkable ability of influencing the surfaces and interfaces, have shown a significant role in the inhibition of acid corrosion of mild steel [188-194]. In aqueous solutions the inhibitory action of surfactant molecules may be due to the physiosorption (electrostatic) or chemisorption onto the metallic surface, depending on the charge of the solid surface. The degree of their adsorption on metal surfaces depend on the nature of the metal, the mode of adsorption, chemical structure of the surfactant, the metal surface condition, and the type of corrosion media. The corrosion inhibition by surfactant molecules is related to the surfactant’s ability to aggregate at interfaces and in solution. The effectiveness of surfactant as corrosion inhibitor can be studied on the basis of their micellar properties in a particular medium. The adsorbed molecules form monolayer or bilayer hemimicelles or admicelles, depending upon the surfactant concentration and prevent the acid to attack the surface, and thus reduce the corrosion attack. Surfactants have been used as corrosion inhibitors either alone or in combination with other compounds to improve their performance as inhibitors.

The inhibition of acid corrosion of steel using cationic surfactants cetylpyridinium chloride (CPC) [195, 196], cetyl trimethyl ammonium bromide (CTAB) [194, 197, and 198] and cetyl pyridinium bromide (CPB) [199] has been studied. The surfactants were found to exhibit excellent IE in acid solutions. The effect of anionic surfactant sodium dodecyl sulphonate (SDS) as inhibitor during the corrosion of mild
steel in sulphuric acid was studied using galvanostatic, potentiostatic and SEM studies [200]. The results obtained revealed that SDS acts as efficient inhibitor and shows very good IE. The corrosion inhibition behavior of anionic surfactant sodium dodecyl benzene sulphonate (SDBS) in acid solution was also studied [201-203]. The maximum inhibition of the inhibitor is observed around its critical micelle concentration (CMC). Surfactant inhibitors have many advantages over traditional corrosion inhibitors. For example, they are easily produced, are economical and possess high inhibition efficiency and low toxicity [204-206]. Surfactants have widely been used for inhibition of pitting corrosion of stainless steel [207], as corrosion inhibitors for carbon steel pipelines in oil fields, aluminum alloys and mild steel [208].

1.13 STATEMENT OF THE WORK PRESENTED IN THE THESIS

As a consequence of the industry’s motivation to achieve improved efficiency and enhanced performance, engineering components are required to operate in environments, which are becoming increasingly severe. The critical industrial components are, therefore, being degraded more aggressively due to surface environment interactions referred to as corrosion. Acid solutions are widely used in various industries, the most important area being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. These processes are generally carried out at temperature up to 60°C. Since the acids solutions are quite aggressive and may lead to the corrosion of the contacting metals if used as such, inhibitors are often used in these processes to control the corrosion of metals. Most of the efficient pickling inhibitors are organic compounds containing hetero atoms such as sulfur, nitrogen, oxygen, phosphorus, and multiple bonds or aromatic rings in their structures.
However, most of the organic compounds used as corrosion inhibitors are toxic and hazardous to both human beings and the environment and needs to be replaced by nontoxic, environment friendly compounds. As a result, the current research trend is towards the development of nontoxic, economical and more environmentally safe green chemicals as corrosion inhibitors.

It has been shown by a number of investigators that some water soluble polymers and their derivatives can act as corrosion inhibitors, which has generated an increasing interest in these compounds. Polymers are attractive as corrosion inhibitors because of their low cost, stability and environmental compatibility. The polymers through their functional groups form complexes with metal ions. On the metal surface these complexes occupy a large surface area thereby blanketing the surface and protecting the metal from corrosion. Surfactants, which have a remarkable ability of influencing the surfaces and interfaces, have shown a significant role in the inhibition of acid corrosion of mild steel. Surfactants have been used as corrosion inhibitors either alone or in combination with other compounds to improve their performance as inhibitors. A survey of literature indicates that the addition of halide ions to the polymers can synergistically improve their corrosion inhibition efficiency. However, corrosion inhibition effect of polymers in presence of surfactants perhaps has yet not been reported. Polymers are likely to interact with the surfactants to form complex structure and help to adhere to mild surface and thus offer greater resistance to corrosion.

The work presented in this thesis deals with the corrosion inhibition behavior of different polymers (both natural and synthetic) separately and in combination with very low concentration of the anionic and cationic surfactants on mild steel in 0.1M
H₂SO₄ solutions. The aim of the surfactants addition was to improve the corrosion inhibition behavior of environment friendly polymers as corrosion inhibitor for mild steel corrosion in acidic medium. The concentration of surfactants was intentionally kept low so that the green nature of polymers is least influenced. The natural polymers considered for the investigations are starch (polysaccharides) and gum acacia (GA) whereas synthetic polymers considered for investigation are polyvinyl alcohol (PVA) and polyethylene glycol (PEG). The surfactants subjected to investigation include both anionic and cationic surfactants. The anionic surfactants include: sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) whereas the cationic surfactants include: cetyltrimethyl ammonium bromide (CTAB) and cetyl pyridinium chloride (CPC). The techniques used are weight loss measurements, solution analysis of metal ions, potentiodynamic polarization measurements, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), atomic force microscopy (AFM) and thermodynamic/kinetic parameters. The breakup of the work contained in various chapters is as follows:

Chapter I

This chapter deals with the general introduction. The general introduction briefly describes the fundamentals of corrosion which includes the definition of corrosion and its importance, cost of corrosion, corrosion reactions, corrosion measurements methods, types of corrosion and method of corrosion control. It presents an exhaustive literature survey exploiting green compounds including natural and synthetic polymers as corrosion inhibitor for mild steel in acid solutions. Except for some early pioneering research papers, the thesis include literature survey from the selected research papers, reviews and reports published on the subject during the
last three decades. Special emphasis has been laid to the work which has direct or indirect bearing on the studies presented in this thesis. It might be possible that some results of the important studies have been left unquoted quite inadvertently, yet there was absolutely no intension to undermine those works.

Chapter II

This chapter deals with the experimental details which includes the materials and methods used during the experimental work. The details of corrosion tests which have been undertaken to investigate the inhibition behavior of polymers and surfactant additives have also been explained in this chapter.

Chapter III

The work presented in this chapter deals with the corrosion inhibition behavior of starch alone and in presence of surfactants, sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB) on mild steel in 0.1M H₂SO₄ solution at 30-60°C. The corrosion inhibition efficiency of starch in acid solution alone and in presence of SDS and CTAB was determined using weight loss and potentiodynamic polarization measurements. The surface morphology of the mild steel before and after immersion in 0.1M H₂SO₄ solution was also examined using SEM. The mode of adsorption of inhibitor molecules on mild steel surface was also elucidated by determination of thermodynamic/kinetic parameters.

Chapter IV

This chapter deals with the corrosion inhibition behavior of polyvinyl alcohol (PVA), surfactants sodium dodecyl sulfate (SDS) and cetyl pyridinium chloride (CPC) and PVA-surfactant mixture on mild steel in 0.1M H₂SO₄ in the temperature range of 30-60°C. The corrosion performance of additives on mild steel corrosion was
investigated by weight loss method and potentiodynamic polarization techniques. To determine if the corrosion inhibition is due to the formation of a protective film by adsorption of inhibitors scanning electron spectroscopy (SEM) has also been performed on the corroded mild steel specimens. The mode of adsorption of inhibitor molecules on mild steel surface was also elucidated by determination of thermodynamic/kinetic parameters.

Chapter V

This chapter deals with the corrosion inhibition behavior of gum acacia (GA) with surfactants mixture. The corrosion behavior of mild steel in 0.1M H₂SO₄ in absence and presence of different concentrations of GA alone and in combination with surfactants SDBS and CTAB, was studied in the temperature range of 30-60°C using weight loss measurement and solution analysis of iron ions. The corrosion protection of mild steel by GA and surfactants additives was confirmed by scanning electron spectroscopy (SEM) and atomic force microscopy (AFM) techniques and determination of thermodynamic/kinetic parameters.

Chapter VI

This chapter presents the results of the investigation concerning with the corrosion inhibition behavior of polyethylene glycol (PEG) and surfactants (SDBS and CTAB) additives on mild steel corrosion in 0.1M H₂SO₄ in the temperature range of 30-60°C. The corrosion performance of the additives was investigated by weight loss measurements, solution analysis of iron ions, scanning electron spectroscopy (SEM), energy dispersive X-ray analysis (EDAX) and atomic force microscopy (AFM) techniques.
Chapter 2

Materials and Methods
2. MATERIALS AND METHODS

2.1 Chemical Used

The chemicals used in the experimental work were all A.R. grade products. Their names and make are given in Table 2.1

2.2 Test Specimens

The specimens of size “2.5 × 2.0 × 0.03 cm” were press cut from the commercially obtained mild steel sheet and utilized in weight loss experiments. For electrochemical experiments the dimension of working electrode is 1 cm². The mild steel coupons having composition (weight %) 0.19% C, 0.055% Si, 0.366% Mn, 0.069% P, 0.087% S, 0.074% Ni, 0.075% Cr, 0.11% Mo and balance Fe or 0.12% C, 0.455% Mn, 0.016% P, 0.002% S, 0.239% Ni, 0.142% Cr, 0.108% Mo, 0.032% Cu, 0.017% Al, 0.033% V, and the balance Fe were used for corrosion inhibition studies. The chemical composition of specimens was obtained by emission spectrophotometer (OES).

2.3 Test Solutions

0.1M H₂SO₄ solution was used for the evaluation of corrosion inhibition behavior of different types of polymers, surfactants and polymer-surfactant additives on the mild steel. The polymers used in the experiments include starch, polyvinyl alcohol (PVA) [molecular weight approximately 125000 g mol⁻¹], gum acacia (GA) and polyethylene glycol (PEG) [molecular weight approximately 4000 g mol⁻¹]. The surfactants used during the experiments include: cetyltrimethyl ammonium bromide (CTAB) [molecular weight 364.46 g mol⁻¹], cetyl pyridinium chloride (CPC)
[molecular weight 358.0 gmol⁻¹], sodium dodecyl sulphate (SDS) [molecular weight 288.38 gmol⁻¹], and sodium dodecyl benzene sulphonate (SDBS) [molecular weight 348.48 gmol⁻¹]. The above chemicals were used as received. Stock solutions of 2000 ppm of polymers as well as surfactants were prepared in 0.1M H₂SO₄ and the desired concentration were obtained by appropriate dilution. The concentration of polymers and surfactants in the solution ranges from 1 to 1500 ppm. All solutions were made using double distilled water.

The molecular structure of the starch, PVA, GA, PEG, CTAB, CPC, SDS and SDBS is given in Figures 2.1-2.8.

2.4 Corrosion Inhibition Studies

The corrosion inhibition behavior of different types of polymers at varying concentrations separately and in combination with fixed and very low concentration of cationic surfactants, cetyltrimethyl ammonium bromide (CTAB), cetyl pyridinium chloride (CPC) and anionic surfactants, sodium dodecyl sulphate (SDS), and sodium dodecyl benzene sulphonate (SDBS) on mild steel in 0.1M H₂SO₄ solution were studied using weight loss, chemical analysis of solution, and potentiodynamic polarization measurements. The surface morphology of the specimens was studied using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and atomic force microscopy (AFM).

2.4.1 Weight loss measurements

The specimens of required dimension were press cut from the mild steel sheet. A hole of 1 mm diameter was made near the edge of the specimen for hooking. The specimens were abraded with a series of emery papers, washed with double-distilled
water, degreased with acetone or absolute ethanol, dried in air and weighed using Sartorius electronic microbalance. Before any experiment, the specimens were prepared as above and used with no further storage. After accurate weighing, the freshly prepared mild steel specimens were immersed in 250 ml beakers containing 200 ml of test solutions maintained at 30-60°C using a thermo-stated water bath. To avoid crevice corrosion the specimens were hanged in the test solution with the help of nylon thread. The experimental conditions were controlled in order to ensure reproducible results. After completion of immersion, the steel specimens were taken out and washed with running water. The corrosion product was removed mechanically by rubbing the steel surface with brush. The steel specimen was then dried and loss in weight was accurately recorded by weighing. The weight loss taken was the difference between the weight at a given time and the original weight of the specimen. The specimens were immersed in triplicate and the average corrosion rate was calculated. The uncertainty for triplicate measurements was less than 5%. All the weight loss experiments were performed for duration of 6 h, as per ASTM designation G1-90 [209]. The corrosion rates were determined using the following equation:

\[
\text{Corrosion rate (mpy)} = \frac{534 \ W}{\rho \ A \ t}
\]  

(2.1)

where \( W \) is weight loss in mg, \( \rho \) is the density of specimen in g/cm\(^3\), \( A \) is the area of specimen in sq. in and \( t \) is exposure time in h.

The % inhibition efficiency (IE) was calculated by using the following equation:

\[
(\%\text{IE}) = \left( \frac{CR_0 - CR}{CR_0} \right) \times 100
\]

(2.2)
where CRo and CRi are the corrosion rates of mild steel in the absence and presence of the inhibitor, respectively.

### 2.4.2 Chemical analysis of solution

In order to confirm the results of weight loss measurements the corrosion rates of mild steel were also estimated by determination of total iron ions (Fe²⁺/Fe³⁺) entered into the test solution during the course of corrosion [210, 211]. The analysis was performed spectrophotometrically (Spectrophotometer model: SPECTRONIC 20D+; Thermo scientific, India) using a calibration curve prepared from standard solutions. 1,10-phenanthroline was used to produce a strongly colored complex with Fe (II) ions. Hydroxyl amine (HCl salt) was added as a reducing agent before color is developed to provide a measure of total Fe ions present into the solution. The corrosion rates were calculated using the following relationship:

\[
\text{Corrosion rate} = \frac{m}{s \times t} \text{ (gm}^{-2} \text{h}^{-1})
\]  

(2.3)

where \(m\) is the metal corroded calculated from total ion content determined in the test solution, \(s\) is the area of test metal in m² and \(t\) is the exposure time in hours.

### 2.4.3 Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were performed using a conventional three electrode cell assembly, using an EG&G Potentiostat/Galvanostat, model 263A. The experiments were carried out using Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and mild steel specimens as working electrode. The working electrode was polished with different grades of
emery paper washed with double distilled water and finally degreased with acetone. Before starting the measurements, the specimens were immersed in the test solution until a steady-state potential was reached. All tests were performed at temperature 30 ± 1°C under unstirred conditions without deaeration. The polarization studies were carried out from a potential of -250 to 250 mV with respect to the steady-state potential at a scan rate of 0.166 mV/s. The linear Tafel segments of the anodic and cathodic curves were extrapolated to obtain corrosion potential (E_{corr}) and corrosion current densities (I_{corr}). The IE was calculated from the measured I_{corr} values using the relationship:

\[
(\%\text{IE}) = \frac{i_{corr}^{0} - i_{corr}}{i_{corr}^{0}} \times 100
\]

where, \(i_{corr}^{0}\) is corrosion current density in the absence of inhibitor and \(i_{corr}\) is corrosion current density in the presence of inhibitor.

2.4.4 Surface morphological studies

2.4.4.1 Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDAX) analysis

The surface morphology of mild steel specimens immersed in uninhibited and inhibited acid solution was evaluated using SEM (Model: JEOL JSM-6510LV) with an EDAX (INCA, Oxford) attachment. To study the surface morphology of mild steel, freshly polished specimens were examined in optical microscope prior to initiation of any corrosion reaction to find out any surface defects, such as pit or noticeable irregularities like cracks etc. Only those specimens, who had a smooth pit-free surface, were subjected to immersion. After completion of immersion the tests
specimens were thoroughly washed with double distilled water, dried and then subjected to SEM and EDAX analysis.

2.4.4.2 Atomic force microscopy (AFM)

The surface morphology of mild steel specimens immersed in uninhibited and inhibited acid solution was also evaluated using AFM (Model: Innova SPM, Veeco or Bruker Innova). AFM is a powerful technique to characterize surface morphology at nano to microscale and has become a new choice to study the influence of inhibitor on the generation and the progress of the corrosion at the metal/solution interface. The mild steel specimens were immersed in 0.1M H₂SO₄ solution without inhibitor, with inhibitor, and inhibitor-surfactant mixtures and were examined by AFM. Again only those specimens, who had a smooth pit-free surface, were subjected to immersion. After completion of the immersion specimens were thoroughly washed with double distilled water, dried and then subjected to AFM examination.

2.5 Calculation of Thermodynamic Parameters

2.5.1 Activation energy

The corrosion rates of mild steel specimen in the absence and presence of polymers, surfactants and polymers in combination with surfactants in 0.1M H₂SO₄ was determined at the temperature range of 30-60°C. In order to elucidate the inhibitive properties of the inhibitors, the apparent activation energy (Eₐ) for the corrosion process in the absence and presence of inhibitors was evaluated from the slope of the plot of logarithm of corrosion rate (log CR) versus reciprocal of absolute temperature (1/T), (Arrhenius equation) given by relationship:
where \( \text{CR} \), is the corrosion rate, \( A \), is the Arrhenius constant, \( E_a \), is the apparent activation energy, \( R \), is the molar gas constant and \( T \), is the absolute temperature.

2.5.2 Enthalpy and entropy of adsorption

The enthalpy of adsorption, \( \Delta H \) and entropy of adsorption, \( \Delta S \) of corrosion process was evaluated from the effect of temperature on corrosion rate. The enthalpy of adsorption, \( \Delta H \) and entropy of adsorption, \( \Delta S \) was obtained by alternative formulation of Arrhenius equation also called transition state plot which is given by the following equation:

\[
\text{CR} = \frac{RT}{Nh} \exp \left( \frac{\Delta S}{R} \right) \exp \left( -\frac{\Delta H}{RT} \right)
\]  

(2.6)

where \( h \), is the Planck’s constant, \( N \) is the Avogadro’s number, \( R \) is the molar gas constant and \( T \) is the absolute temperature. From the slope \(-\frac{\Delta H}{2.303 R}\) and intercept \( \log \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S}{2.303 R} \right) \) of the linear plots of \( \log (\text{CR}/T) \) versus \( 1/T \), \( \Delta H \) and \( \Delta S \) respectively were obtained.

2.5.3 Free energy of adsorption

The plots of \( C/\theta \) against \( C \) are drawn which is characteristics of Langmuir adsorption isotherm given by the following equation:

\[
\frac{C}{\theta} = \frac{1}{k} + C
\]  

(2.7)
where \( \theta \) is the degree of surface coverage, \( K \) is the adsorptive equilibrium constant of the adsorption process and \( C \) is the inhibitor concentration. The value of \( K \) is related to the free energy of adsorption, \( \Delta G_{ads} \) by the following equation:

\[
K_{ah} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)
\]  

(2.8)

where \( R \) is the gas constant and \( T \) the absolute temperature. The value of 55.5 is the concentration of water in solution expressed in molL\(^{-1}\).

The free energy of adsorption, \( \Delta G_{ads} \) was also obtained from the intercept of plot of log (\% IE) versus log \( C \) using the following equation:

\[
\log C' = \log \left(\frac{\theta}{1-\theta}\right) - \log B
\]  

(2.9)

where, \( \log B = -1.74 - \frac{\Delta G_{ads}}{2.303RT} \) and \( C' \) is the concentration of the system studied.

### 2.5.4 Heat of adsorption

The value of heat of adsorption (\( Q_{ads} \)) for inhibitors and inhibitors in combination with surfactants at the metal surface was determined by plotting log \( \left(\frac{\theta}{1-\theta}\right) \) versus 1/T. From the slope of the linear plot, heat of adsorption, \( Q_{ads} \) was obtained.

\[
Slope = -\frac{Q_{ads}}{2.303R}
\]  

(2.10)
2.6 Determination of Synergistic Parameter

The synergism parameter, $S_i$ for the interaction of polymers and surfactants was estimated using the following equation initially proposed by Aramaki and Hackermann [212].

$$S_i = \frac{1 - I_{1,2}}{I_1 + I_2 - 1}$$

(2.11)

where $I_{1,2} = (I_1 + I_2)$, $I_1$ and $I_2$ is IE observed for polymers and surfactants respectively, acting alone, and $I_{1,2}$ is the experimentally observed IE for the polymers in combination with the surfactants. $S_i$ approaches 1 when no interaction between the polymer and the surfactant exist, while $S_i > 1$ points to a synergistic effect. In the case of $S_i < 1$, the antagonistic interaction prevails, which may be attributed to competitive adsorption.
### Table 2.1

Name and make of chemicals used in all the experiments

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name</th>
<th>Make</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Starch soluble extra pure</td>
<td>Merck, India</td>
</tr>
<tr>
<td>2</td>
<td>Polyvinyl alcohol (PVA)</td>
<td>CDH product</td>
</tr>
<tr>
<td>3</td>
<td>Gum acacia (GA)</td>
<td>Merck, India</td>
</tr>
<tr>
<td>4</td>
<td>Polyethylene glycol (PEG)</td>
<td>Merck, India</td>
</tr>
<tr>
<td>5</td>
<td>Cetyltrimethyl ammonium bromide (CTAB)</td>
<td>Merck, India</td>
</tr>
<tr>
<td>6</td>
<td>Cetyl pyridinium chloride (CPC)</td>
<td>Himedia, India</td>
</tr>
<tr>
<td>7</td>
<td>Sodium dodecyl sulphate (SDS)</td>
<td>Merck, India</td>
</tr>
<tr>
<td>8</td>
<td>Sodium dodecyl benzene sulphonate (SDBS)</td>
<td>Himedia, India</td>
</tr>
<tr>
<td>9</td>
<td>Ammonium ferrous sulphate</td>
<td>Qualigens</td>
</tr>
<tr>
<td>10</td>
<td>1,10- phenanthroline</td>
<td>CDH product</td>
</tr>
<tr>
<td>11</td>
<td>Hydroxyl amine hydrochloride</td>
<td>CDH product</td>
</tr>
<tr>
<td>12</td>
<td>Sodium acetate anhydrous</td>
<td>CDH product</td>
</tr>
<tr>
<td>13</td>
<td>Sulphuric acid</td>
<td>Merck, India</td>
</tr>
<tr>
<td>14</td>
<td>Acetone</td>
<td>Merck, India</td>
</tr>
</tbody>
</table>
Figure 2.1 Molecular structure of the starch

Figure 2.2 Molecular structure of the polyvinyl alcohol
Figure 2.3 Molecular structures of the gum acacia

Figure 2.4 Molecular structure of the polyethylene glycol
Figure 2.5 Molecular structure of the cetyl trimethyl ammonium bromide

Figure 2.6 Molecular structure of the cetyl pyridinium chloride
Figure 2.7 Molecular structure of the sodium dodecyl sulphate

Figure 2.8 Molecular structure of the sodium dodecyl benzene sulphonate
Chapter 3

Inhibition of Mild Steel Corrosion Using Starch (Polysaccharide) and Synergistic Surfactants Additives
3. RESULTS AND DISCUSSION

3.1 Weight Loss Measurements

The corrosion of mild steel in 0.1M H₂SO₄ in the absence and presence of starch (polysaccharide) as inhibitor was studied using weight loss technique at temperature range of 30-60°C. The calculated value of corrosion rates and inhibition efficiency (IE) for the starch at different concentrations and temperatures is shown in Table 3.1. The results are graphically presented in Figure 3.1. From the table it is clearly seen that the corrosion rates are reduced in presence of starch as compared to the free acid solution. Also the corrosion rate increased with increase in temperature at all concentrations. The plot of %IE as a function of starch concentrations at 30-60°C reveals that IE increases with increase in starch concentration showing a maximum efficiency of 66.21% at 30°C in presence of starch concentration of 200 ppm; further addition of starch does not significantly influence the IE.

Starch is a natural polymer, available in abundance at low cost, is renewable and biodegradable. Chemically it is a polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. Starch is produced by all green plants as an energy store. It contains two structurally different components namely, amylose (15-20%) and amylopectin (80-85%). The amylose is composed of large linear chain of α (1-4) linked α-D-glucopyanosyl residue, where as amylopectin is a branching form of α-glycon linked by α (1-6) linkages. The molecular structure of the starch (Figure 2.1) suggests that it has strong potential to become an effective corrosion inhibitor. A survey of literature indicates that only few references are available dealing with the
corrosion inhibition effect of starch on aluminum [213, 214] and steel [215]. More recently, modified cassava starches were evaluated as corrosion inhibitor for carbon steel under alkaline conditions in 200 ppm NaCl solutions [72]. The starches were found to show corrosion inhibitive properties; their protection level depended on the type and amount of active groups present in the molecules. Considering the present investigation, the inhibition of mild steel corrosion in the presence of starch could be attributed to the adsorption of the compound on to mild steel surface, which blocks the metal and thus do not permit the corrosion process to take place. Starch can be adsorbed by the interaction between the lone pair of electrons of the oxygen atom and the steel surface. The presence of d π vacant orbital of low energy in the iron atom, as observed in transition group metals, facilitates the adsorption process. In acid medium starch may be partially hydrolyzed into simpler carbohydrates but the products with higher hydrophilicity than starch is likely to go into the bulk water. Since the hydrolysis is quite slow only negligible starch molecules are expected to hydrolyze and desorbs from the steel surface. Also, the starch in bulk water may occupy the steel surface as the molecules are in dynamic equilibrium. So, even after slow hydrolysis, inhibition by starch is effective. The increased IE with increasing starch concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film [216]. A decrease in IE with increasing temperature suggests possible desorption of some of the adsorbed starch molecules from the metal surface at higher temperatures. This behavior shows that the starch was physically adsorbed on the metal surface [217]. As the temperature increases the quantity of equilibrium of adsorption decreases [218] and as a result, the plot of higher temperatures is below the lower ones. This is clearly
demonstrated in Figure 3.1 which shows that starch is physically adsorbed on the steel surface since the plots of higher temperatures are under that of lower ones. The decrease in IE with increasing temperature may be due the fact that most effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the starch to be adsorbed on the steel surface.

To observe the effect of surfactants sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) on the corrosion inhibition behavior of starch, the corrosion of mild steel in 0.1M H₂SO₄ in absence and presence of varying concentration of starch in combination with SDS (5 ppm) and CTAB (1 ppm) was separately studied in the temperature range of 30-60°C by weight loss technique. The results are shown in Tables 3.2 and 3.3. It is observed that the corrosion rates of mild steel in 0.1M H₂SO₄ in presence of starch in combination with surfactants is further reduced in comparison to starch alone. Plots of IE versus concentration of starch in combination with surfactants at 30-60°C are shown in Figures 3.2 and 3.3. The anionic SDS binds with starch through electrostatic interaction, thus helps to adsorb at the metal surface more firmly and display higher IE. The IE of starch in presence of 1 ppm of CTAB is also higher than the starch alone. It may be due to the adsorption of starch to the metal surface by binding with CTAB as co-ions or through hydrophobic interaction. The effect of surfactants on the IE of starch in 0.1M H₂SO₄ appears to be synergistic in nature.

3.2 Synergism Considerations

Synergism is an important phenomenon in corrosion inhibition processes and serves as a basis for many corrosion inhibitor formulations. By taking advantage of
synergism the amount of inhibitor applied can be decreased or an environmental friendly but less effective corrosion inhibitor can be used more effectively. Synergism of corrosion inhibition is either due to the interaction between the constituents of inhibitors or due to interaction between the inhibitor and one of the ions present in the aqueous medium. The values of the synergism parameter for the various concentrations of starch with surfactant additives were calculated from the gravimetric data at 30-60°C using the relationship given by equation 2.11. The results are presented in Tables 3.4 and 3.5. The synergism parameter $S_1$ is found to be greater than unity indicating that the enhanced IE of starch caused by the addition of surfactants is only due to synergism. The addition of a very small amount of surfactants can improve the adsorption of starch on the mild steel.

3.3 Adsorption Considerations

The adsorption of organic compounds on metal surfaces can be described by two main types of interactions namely, physical adsorption and chemical adsorption. These adsorptions are dependent on the electronic structure of the metal, the nature of the electrolyte and the chemical structure of the organic compounds. The character of adsorption of starch alone and starch in combination with SDS and CTAB was elucidated from the values of degree of surface coverage ($\theta$) calculated from the weight loss data. Attempts were made to fit the $\theta$ values to various adsorption isotherms but best results were obtained for Langmuir adsorption isotherm given by equation 2.7. In the equation $\theta$ is the degree of surface coverage; $K$ is the equilibrium constant of the adsorption process and $C$ is the starch concentration. The plots of $C/\theta$ versus $C$ for mild steel corrosion in 0.1M $H_2SO_4$ for starch alone and starch in combination with SDS and CTAB at temperature 30-60°C is shown in Figures 3.4-3.6. A linear correlation of slope close to
unity suggest that adsorption of starch alone and starch in combination with SDS and CTAB on mild steel interface obeys Langmuir adsorption isotherm at all the temperatures studied.

3.4 Effect of Temperature

The corrosion of mild steel was studied in the temperature range of 30-60°C in the absence and presence of starch, surfactants and starch in combination with the surfactants. The logarithm of corrosion rate (log CR) versus reciprocal of absolute temperature (1/T) for 0.1M H₂SO₄ is presented for blank, starch, surfactants and starch-surfactant mixtures in Figure 3.7. Linear plot was obtained which indicates that it follows Arrhenius equation [219] given by the equation 2.5. The values of activation energy Eₐ obtained from the slope of the linear plot are presented in Table 3.6. The increase in Eₐ values in presence of the additives compared to the blank indicate the decrease in adsorption process of the inhibitor on the mild steel surface with rise in temperature and a corresponding increase in reaction rate of greater area of metal that is exposed to acid [220]. This shows physical adsorption [221].

Enthalpy of adsorption, ΔH and entropy of adsorption, ΔS for the corrosion of mild steel in 0.1M H₂SO₄ in the presence of starch, surfactants and starch-surfactant mixtures was obtained by the relationship given in the equation 2.7. Figure 3.8 shows the plot of log (CR/T) versus 1/T for blank, starch and starch in combination with surfactants. Linear plot was obtained and from the slope \(-\frac{\Delta H}{2.303R}\) and intercept \(\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{2.303R}\right)\) of the linear plot, the values of ΔH and ΔS, respectively
were obtained. The calculated values are presented in Table 3.6. The enthalpy of adsorption increases in presence of the additives compared to the free acid solution; this indicates physical adsorption. The values of $\Delta S$ are positive which indicates a decrease in the system order in the presence of additives [222]. Figure 3.9 shows the plot of \[
\left( \frac{\theta}{1-\theta} \right) \text{versus} \frac{1}{T} \text{for} \text{starch and starch in combination with the surfactants. Linear plot was obtained and from the slope } \left[ \frac{-Q}{2.303R} \right] \text{of the linear plot, heat of adsorption, } Q_{\text{ads}} \text{ was obtained. The calculated values of } Q_{\text{ads}} \text{ were negative (Table 3.6) indicating that the adsorption of starch, SDS, CTAB and starch-surfactant mixture on mild steel surface is exothermic [223].}
\]

Free energy of adsorption, $\Delta G_{\text{ads}}$ was obtained from the intercept of plot of log %IE versus log inhibitor concentration (log C) and evaluated using the equation 2.9. The calculated values of $\Delta G_{\text{ads}}$ from 30°C to 60°C for the various systems studied are presented in Table 3.6. The $\Delta G_{\text{ads}}$ values obtained are negative which indicate the spontaneous adsorption of the starch and starch in combination with surfactants on the mild steel surface. The value of $\Delta G_{\text{ads}}$ of -40 kJmol$^{-1}$ is usually accepted as a threshold value between chemisorptions and physisorption. The values of $\Delta G_{\text{ads}}$ obtained in this study are below -40 kJmol$^{-1}$ (Between -9.96 and -35.54 kJmol$^{-1}$). This is consistent with electrostatic interactions between the charged molecules and the charge metals, which are indicative of physical adsorption.
3.5 Potentiodynamic Polarization Measurements

The potentiodynamic polarization curves for the corrosion of mild steel in 0.1M H$_2$SO$_4$ in absence and presence of varying concentration of starch and starch in combination with 5 ppm of SDS and 1 ppm of CTAB are shown in Figures 3.10 and 3.11. The values of electrochemical parameters as deduced from these curves e.g., corrosion potential (E$_{corr}$) corrosion current density (i$_{corr}$), the anodic tafel slope ($\beta$a), the cathodic tafel slope ($\beta$c), corrosion rate and %IE are shown in Table 3.7.

The study of electrochemical data reveals that the value of i$_{corr}$ continuously decreases in presence of starch. The maximum IE of about 61.75% was observed at a concentration of 200 ppm indicating that a higher coverage of starch on steel surface is obtained in the solution with highest concentration of inhibitor. The values of E$_{corr}$ shifts to more positive value compared to the blank, indicating that starch acts more anodic than cathodic inhibitor. The addition of 5 ppm of SDS to varying concentration of starch improved the IE of starch significantly. However, the effect of SDS is more pronounced at lower concentrations of starch. The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

3.6 Surface Analysis

The surface morphology of the mild steel before and after immersion in 0.1M H$_2$SO$_4$ solution was also examined using scanning electron microscopy (SEM). Surface photomicrographs of the blank mild steel and steel exposed to 0.1M H$_2$SO$_4$ in absence and presence of starch and starch-CTAB mixture were obtained to establish if the inhibition by additives is due to the formation of a protective film by adsorption. The
SEM photomicrographs are shown in Figures 3.12-4.15. Figure 3.12 shows the surface morphology of the mild steel sample prior to immersion in acid solution. Except the scratch marks on the surface produced during polishing with emery papers the surface is free from any noticeable defects. Figure 3.13 shows the photomicrograph of mild steel surface obtained after immersion in uninhibited acid solution. A damaged and heterogeneous surface is observed due to the corrosive action of uninhibited acid. The surface heterogeneity is considerably decreased in the presence of starch (200 ppm) and starch (200 ppm)-CTAB (1 ppm) inhibited acid solution (Figure 3.14 and 3.15). The decrease in the surface heterogeneity is caused by the adsorption of the additives molecules on the mild steel surface which protected the surface from the attack of corrosive acid.

3.7 Conclusions

- Starch showed good performance as corrosion inhibitor for mild steel in 0.1M H₂SO₄, which is further improved in presence of surfactants SDS and CTAB. The effect of surfactants on corrosion inhibition behavior of starch appears to be synergistic in nature.

- Phenomenon of physical adsorption is proposed from the trend of inhibition efficiency with temperature.

- The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir adsorption isotherm at all the concentrations and temperatures studied.
• The results of potentiodynamic polarization measurements show that starch acts more anodic than cathodic inhibitor. The results are consistent with the results of the weight loss measurements.

• The results of SEM studies further confirmed the inhibitive character of the starch and starch-surfactant additives.
Table 3.1

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H₂SO₄ in the absence and the presence of starch at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>Starch conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Blank</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>90.99</td>
<td>294.71</td>
</tr>
<tr>
<td>5</td>
<td>77.22</td>
<td>227.75</td>
</tr>
<tr>
<td>10</td>
<td>71.28</td>
<td>217.18</td>
</tr>
<tr>
<td>50</td>
<td>69.66</td>
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<td>209.53</td>
</tr>
<tr>
<td>200</td>
<td>67.88</td>
<td>200.49</td>
</tr>
<tr>
<td>500</td>
<td>70.74</td>
<td>201.39</td>
</tr>
</tbody>
</table>
Table 3.2

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H$_2$SO$_4$ in the absence and the presence of varying concentration of starch with SDS at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>Starch conc. (ppm)</th>
<th>SDS conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Blank</td>
<td>Blank</td>
<td>200.88</td>
<td>522.74</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>138.96</td>
<td>383.16</td>
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<td>61.40</td>
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<td>62.78</td>
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<td>5</td>
<td>5</td>
<td>65.46</td>
<td>178.14</td>
</tr>
</tbody>
</table>
Table 3.3

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H₂SO₄ in the absence and the presence of varying concentration of starch with CTAB at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>Starch conc. (ppm)</th>
<th>CTAB conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
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83
Table 3.4

Calculated values synergism parameter ($S_i$) for mild steel in 0.1 M $H_2SO_4$ in the presence of varying concentration of starch with SDS at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>Starch conc. (ppm)</th>
<th>SDS conc. (ppm)</th>
<th>Synergism parameter ($S_i$)</th>
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<td></td>
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Table 3.5

Calculated values synergism parameter (S₁) for mild steel in 0.1M H₂SO₄ in the presence of varying concentration of starch with CTAB at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>Starch conc. (ppm)</th>
<th>CTAB conc. (ppm)</th>
<th>Synergism parameter (S₁)</th>
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<tbody>
<tr>
<td></td>
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Table 3.6

Calculated values of kinetic/thermodynamic parameters for mild steel in 0.1M H₂SO₄ in the absence and the presence of starch and starch-surfactant mixtures from weight loss measurements

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conc. (ppm)</th>
<th>Eₐ  (kJmol⁻¹)</th>
<th>ΔH  (kJmol⁻¹)</th>
<th>ΔS  (Jmol⁻¹K⁻¹)</th>
<th>Q   (kJmol⁻¹)</th>
<th>ΔG₂₉₈ (kJmol⁻¹)</th>
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<tbody>
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<td></td>
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<td>70.19</td>
<td>27.79</td>
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<td>71.90</td>
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<td>-17.73</td>
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<td>-30.54</td>
</tr>
<tr>
<td>Starch+SDS</td>
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<td>76.89</td>
<td>74.27</td>
<td>34.68</td>
<td>-19.84</td>
<td>-35.54</td>
</tr>
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<td>-27.30</td>
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<td>-32.91</td>
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<td></td>
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<td></td>
<td>-14.95</td>
</tr>
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</table>
Table 3.7

Potentiodynamic polarization parameters for corrosion of mild steel in 0.1M H$_2$SO$_4$ in the absence and the presence of various concentrations of starch and starch-SDS
Mixtures at 30°C

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conc. (ppm)</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (μA/cm$^2$)</th>
<th>$\beta_a$ (mV)</th>
<th>$\beta_c$ (mV)</th>
<th>CR (mpy)</th>
<th>(%IE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Blank</td>
<td>-667.318</td>
<td>4194.00</td>
<td>265.164</td>
<td>301.354</td>
<td>382.70</td>
<td>-----</td>
</tr>
<tr>
<td>SDS</td>
<td>5</td>
<td>-589.965</td>
<td>3458.00</td>
<td>165.884</td>
<td>237.081</td>
<td>319.70</td>
<td>17.55</td>
</tr>
<tr>
<td>Starch</td>
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<td>1906.00</td>
<td>158.690</td>
<td>194.560</td>
<td>174.30</td>
<td>54.55</td>
</tr>
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<td>Starch</td>
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<td>1850.00</td>
<td>167.666</td>
<td>204.066</td>
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<td>55.89</td>
</tr>
<tr>
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<td>1604.00</td>
<td>188.320</td>
<td>221.253</td>
<td>151.80</td>
<td>61.75</td>
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<tr>
<td>Starch+SDS</td>
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<td>257.634</td>
<td>351.972</td>
<td>145.90</td>
<td>62.16</td>
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<td>Starch+SDS</td>
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<td>-577.109</td>
<td>1983.00</td>
<td>181.419</td>
<td>229.033</td>
<td>183.30</td>
<td>52.72</td>
</tr>
<tr>
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<td>1754.00</td>
<td>179.350</td>
<td>215.878</td>
<td>161.30</td>
<td>58.18</td>
</tr>
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</table>
Figure 3.1  Plots of inhibition efficiency (%IE) against starch concentration for mild steel in 0.1M H₂SO₄ at different temperatures

Figure 3.2  Plot of inhibition efficiency (%IE) against (starch+5 ppm SDS) concentration for mild steel in 0.1M H₂SO₄ at different temperatures
Figure 3.3  Plots of inhibition efficiency (%IE) against (starch+1 ppm CTAB) concentration for mild steel in 0.1 M H$_2$SO$_4$ at different temperatures

Figure 3.4  Langmuir adsorption isotherm for starch adsorbed on mild steel surface in 0.1M H$_2$SO$_4$ at different temperatures
Figure 3.5  Langmuir adsorption isotherm for (starch+5 ppm SDS) adsorbed on mild steel surface in 0.1M H$_2$SO$_4$ at different temperatures

Figure 3.6  Langmuir adsorption isotherm for (starch+1 ppm CTAB) adsorbed on mild steel surface in 0.1M H$_2$SO$_4$ at different temperatures
Figure 3.7  Adsorption isotherm plot for log CR versus 1/T in the absence and presence of starch, SDS, CTAB and starch in combination with SDS/CTAB

Figure 3.8  Adsorption isotherm plot for log CR/T versus 1/T in the absence and presence of starch, SDS, CTAB and starch in combination with SDS/CTAB
Figure 3.9 Adsorption isotherm plots for log (θ/1-θ) versus 1/T in the absence and presence of starch, SDS, CTAB and starch in combination with SDS/CTAB
Figure 3.10  Potentiodynamic polarization curves for mild steel in 0.1M H₂SO₄ in the absence and presence of various concentration of starch (1) Blank, (2) Starch 5 ppm, (3) Starch 100 ppm and (4) Starch 200 ppm
Figure 3.11  Potentiodynamic polarization curves for mild steel in 0.1M H₂SO₄ in the absence and presence of various concentration of additives (1) Blank, (2) SDS 5 ppm, (3) Starch 5 ppm+SDS 5 ppm, (4) Starch 100 ppm+SDS 5 ppm and (5) Starch 200 ppm+SDS 5 ppm
Figure 3.12 SEM photomicrograph of the surface of mild steel before immersion in 0.1M H₂SO₄ solution

Figure 3.13 SEM photomicrograph of the surface of mild steel after immersion in 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 3.14  SEM photomicrograph of the surface of mild steel after immersion in (0.1M H₂SO₄+200 ppm starch) solution for 6 h at 30°C

Figure 3.15  SEM photomicrograph of the surface of mild steel after immersion in (0.1M H₂SO₄+200 ppm starch+1 ppm CTAB) solution for 6 h at 30°C
Chapter 4

Inhibition of Mild Steel Corrosion Using Polyvinyl Alcohol and Synergistic Surfactants Additives
4. RESULTS AND DISCUSSION

4.1 Weight Loss Measurements

The corrosion of mild steel in 0.1M H₂SO₄ in the absence and presence of polyvinyl alcohol (PVA), surfactants sodium dodecyl sulfate (SDS) and cetyl pyridinium chloride (CPC) and SDS and CPC in combination with PVA was studied using weight loss technique at temperature 30-60°C. The variation of weight loss with time (days) for mild steel dissolution in 0.1M H₂SO₄, in the presence of surfactants, PVA and PVA in combination with surfactants at temperature 30°C is shown in Figure 4.1. Inspection of the figure revealed that the weight loss of mild steel decreases upon addition of inhibitor and surfactants to the acid solution as compared to the blank and the highest weight loss reduction was obtained with PVA-CPC mixture. The corrosion inhibition of mild steel in 0.1M H₂SO₄ at 30-60°C in absence and presence of different concentrations of PVA and surfactants was studied separately using weight loss technique and the data obtained after 6 h of immersion have been recorded in Table 4.1 and 4.2 respectively. The corrosion rates are reduced in presence of PVA as compared to the free acid solution. Also the corrosion rate increased with increase in temperature at all concentrations studied. The plot of inhibition efficiency (%IE) as a function of PVA concentrations at 30-60°C is shown in Figure 4.2. The figure reveals that IE increases with increase in PVA concentration showing a maximum IE of 81.41% at 30°C at PVA concentration of 100 ppm; further increase in PVA concentration does not significantly affect the corrosion rate. The increased IE with increasing PVA concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective
film. A decrease in IE with increasing temperature suggests possible desorption of some of the adsorbed PVA molecules from the metal surface at higher temperatures. This behavior shows that the PVA was physically adsorbed on the metal surface. As the temperature increases the quantity of equilibrium of adsorption decreases [218] and as a result, the plot of higher temperatures is below the lower ones. This is clearly demonstrated in Figure 4.2 which shows that PVA is physically adsorbed on the steel surface as the plots of higher temperatures are under that of lower ones. The decrease in IE with increasing temperature may be due the fact that most effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the PVA to be adsorbed on the steel surface.

PVA is a kind of water-soluble resin produced by polymerization and alcoholysis of vinyl acetate. It is a high polymer (Figure 2.2) with excellent characters to dissolve easily in water but not to dissolve in common organic solvent and organic acids, and with excellent film-forming property, oil and chemical resistant. The inhibition behavior of PVA on mild steel in 0.1M H₂SO₄ can be explained in terms of the adsorption of its molecules on the surface of steel. It may interact with the corroding steel and affect the corrosion reaction in more than one way. In the acidic medium the PVA can be easily protonated at the OH group and could interact with the corroding steel surface via protonated OH, which can be adsorbed at the cathodic sites and hinder the hydrogen evolution reaction. The oxygen atom carrying two lone pair of electrons could also be adsorbed on the anodic sites of the steel surface and retard the iron electro dissolution. Therefore, PVA is expected to involve both physical and chemical adsorption. However, the variation in the values of %IE with temperature in presence of PVA compared to blank suggested dominant role of physisorption in the
adsorption process. When the surface of steel is saturated with PVA molecules, the further increase in PVA concentration causes desorption from the steel surface and does not significantly affect the corrosion rate.

The surfactants SDS and CPC also exhibit corrosion inhibition of mild steel in 0.1M H₂SO₄. Also the corrosion rate increased with increase in temperature at all concentrations studied (Table 4.2). In presence of SDS, the IE increases with increase in surfactant concentration showing a maximum IE of 93.96% at 30°C at SDS concentration of 50 ppm; further increase in SDS concentration results in a decrease in IE. However, in presence of CPC the maximum IE is observed at CPC concentration of 5 ppm; further increase in CPC concentration does not significantly affect the corrosion rate. To observe the effect of SDS and CPC on the corrosion inhibition behavior of PVA, the corrosion of mild steel in 0.1M H₂SO₄ in absence and presence of varying concentration of PVA in combination with SDS (5 ppm) and CPC (1 ppm) was separately studied in the temperature range of 30-60°C by weight loss measurement. The results are shown in Tables 4.3. Plots of %IE versus concentration of PVA in combination with surfactants at 30-60°C are shown in Figures 4.3 and 4.4. It is observed that the IE of PVA in presence of SDS and CPC is further increased. The observed increase in IE of PVA in presence of SDS and CPC can be explained in terms of the interaction between the PVA and surfactant molecules leading to the improved adsorption on the steel surface. The cationic CP⁺ ions (after ionization of chloride ions) bind with electronegative oxygen atoms of PVA molecules via lone pair of electrons, thus helps to adsorb at the steel surface more firmly and display higher IE. The direct PVA-SDS interaction seems to be unfavorable due to repulsion between the anionic nature of DS⁻ (after ionization of sodium ions) and electron rich-
oxygen atom. However, in acidic solution, the protonated OH may strongly interact with DS’ ions and favor greater adsorption over the steel surface. Additionally, the surfactant molecules also adhere to the steel surface unoccupied by the PVA molecules. The effect of surfactants on the IE of PVA in 0.1M H₂SO₄ appears to be synergistic in nature.

4.2 Synergism Considerations

Synergism is an important phenomenon in corrosion inhibition processes and serves as a basis for many corrosion inhibitor formulations [225]. By taking advantage of synergism the amount of inhibitor applied can be decreased or an environmental friendly but less effective corrosion inhibitor can be used more effectively. Synergism of corrosion inhibition is either due to the interaction between the constituents of inhibitors or due to interaction between the inhibitor and one of the ions present in the aqueous medium. The values of synergism parameter, Sᵢ for the various concentrations of PVA and surfactant additives was calculated from gravimetric data at 30-60°C using the relationship given by equation 2.11. The results are presented in Table 4.4 and 4.5. It can be seen that the values of Sᵢ are greater than 1, which clearly shows that the corrosion inhibition brought about by the PVA and surfactant is synergistic. The addition of a very small amount of surfactant can improve the adsorption of PVA on the mild steel. Sᵢ approaches 1 when no interaction between inhibitor and the surfactant exist, while Sᵢ>1 indicate a synergistic effect. In the case of Sᵢ<1, antagonistic behavior prevails which may be attributed to competitive adsorption.
4.3 Adsorption Isotherms

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reaction. In present study, Langmuir adsorption isotherm was found to be suitable for the experimental findings. The isotherm is already described by equation 2.7. The plots of C/θ versus C for mild steel corrosion in 0.1M H₂SO₄ for PVA alone and PVA in combination with surfactants at temperature 30-60°C is shown in Figures 4.5-4.7. The values of adsorption parameters deduced from the Langmuir adsorption isotherm (linear regression parameters) such as linear regression coefficient, slope and adsorptive equilibrium constants are presented in Table 4.6. A linear correlation of slope close to unity suggests that adsorption of PVA alone and PVA in combination with surfactants on mild steel interface obeys Langmuir adsorption isotherm at all the temperatures studied. The plots shown in the figure are linear (Correlation is 1 or >0.9) but slopes are not equal to unity as could be expected for ideal Langmuir adsorption isotherm equation. The deviation from unity may be explained on the basis of interaction among the adsorbed species on the mild steel surface. The interaction is due to the presence of polar atoms in the inhibitor molecules which are adsorbed on the cathodic and anodic sites of the steel surface. The high values of K indicate that the additives are strongly adsorbed on the steel surface. The values of K for PVA-surfactant mixture is more than the PVA alone, this implies more efficient adsorption of mixed PVA-surfactants and hence better IE. The mixed PVA and CPC is more effective as an inhibitor for steel corrosion than that the mixture of PVA and SDS.
4.4 Effect of Temperature

The adsorption of organic compounds on metal surfaces can be described by two main types of interactions namely, physical adsorption and chemical adsorption. These adsorptions are influenced by the charge of the metal, chemical structure of the inhibitor, the type of the electrolyte and temperature. In order to elucidate the inhibitive properties of the PVA and the temperature dependence on the corrosion rates, the apparent activation energy \( (E_a) \) for the corrosion process in the absence and presence of inhibitor were evaluated from Arrhenius equation given by equation 2.5. The logarithm of corrosion rate \( (\log CR) \) versus reciprocal of absolute temperature \( (1/T) \) for 0.1M H\(_2\)SO\(_4\) for blank, PVA, surfactants and PVA-surfactant mixtures is presented in Figure 4.8. The values of \( E_a \) obtained from the slope of the linear plot are presented in Table 4.7. Other kinetic parameters such as enthalpy of adsorption, \( \Delta H \) and entropy of adsorption, \( \Delta S \) of corrosion process may be evaluated from the effect of temperature. An alternative formulation of Arrhenius equation also called transition state plot is given by equation 2.6. Figure 4.9 shows the plot of \( \log (CR/T) \) versus \( 1/T \) for blank, PVA and PVA in combination with surfactants. Enthalpy and entropy of activation were obtained from the slope \( \left(-\frac{\Delta H}{2.303R}\right) \) and intercept \( \left[\log \left(\frac{R}{Nh}\right) + \left(-\frac{\Delta S}{2.303R}\right)\right] \) of the linear plot, respectively. The calculated values are presented in Table 4.7. Considering the kinetic/thermodynamic parameters for mild steel in 0.1M H\(_2\)SO\(_4\) in absence and presence of PVA, surfactants and PVA-surfactant mixtures. The values of \( E_a \) and \( \Delta H \) in presence of additives are higher than in absence of additives. This is due to an increase of the energy barrier of the corrosion reaction occurring at the steel surface. A change in the value of \( E_a \) in presence of additives
may be due to the modification of the mechanism of the corrosion process in presence of adsorbed inhibitor molecules. In general, higher values of $E_a$ in presence of additives support physical adsorption mechanism whereas an unchanged or lower value of $E_a$ for inhibited systems compared to the blank is indicative of chemisorption mechanism. The inhibitor causing an increase in the values of $E_a$ compared to blank retard the corrosion at ordinary temperature, but the inhibition is diminished at elevated temperature. In the present investigation the value of $E_a$ in presence of additives is higher compared to the blank and hence supports physical adsorption mechanism [221]. The values of $\Delta S$ are more positive in presence of PVA indicating a decrease in the system order [222]. This suggests an increase in the disordering of the inhibited system which took place while going from reactants to activated complex [226]. The more positive values of $\Delta S$ in presence of PVA-surfactant mixtures is again due to more disordering in the inhibited system due to presence of additional surfactants. The enthalpy of adsorption increases in presence of the additives compared to the free acid solution; this indicates physical adsorption. Free energy of adsorption values $\Delta G_{ads}$ were obtained from the equation 2.9 [227]. The calculated values of $\Delta G_{ads}$ from 30°C to 60°C for the various systems studied are presented in Table 4.8. Results obtained indicate that the values of $\Delta G_{ads}$ are negative in all cases indicating that the PVA is strongly adsorbed on the mild steel surface [224]. It is an established fact that values of $\Delta G_{ads}$ around -20 kJmol$^{-1}$ or less indicates physiosorption. The adsorption is attributed to the electrostatic attraction between the charged organic molecules and charged metal surface. The values of $\Delta G_{ads}$ around -40 kJmol$^{-1}$ or more are considered as chemisorptions. However, the values of $\Delta G_{ads}$ between -20 and -40 kJmol$^{-1}$ gives a disputed Judgment about the type of adsorption.
In the present investigation, the values of \( \Delta G_{\text{ads}} \) are in the range of -14.17 to -36.75 \( \text{kJ mol}^{-1} \) suggesting a mixed type of adsorption involving both physiosorption and chemisorption. However, the variation in the values of %IE with temperature and higher values of \( E_a \) in presence of additives compared to blank suggest major contribution of physiosorption in the adsorption process.

### 4.5 Potentiodynamic Polarization Measurements

The potentiodynamic polarization curves for the corrosion of mild steel in 0.1M \( \text{H}_2\text{SO}_4 \) in absence and presence of varying concentration of PVA and PVA in combination with 1 ppm of CPC, are shown in Figures 4.10 and 4.11. The polarization experiments were carried out at room temperature. The values of electrochemical parameters such as corrosion potential (\( E_{\text{corr}} \)), corrosion current density (\( I_{\text{corr}} \)), the anodic Tafel slope (\( \beta_a \)), the cathodic Tafel slope (\( \beta_c \)) calculated using Tafel fit are listed in Table 4.9. In presence of inhibitor the value of corrosion current density is lowered indicating that corrosion of mild steel is inhibited by PVA and surfactants. The maximum IE of about 77.49% was observed at a concentration of 100 ppm indicating that a higher coverage of PVA on steel surface is obtained in the solution with highest concentration of inhibitor. The addition of 1 ppm of CPC to varying concentration of PVA improved the IE of PVA. The IE calculated from corrosion current density for the mixture reaches a considerably high value of 83.10%. There is a change in the values of both \( \beta_a \) and \( \beta_c \) indicating that the corrosion of mild steel in presence of inhibitor is under both anodic and cathodic control. The magnitude of the shift in \( E_{\text{corr}} \) in presence of PVA suggests that it acts as a mixed inhibitor and affects both anodic and cathodic reaction [230]. However, it acts more cathodic than anodic inhibitor. The values of IE obtained from weight loss and
electrochemical methods remain slightly different, this may be due to the fact that IE calculated from weight loss method is an average value whiles the IE obtained from electrochemical method in an instantaneous value. The electrochemical results on the whole, are in good agreement with the weight loss results.

4.6 Surface Analysis

Surface photomicrographs of the blank mild steel and steel exposed to 0.1M H₂SO₄ in absence and presence of PVA and PVA-surfactants mixtures were obtained by means of SEM so as to determine if the mild steel corrosion inhibition is due to the formation of a protective film by adsorption of inhibitor. The SEM photomicrographs are depicted in Figures 4.12-4.16. The surface morphology of the sample before immersion in 0.1M H₂SO₄ solution (Figure 4.12) shows a freshly polished mild steel surface which is free from any noticeable defects such as cracks and pits. The marks on the surface are the streaks made during polishing with emery papers. Figure 4.13 shows the photomicrograph of mild steel surface obtained after immersion in uninhibited 0.1M H₂SO₄. In uninhibited acid solution a damaged and heterogeneous surface is observed. The surface heterogeneity is considerably decreased in the presence of PVA inhibited acid solution (Figure 4.14) which is further decreased in presence of surfactant additives (Figure 4.15-4.16). The decrease in the surface heterogeneity would have been caused by the deposition of the additives molecules on the mild steel surface which protected the surface from the attack of corrosive medium.
4.7 Conclusions

- Polyvinyl alcohol was found to be an efficient corrosion inhibitor for mild steel in 0.1M H₂SO₄. The inhibition efficiency increased with an increase in inhibitor concentration up to 100 ppm and reached a value of 81.41% at 30°C, but decreased with rise in temperature.

- The corrosion process is inhibited by adsorption of the polyvinyl alcohol on the mild steel surface following the Langmuir adsorption isotherm.

- Addition of both surfactants synergistically increased the inhibition efficiency of polyvinyl alcohol.

- The negative free energy of adsorption ΔG_ads indicates strong and spontaneous adsorption of polyvinyl alcohol on the mild steel surface.

- The results of potentiondynamic polarization measurements showed that the polyvinyl alcohol acts as mixed inhibitor. The results are in reasonably good agreement with the weight loss measurements.

- SEM studies further confirm the inhibitive character of the additives.
Table 4.1

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H₂SO₄ in the absence and the presence of PVA at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>PVA conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Blank</td>
<td>817.55</td>
<td>1499.38</td>
</tr>
<tr>
<td>5</td>
<td>179.22</td>
<td>429.88</td>
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<td>157.79</td>
<td>399.36</td>
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<td>151.95</td>
<td>379.38</td>
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<td>394.16</td>
</tr>
<tr>
<td>400</td>
<td>164.94</td>
<td>400.66</td>
</tr>
<tr>
<td>500</td>
<td>168.18</td>
<td>405.85</td>
</tr>
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</table>
Table 4.2
Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H₂SO₄ in the absence and the presence of SDS and CPC at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>Surfactant conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
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</thead>
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<td></td>
<td>30°C</td>
<td>40°C</td>
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<tr>
<td>Blank</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDS</td>
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<td></td>
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<tr>
<td>1</td>
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<td>200</td>
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<tr>
<td>PVA conc. (ppm)</td>
<td>Surfactant conc. (ppm)</td>
<td>Corrosion rate (mpy) 30°C</td>
</tr>
<tr>
<td>-----------------</td>
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<tr>
<td>Blank</td>
<td></td>
<td>817.55</td>
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Table 4.4

Calculated values of synergism parameter ($S_i$) for mild steel in 0.1M H$_2$SO$_4$ in the presence of varying concentration of PVA with SDS at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>PVA conc. (ppm)</th>
<th>SDS conc. (ppm)</th>
<th>Synergism parameter ($S_i$)</th>
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<td>1.171</td>
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Table 4.5

Calculated values of synergism parameter ($S_i$) for mild steel in 0.1M H$_2$SO$_4$ in the presence of varying concentration of PVA with CPC at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>PVA conc. (ppm)</th>
<th>CPC conc. (ppm)</th>
<th>Synergism parameter ($S_i$)</th>
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Table 4.6

The values of linear regression coefficient ($R^2$), slope and adsorptive equilibrium constant ($K$) for mild steel in 0.1M $\text{H}_2\text{SO}_4$ in the presence of PVA and PVA-surfactants mixtures at 30-60°C from weight loss measurements

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<thead>
<tr>
<th>Additives</th>
<th>$R^2$</th>
<th>Slope</th>
<th>$K \times 10^7$</th>
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<td>$50°C$</td>
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<tr>
<td>PVA</td>
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<tr>
<td>PVA+SDS</td>
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<tr>
<td>PVA+CPC</td>
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<td>1.00</td>
<td>0.9997</td>
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Table 4.7

Calculated values of kinetic/thermodynamic parameters for mild steel in 0.1M H₂SO₄ in the absence and the presence of PVA, surfactants and PVA-surfactant mixtures from weight loss measurements

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<thead>
<tr>
<th>Additives</th>
<th>Conc. (ppm)</th>
<th>$E_a$ (kJmol⁻¹)</th>
<th>$\Delta H$ (kJmol⁻¹)</th>
<th>$\Delta S$ (Jmol⁻¹K⁻¹)</th>
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</thead>
<tbody>
<tr>
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<td>43.84</td>
<td>46.48</td>
<td>1.92</td>
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<td>51.68</td>
<td>17.28</td>
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<td>79.80</td>
<td>82.44</td>
<td>106.36</td>
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### Table 4.8

Calculated values of $\Delta G_{\text{ads}}$ for mild steel in 0.1M H$_2$SO$_4$ in the presence of PVA and PVA-surfactant mixtures at 30-60°C from weight loss measurements.

<table>
<thead>
<tr>
<th>Additives</th>
<th>$\Delta G_{\text{ads}}$ (kJmol$^{-1}$)</th>
</tr>
</thead>
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<tr>
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<tr>
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<td>PVA+CPC</td>
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### Table 4.9

The values of electrochemical parameters for corrosion of mild steel in 0.1M H$_2$SO$_4$ in the absence and the presence of various concentrations of PVA and PVA-CPC mixtures at 30°C.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conc. (ppm)</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$I_{\text{corr}}$ ($\mu$A/cm$^2$)</th>
<th>$\beta_a$ (mV)</th>
<th>$\beta_c$ (mV)</th>
<th>(%IE)</th>
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</thead>
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<td>2129.44</td>
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<td>2209</td>
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<td>257.16</td>
<td>83.10</td>
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Figure 4.1  Variation of weight loss with time (days) for the corrosion of mild steel in 0.1M H₂SO₄ in the absence and presence of PVA, surfactants, and PVA-surfactant mixtures at 30°C

Figure 4.2  Plots of inhibition efficiency (%IE) against PVA concentration for mild steel in 0.1M H₂SO₄ at different temperatures
Figure 4.3  Plots of inhibition efficiency (%IE) against (PVA+5 ppm SDS) concentration for mild steel in 0.1M H$_2$SO$_4$ at different temperatures

Figure 4.4  Plots of inhibition efficiency (%IE) against (PVA+1 ppm CPC) concentration for mild steel in 0.1M H$_2$SO$_4$ at different temperatures
Figure 4.5  Langmuir adsorption isotherm for PVA adsorbed on mild steel surface in 0.1M H₂SO₄ at different temperatures

Figure 4.6  Langmuir adsorption isotherm for (PVA+5 ppm SDS) adsorbed on mild steel surface in 0.1M H₂SO₄ at different temperatures
Figure 4.7 Langmuir adsorption isotherm for (PVA+1 ppm CPC) adsorbed on mild steel surface in 0.1M H₂SO₄ at different temperatures

Figure 4.8 Adsorption isotherm plots for log CR versus 1/T in the absence and presence of PVA, SDS, CPC and PVA in combination with SDS/CPC
Figure 4.9 Adsorption isotherm plots for log CR/T versus 1/T in the absence and presence of PVA, SDS, CPC and PVA in combination with SDS/CPC
Figure 4.10 Potentiodynamic polarization curves for mild steel in 0.1M H₂SO₄ in the absence and presence of various concentration of PVA (1) Blank, (2) PVA 5 ppm, (3) PVA 100 ppm and (4) PVA 300 ppm
Figure 4.11  Potentiodynamic polarization curves for mild steel in 0.1M H_2SO_4 in the absence and presence of various concentration of additives (1) Blank, (2) CPC 1 ppm, (3) PVA 5 ppm+CPC 1 ppm, (4) PVA 100 ppm+CPC 1 ppm and (5) PVA 300 ppm+CPC 1 ppm
Figure 4.12  SEM photomicrograph of the surface of mild steel before immersion in 0.1M H₂SO₄ solution

Figure 4.13  SEM photomicrograph of the surface of mild steel after immersion in 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 4.14  SEM photomicrograph of the surface of mild steel after immersion in (0.1M H₂SO₄+200 ppm PVA) solution for 6 h at 30°C

Figure 4.15  SEM photomicrograph of the surface of mild steel after immersion in (0.1M H₂SO₄+200 ppm PVA+5 ppm SDS) solution for 6 h at 30°C
Chapter 5

Inhibition of Mild Steel Corrosion Using Gum Acacia and Synergistic Surfactants Additives
5. RESULTS AND DISCUSSION

5.1 Weight Loss Measurements

The corrosion inhibition of mild steel in 0.1M H\textsubscript{2}SO\textsubscript{4} at 30-60°C in absence and presence of different concentrations of gum acacia (GA), surfactants sodium dodecyl benzene sulphonate (SDBS) and cetyltrimethyl ammonium bromide (CTAB) and GA-surfactants mixture was studied using weight loss technique and the data obtained after 6 h of immersion have been recorded in Tables 5.1-5.3. The results are graphically presented in Figures 5.1-5.3. The corrosion rates are reduced in presence of GA, surfactants and GA-surfactants mixture as compared to the free acid solution. Also the corrosion rate increased with increase in temperature at all concentrations studied. The plots of %IE as a function of GA concentrations at 30-60°C (Figure 5.1) reveals that IE progressively increases as the concentration of GA increased in the acid solution. The above observation shows that addition of GA to 0.1M H\textsubscript{2}SO\textsubscript{4} solution retards the corrosion rate of mild steel and that the extent of retardation is concentration and temperature dependent.

Gum acacia or gum arabic is a dried exudation obtained mainly from \textit{Acacia Senegal} (L) or closely related species of \textit{Acacia}. It is cheap, eco-friendly and possesses suitable functional group containing nitrogen atom that could serve as adsorption centre hence suitable corrosion inhibitor (Figure 2.3). The inhibition of mild steel corrosion by GA can be explained in terms of its adsorption on the steel surface. The adsorption of GA on mild steel surface makes a barrier for mass and charge transfer and consequently, mild steel is protected from aggressive anions of acid. GA is a complex mixture of arabinogalactan, oligosaccharides, polysaccharides.
and glycoproteins [231]. This is suggestive of the fact that GA contains constituents which contain active adsorption sites in the form of hetero atoms such as oxygen and nitrogen. However, owing to the complex chemical composition of GA it is quite difficult to assign the inhibitive effect to a particular constituent. Further, in acidic solution some of the constituents of GA (eg. Glycoproteins) may exist in protonated form and could be electrostatically attracted to the cathodic sites on steel surface, thereby decreasing the hydrogen evolution reaction and indicating physical adsorption [232]. The increased IE with increasing GA concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film [216]. A decrease in IE with increasing temperature suggests possible desorption of some of the adsorbed GA molecules from the metal surface at higher temperatures. This behavior shows that the GA was physically adsorbed on the metal surface [217]. As the temperature increases the quantity of equilibrium of adsorption decreases [218] and as a result, the plot of higher temperatures is below the lower ones. This is clearly demonstrated in Figure 5.1 which shows that GA is physically adsorbed on the steel surface as the plots of higher temperatures are under that of lower ones. The decrease in IE with increasing temperature may be due the fact that most effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the GA to be adsorbed on the steel surface.

The surfactants SDBS and CTAB also exhibit corrosion inhibition of mild steel in 0.1M H₂SO₄ (Table 5.2). Also the corrosion rate increased with increase in temperature at all concentrations studied. In presence of SDBS, the IE increases with increase in surfactant concentration showing a maximum IE of 97.67% at 30°C at
SDBS concentration of 300 ppm; further increase in SDBS concentration does not significantly affect the IE. However, in presence of CTAB the maximum IE is observed at CTAB concentration of 5 ppm and further increase in CTAB concentration does not significantly affect the corrosion rate. To observe the effect of SDBS and CTAB on the corrosion inhibition behavior of GA, the corrosion of mild steel in 0.1M H₂SO₄ in absence and presence of varying concentration of GA in combination with SDBS (5 ppm) and CTAB(1 ppm) was separately studied in the temperature range of 30-60°C (Table 5.3). It is observed that the IE of GA in presence of SDBS and CTAB is further increased (Figures 5.2 and 5.3). The observed increase in IE of GA in presence of SDBS and CTAB can be explained in terms of the interaction between the GA and surfactant molecules leading to the improved adsorption on the steel surface. In acidic solution, the constituents of GA in protonated form may strongly interact with DS⁻ ions and favor greater adsorption over the steel surface. The CTAB may bind as co-ions or through hydrophobic interaction. Additionally, the surfactant molecules also adhere to the steel surface unoccupied by the GA molecules. The effect of surfactants on the IE of GA in 0.1M H₂SO₄ appears to be synergistic in nature.

5.2 Chemical Analysis of Solution

The corrosion rate and IE of mild steel was also investigated from determination of total iron ions (Fe²⁺/Fe³⁺) entered in the solution during time period for which reaction is carried out and the result is shown in Tables 5.4-5.6. The %IE as obtained by chemical analysis of solution is highly consistent with %IE obtained by weight loss measurements.
5.3 Synergism Considerations

To judge whether synergism is taking place between GA and surfactant SDBS/CTAB molecules, the synergism parameter, $S_i$, was calculated following equation 2.11. $S_i$ approaches 1 when no interaction between the inhibitor and the surfactant exist, while $S_i > 1$ points to a synergistic effect. In the case of $S_i < 1$, the antagonistic interaction prevails, which may be attributed to competitive adsorption. The values of synergism parameter for the various concentrations of GA in combination with SDBS/CTAB at 30-60°C as obtained by weight loss measurement and chemical analysis of solution are listed in Table 5.7. The values given in the table are more than unity, thereby suggesting that the enhanced IE caused by the addition of surfactant to the inhibitor is only due to synergistic effect. The values of synergism parameter, $S_i$ calculated from chemical analysis of solution is consistent with the values calculated from weight loss measurements.

5.4 Adsorption Isotherms

Basic information on the interaction between the inhibitors and the mild steel surface is provided by the adsorption isotherm. The adsorption of organic inhibitors at an electrolyte-electrode interface may take place through displacement of adsorbed water molecules. Surface coverage data ($\theta$) was used in determining inhibitor adsorption characteristics, which resulted in fitting the data to different isotherm type models, including Freundlich, Frumkin, Temkin, and Langmuir. The degree of surface coverage ($\theta$) for different concentrations of the inhibitor in 0.1M H$_2$SO$_4$ has been evaluated from weight loss measurements. The plots of logarithm of IE versus logarithmic concentration of additives displayed a straight line for mild steel
corrosion in 0.1M H₂SO₄ for GA alone and GA in combination with SDBS and CTAB at temperature 30-60°C (Figures 5.4-5.7). It is found that the linear correlation coefficients are close to unity, which indicates a very good fit between the Freundlich isotherm, and the experimental data that is the Freundlich adsorption model is applicable in the corrosion inhibition mechanism for GA alone and GA in combination with SDBS and CTAB on mild steel surface at all the temperatures studied.

5.5 Effect of Temperature

The effect of temperature on inhibition reaction is highly complex, because many changes may occur on the metal surface such as etching, rupture and desorption of inhibitor. Thus temperature can modify the interaction between the mild steel and the solution medium. Generally the corrosion rate increases with rise of temperature [233]. In order to elucidate the inhibitive properties of the GA and the temperature dependence on the corrosion rates, the apparent activation energy (Eₐ) for the corrosion process is calculated from Arrhenius equation 2.5. The logarithm of corrosion rate (log CR) versus reciprocal of absolute temperature (1/T) for 0.1M H₂SO₄ for blank, GA, surfactants and GA-surfactant mixtures is presented in Figure 5.8. The values of Eₐ obtained from the slope of the linear plots are presented in Table 5.8. A change in the value of Eₐ in presence of GA and GA-surfactants mixture may be due to the modification of the mechanism of the corrosion process in presence of adsorbed inhibitor molecules. In general, higher values of Eₐ in presence of additives support physical adsorption mechanism whereas an unchanged or lower value of Eₐ for inhibited systems compared to the blank is indicative of chemisorption mechanism. The inhibitor causing an increase in the values of Eₐ compared to blank
retard the corrosion at ordinary temperature, but the inhibition is diminished at elevated temperature. In the present investigation the values of $E_a$ in presence of additives is higher compared to the blank and hence supports physical adsorption mechanism which leads to the formation of an adsorptive film of electrostatic character [234]. Other kinetic parameters such as enthalpy of adsorption, $\Delta H$ and entropy of adsorption, $\Delta S$ were obtained from Transition state equation 2.6. The plots of $\log (CR/T)$ versus $1/T$ for blank, GA and GA in combination with surfactants gave a straight line (Figure 5.9) with a slope $\left( \frac{-\Delta H}{2.303R} \right)$ and an intercept of $\left[ \log \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S}{2.303R} \right) \right]$ from which enthalpy and entropy of activation were calculated and presented in Table 5.8. The positive signs of enthalpies reflect the endothermic nature of mild steel dissolution process and mean that the dissolution of mild steel is difficult [235]. The enthalpy of adsorption increases in presence of the additives compared to the free acid solution; this is indicative of physical adsorption. The values of $\Delta S$ are negative which indicates an increase in the system order in the presence of GA and GA-surfactants mixture. Free energy of adsorption, $\Delta G_{ads}$ for mild steel dissolution in 0.1M H$_2$SO$_4$ containing GA, GA in combination with surfactant SDBS/CTAB from 30°C to 60°C were calculated from the equation 2.9. The calculated values of $\Delta G_{ads}$ are presented in Table 5.9. From the Table it is evident that in all cases the values of $\Delta G_{ads}$ are negative, indicating that the GA is strongly adsorbed on the mild steel surface [224]. The values of $\Delta G_{ads}$ around -20 kJmol$^{-1}$ or less indicates physisorption whereas the values around -40 kJmol$^{-1}$ or more are considered as chemisorptions. In the present investigation the values of $\Delta G_{ads}$ are between -30.13 and -34.98 kJmol$^{-1}$ suggesting a mixed type of adsorption involving
both physiosorption and chemisorption. However, the variation in the values of %IE with temperature and higher values of $E_a$ and $\Delta H$ in presence of additives compared to blank suggest major contribution of physiosorption in the adsorption process.

### 5.6 Surface Analysis

Surface photographs were obtained by means of SEM and AFM so as to determine if the mild steel corrosion inhibition is due to the formation of a protective film by adsorption of inhibitor. The SEM photomicrographs of the blank mild steel surface and steel surface exposed to 0.1M $H_2SO_4$ in absence and presence of GA and GA-surfactants mixtures are shown in Figure 5.10-5.14. The surface morphology of the sample before immersion in 0.1M $H_2SO_4$ solution (Figure 5.10) shows a freshly polished mild steel surface which is free from any noticeable defects such as cracks and pits. The marks on the surface are the streaks made during polishing with emery papers. Figure 5.11 shows the photomicrograph of mild steel surface obtained after immersion in uninhibited 0.1M $H_2SO_4$. In uninhibited acid solution a damaged and heterogeneous surface is observed. The surface heterogeneity is considerably decreased in the presence of GA inhibited acid solution (Figure 5.12) which is further decreased in presence of surfactant additives (Figure 5.13 and 5.14). The decrease in the surface heterogeneity would have been caused by the deposition of the additives molecules on the mild steel surface which protected the surface from the attack of corrosive medium. The SEM results are further proved by AFM photographs of steel specimens taken in absence and presence of inhibitors at room temperature in the range of 0-0.5 $\mu$m. The surface roughness parameters of steel samples as obtained by AFM photographs (Figure 5.15-5.18) are shown in Table 5.10. The average surface roughness of mild steel specimen before subjecting to corrosion inhibition studies in
0.0009 nm. When the steel specimen was exposed to uninhibited 0.1M H₂SO₄ the average roughness increased to 3.00 nm due to excessive corrosive action of the acid. However, when the steel was exposed to GA inhibited acid solution the average roughness considerably reduced to 0.753 nm; which is further reduced to a value of 0.2426 nm in presence of GA-surfactant mixture. A smoother layer with clearly different morphology is as a result of the formation of a protective layer by the adsorbed inhibitor.

5.7 Conclusions

- Gum acacia was found to be an efficient corrosion inhibitor for mild steel in 0.1M H₂SO₄. The inhibition efficiency increased with an increase in inhibitor concentration but decreased with rise in temperature.
- The corrosion process is inhibited by adsorption of the gum acacia on the mild steel surface following the Freundlich adsorption isotherm.
- Addition of SDBS and CTAB synergistically increased the inhibition efficiency of gum acacia.
- The negative free energy of adsorption ΔGₐds indicates strong and spontaneous adsorption of gum acacia on the mild steel surface.
- The results obtained from chemical analysis of solution are highly consistent with the results of weight loss measurements.
- SEM and AFM studies further confirm the inhibitive character of the additives.
Table 5.1

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H₂SO₄ in the absence and the presence of GA at 30-60°C from weight loss measurements

<table>
<thead>
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<th>GA conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
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<td></td>
<td>30°C</td>
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<td>809.66</td>
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Table 5.2
Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1 M H₂SO₄ in the absence and the presence of SDBS and CTAB at 30-60°C from weight loss measurements

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<th>Surfactant conc. (ppm)</th>
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<th>Inhibition efficiency (%IE)</th>
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<td>40°C</td>
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Table 5.3

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H₂SO₄ in the absence and the presence of varying concentration GA with SDBS and CTAB at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>GA conc. (ppm)</th>
<th>Surfactant conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
</tr>
</thead>
<tbody>
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<td>40°C</td>
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<td>Blank</td>
<td>809.66</td>
<td>1413.98</td>
</tr>
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</tr>
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Table 5.4

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1 M H₂SO₄ in the absence and the presence of GA at 30-60°C from chemical analysis of solution.

<table>
<thead>
<tr>
<th>GA conc. (ppm)</th>
<th>Corrosion rate (gm⁻²h⁻¹)</th>
<th>Inhibition efficiency (%IE)</th>
</tr>
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<td>30°C</td>
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<tr>
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<td>5.36</td>
<td>11.01</td>
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<td>100</td>
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<td>10.41</td>
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<td>8.63</td>
</tr>
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<td>500</td>
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<td>8.03</td>
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<tr>
<td>1500</td>
<td>2.97</td>
<td>6.25</td>
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</table>
Table 5.5

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1 M H₂SO₄ in the absence and the presence of SDBS and CTAB at 30-60°C from chemical analysis of solution

<table>
<thead>
<tr>
<th>Surfactant conc. (ppm)</th>
<th>Corrosion rate (gm⁻²h⁻¹)</th>
<th>Inhibition efficiency (%IE)</th>
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<tr>
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<td>30°C</td>
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</tr>
<tr>
<td></td>
<td>17.85</td>
<td>31.24</td>
</tr>
<tr>
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<tr>
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<td>0.59</td>
<td>2.23</td>
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<tr>
<td>CTAB</td>
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<td></td>
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<td>12.64</td>
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<td>1.26</td>
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Table 5.6

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H₂SO₄ in the absence and the presence of varying concentration of GA with SDBS and CTAB at 30-60°C from chemical analysis of solution

<table>
<thead>
<tr>
<th>GA conc. (ppm)</th>
<th>Surfactant conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
</tr>
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<td>28.27</td>
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<td>5.36</td>
<td>11.31</td>
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Table 5.7

Calculated values of synergism parameter ($S_i$) for mild steel in 0.1M H$_2$SO$_4$ in the absence and the presence of varying concentration of GA with SDBS and CTAB at 30-60°C from weight loss measurements and chemical analysis of solution

<table>
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<th>GA conc. (ppm)</th>
<th>Surfactant conc. (ppm)</th>
<th>Synergism parameter ($S_i$) weight loss measurement</th>
<th>Synergism parameter ($S_i$) chemical analysis of solution</th>
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<td>---</td>
</tr>
<tr>
<td>5</td>
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Table 5.8

Calculated values of kinetic/thermodynamic parameters for mild steel in 0.1M H₂SO₄ in the absence and the presence of GA, surfactants and GA-surfactant mixtures from weight loss measurements

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<th>Conc. (ppm)</th>
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<th>$\Delta S$ (Jmol⁻¹K⁻¹)</th>
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### Table 5.9

Calculated values of $\Delta G_{ads}$ for mild steel in 0.1M H$_2$SO$_4$ in the presence of GA and GA-surfactant mixtures at 30-60°C from weight loss measurements

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<th>Additives</th>
<th>$\Delta G_{ads}$ (kJmol$^{-1}$)</th>
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<tr>
<td>GA+CTAB</td>
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### Table 5.10

Surface roughness parameters as obtained by AFM

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<th>Surface roughness parameters</th>
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<td></td>
<td></td>
<td>Average roughness (nm)</td>
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<td>1</td>
<td>Mild steel before subjecting to immersion</td>
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</tr>
<tr>
<td>2</td>
<td>Mild steel after immersion in uninhibited acid solution</td>
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</tr>
<tr>
<td>3</td>
<td>Mild steel after immersion in GA inhibited acid solution</td>
<td>0.7534</td>
</tr>
<tr>
<td>4</td>
<td>Mild steel after immersion in GA-SDBS inhibited acid solution</td>
<td>0.2426</td>
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</table>
Figure 5.1  Plots of inhibition efficiency (%IE) against GA concentration for mild steel in 0.1M H₂SO₄ at different temperatures

Figure 5.2  Plots of inhibition efficiency (%IE) against (GA+5 ppm SDBS) concentration for mild steel in 0.1M H₂SO₄ at different temperatures
Figure 5.3  Plots of inhibition efficiency (%IE) against (GA+1 ppm CTAB) concentration for mild steel in 0.1M H_2SO_4 at different temperatures

Figure 5.4  Freundlich adsorption isotherm plot for GA, (GA+5 ppm SDBS) and (GA+1 ppm CTAB) adsorbed on mild steel surface in 0.1M H_2SO_4 at 30°C
Figure 5.5  Freundlich adsorption isotherm plot for GA, (GA+5 ppm SDBS) and (GA+1 ppm CTAB) adsorbed on mild steel surface in 0.1M H₂SO₄ at 40°C

Figure 5.6  Freundlich adsorption isotherm plot for GA, (GA+5 ppm SDBS) and (GA+1 ppm CTAB) adsorbed on mild steel surface in 0.1M H₂SO₄ at 50°C
Figure 5.7  Freundlich adsorption isotherm plot for GA, (GA+5 ppm SDBS) and (GA+1 ppm CTAB) adsorbed on mild steel surface in 0.1M H₂SO₄ at 60°C

Figure 5.8  Adsorption isotherm plot for log CR versus 1/T in the absence and presence of GA, SDBS, CTAB and GA in combination with SDBS/CTAB
Figure 5.9  Adsorption isotherm plots for log (CR/T) versus 1/T in the absence and presence of GA, SDBS, CTAB and GA in combination with SDBS/CTAB
**Figure 5.10** SEM photomicrograph of the surface of mild steel before immersion in 0.1M H₂SO₄ solution

**Figure 5.11** SEM photomicrograph of the surface of mild steel after immersion in 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 5.12  SEM photomicrograph of the surface of mild steel after immersion in GA (1000 ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C

Figure 5.13  SEM photomicrograph of the surface of mild steel after immersion in GA (1000 ppm)-SDBS (5 ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 5.14  SEM photomicrograph of the surface of mild steel after immersion in GA (1000 ppm)-CTAB (1 ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 5.15  AFM photograph of the surface of mild steel before immersion in 0.1M H₂SO₄ solution
Figure 5.16  AFM photograph of the surface of mild steel after immersion in 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 5.17  AFM photograph of the surface of mild steel after immersion in GA (1000 ppm) inhibited 0.1M H$_2$SO$_4$ solution for 6 h at 30°C
Figure 5.18  AFM photograph of the surface of mild steel after immersion in GA (1000 ppm)-SDBS (5 ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C.
Chapter 6

Inhibition of Mild Steel Corrosion Using Polyethylene Glycol and Synergistic Surfactants Additives
6. RESULTS AND DISCUSSION

6.1 Weight Loss Measurements

The corrosion inhibition of mild steel in 0.1M H₂SO₄ at 30-60°C in absence and presence of different concentrations of polyethylene glycol (PEG), surfactants sodium dodecyl benzene sulphonate (SDBS) and cetyltrimethyl ammonium bromide (CTAB) and PEG-surfactants mixture was studied using weight loss technique and the data obtained after 6 h of immersion have been recorded in Tables 6.1-6.3. The results are graphically presented in Figures 6.1-6.3. The corrosion rates are reduced in presence of PEG, surfactants and PEG-surfactants mixture as compared to the free acid solution. Also the corrosion rate increased with increase in temperature at all concentrations studied. It can be seen that PEG efficiently inhibit the corrosion of mild steel in 0.1M H₂SO₄ and the extent of corrosion inhibition is concentration and temperature dependent. The calculated values of %IE of PEG indicate that IE increases with increasing PEG concentration. A further increase in PEG concentration does not significantly change the protective effect of PEG. The %IE decreases with increasing temperature at all the concentrations studied.

PEG is cheap, eco-friendly and possesses suitable functional group containing oxygen heteroatom that could serve as adsorption centre, hence suitable corrosion inhibitor (Figure 2.4). The corrosion inhibition by PEG is attributed to the presence of heteroatom oxygen in the inhibitor molecules and can be explained in terms of its adsorption on the steel surface through the lone pairs of electrons present on the oxygen atom. It has been reported that the hydroxyl group of polyethylene glycol could act as bridge between the polymer and the surface of metal and result in an
inhibiting effect in acidic solution [145]. The adsorption of PEG is assumed to be a quasi-substitution process between water molecules on the steel surface and the PEG molecules. The adsorption of PEG on mild steel surface makes a barrier for mass and charge transfer and consequently, mild steel is protected from aggressive anions of acid. Further, in acidic solution PEG may exist in protonated form and could be electrostatically attracted to the cathodic sites on steel surface, thereby decreasing the hydrogen evolution reaction and indicating physical adsorption [232]. The increased IE with increasing PEG concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film [216].

Considering the effect of temperature on the corrosion inhibition behavior of PEG, the IE decreases with increasing temperature. Adsorption and desorption of inhibitor molecules continuously occur at the mild steel surface and an equilibrium exist between the two processes at a particular temperature. With increase in temperature, the equilibrium between adsorption and desorption processes is shifted towards desorption until equilibrium is established again at a different value of equilibrium constant. This explains the lower IE at higher temperatures. This behavior shows that the mechanism of adsorption of the PEG is physisorption [217], because the physisorption is due to electrostatic interactions, which disappear at elevated temperatures. As the temperature increases the quantity of equilibrium of adsorption decreases [218] and as a result, the plot of higher temperatures is below the lower ones. This is clearly demonstrated in Figure 6.1 which shows that PEG is physically adsorbed on the steel surface. The decrease in IE with increasing temperature may be due the fact that most effects at elevated temperatures are adverse to corrosion
inhibition by increasing the corrosion rate and decreasing the tendency of the PEG to be adsorbed on the steel surface.

The surfactants SDBS and CTAB also exhibit corrosion inhibition of mild steel in 0.1M H₂SO₄ (Table 6.2). Also the corrosion rate increased with increase in temperature at all concentrations studied. In presence of SDBS, the IE increases with increase in surfactant concentration showing a maximum IE of 95.69% at 30°C at SDBS concentration of 200 ppm; further increase in SDBS concentration does not significantly affect the IE. However, in presence of CTAB the maximum IE is observed at CTAB concentration of 5 ppm and further increase in CTAB concentration does not significantly affect the corrosion rate. To observe the effect of SDBS and CTAB on the corrosion inhibition behavior of PEG, the corrosion of mild steel in 0.1M H₂SO₄ in absence and presence of varying concentration of PEG in combination with SDBS (5 ppm) and CTAB(1 ppm) was separately studied in the temperature range of 30-60°C (Table 6.3). It is observed that the IE of PEG in presence of SDBS and CTAB is further increased (Figures 6.2 and 6.3). The observed increase in IE of PEG in presence of SDBS and CTAB can be explained in terms of the interaction between the PEG and surfactant molecules leading to the improved adsorption on the steel surface. In acidic solution, the PEG in protonated form may strongly interact with DS⁻ ions furnished by SDBS and favor greater adsorption over the steel surface. The CTAB may bind with the PEG as co-ions or through hydrophobic interaction and result in higher adsorption. Additionally, the surfactant molecules also adhere to the steel surface unoccupied by the PEG molecules. The effect of surfactants on the IE of PEG in 0.1M H₂SO₄ appears to be synergistic in nature.
6.2 Chemical Analysis of Solution

The corrosion rate and IE of mild steel was also investigated from determination of total iron ions (Fe²⁺/Fe³⁺) entered in the solution during time period for which reaction is carried out and the result is shown in Tables 6.4-6.6. The results as obtained by chemical analysis of solution are consistent with the results obtained by weight loss measurements.

6.3 Synergism Considerations

The values of synergism parameter, $S_1$ for the various concentrations of PEG in combination with SDBS/CTAB at 30-60°C as obtained by weight loss measurement and chemical analysis of solution are listed in Table 6.7. The values were calculated following the relationship given in equation 2.11. The values given in the tables are more than unity, thereby suggesting that the enhanced IE caused by the addition of surfactant to the PEG is only due to synergistic effect. The values of synergism parameter, $S_1$ calculated from chemical analysis of solution is consistent with the values calculated from weight loss measurements.

6.4 Adsorption Isotherms

Surface coverage data ($\theta$) was used in determining inhibitor adsorption characteristics, which resulted in fitting the data to different isotherm type models, including Langmuir, Freundlich, Frumkin, and Temkin. But the Langmuir adsorption isotherm given by equation 2.7 was found to be the best description of the adsorption behavior of PEG and PEG-surfactant mixture. The plots of $C/\theta$ against $C$ (Figures 6.4-6.6) displayed a straight line for mild steel corrosion in 0.1M H₂SO₄ for PEG alone
and PEG in combination with SDBS and CTAB at temperature 30-60°C. The values of adsorption parameters deduced from the Langmuir adsorption isotherm (linear regression parameters) such as linear regression coefficient and adsorptive equilibrium constants are presented in Table 6.8. It is found that almost all the linear correlation coefficients are close to unity, suggesting that the adsorption of PEG alone and PEG in combination with SDBS and CTAB on mild steel surface at all the temperatures studied obeys Langmuir adsorption isotherm. Langmuir’s isotherm assumes that there is no interaction between the adsorbed molecules, the energy of adsorption is independent on the surface coverage (θ), the solid surface contains a fixed number of adsorption sites, and each site hold one adsorbed species. From the values of adsorptive equilibrium coefficient (K) it is apparent that the values of K decreased with increasing temperature. A large value of K (at lower temperature) means better inhibition efficiency of a given inhibitor, strong interaction between the double layer existing at the phase boundary and the adsorbed species. Small values of K. (at higher temperature) however, show that such interactions are weaker, denoting that the adsorbed species are easily removable by the solvent molecules from the surface. In addition, large values of K mean better inhibition efficiency of the given inhibitor.

6.5 Effect of Temperature

The effect of temperature on the corrosion parameters of mild steel in free and inhibited solution of 0.1M H₂SO₄ was studied at a temperature range of 30-60°C. Acid solutions were inhibited by adding different concentration of inhibitors. The effect of temperature on inhibition reaction is highly complex, because many changes may occur on the metal surface such as etching, rupture and desorption of inhibitor.
Thus temperature can modify the interaction between the mild steel and the solution medium. Generally the corrosion rate increases with rise of temperature [51, 249]. In order to elucidate the inhibitive properties of the PEG and the temperature dependence on the corrosion rates, the apparent activation energy (E_a) for the corrosion process is calculated from Arrhenius type plot given by the equation 2.5. The logarithm of corrosion rate (log CR) versus reciprocal of absolute temperature (1/T) for 0.1M H_2SO_4 for blank, PEG, surfactants and PEG-surfactant mixtures is presented in Figure 6.7. The values of E_a obtained from the slope of the linear plot are presented in Table 6.9. A change in the value of E_a in presence of PEG and PEG-surfactants mixture may be due to the modification of the mechanism of the corrosion process in presence of adsorbed inhibitor molecules. In general, higher values of E_a in presence of additives support physical adsorption mechanism whereas an unchanged or lower value of E_a for inhibited systems compared to the blank is indicative of chemisorption mechanism. The inhibitor causing an increase in the values of E_a compared to blank retard the corrosion at ordinary temperature, but the inhibition is diminished at elevated temperature. In the present investigation the values of E_a in presence of additives is higher compared to the blank and hence supports physical adsorption mechanism which leads to the formation of an adsorptive film of electrostatic character [235]. Other kinetic parameters such as enthalpy of adsorption, \( \Delta H \) and entropy of adsorption, \( \Delta S \) were obtained from Transition state equation 2.6. A plot of Log (CR/T) versus 1/T for blank, PEG and PEG in combination with surfactants (Figure 6.8) gave a straight line with a slope \( \frac{\Delta H}{2.303R} \) and an intercept of \( \log \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S}{2.303R} \right) \) from which enthalpy and entropy of activation were
calculated and presented in Table 6.9. The enthalpy of adsorption increases in presence of the additives compared to the free acid solution; this is indicative of physical adsorption. The values of $\Delta S$ in the absence of PEG and PEG in combination of surfactants is large and negative, this suggests decrease in disorder taking place on going from reactants to the activated complex [201].

Figure 6.9 shows the plots of $\log \left( \frac{\theta}{1-\theta} \right)$ versus $1/T$ for PEG and PEG in combination with the surfactants. Linear plot was obtained and from the slope $\left[ \frac{-Q}{2.303R} \right]$ of the linear plot, heat of adsorption, $Q_{\text{ads}}$ was calculated. The values of $Q_{\text{ads}}$ are presented in Table 6.9. The negative $Q_{\text{ads}}$ values imply that inhibitor’s adsorption is physical in nature (inhibition efficiency decreases at high temperature) while positive values suggest increased efficiency at high temperature (chemisorption) [223]. From Table 6.9, at is apparent that in all cases the values of $Q_{\text{ads}}$ are negative and ranges from -35.64 to -52.77 kJmol$^{-1}$. This is in support of physiosorption mechanism. Thus the adsorption of PEG, SDBS, CTAB and PEG-surfactant mixture on mild steel surface follow physiosorption mechanism.

The values of free energy of adsorption, $\Delta G_{\text{ads}}$ were obtained following equation 2.9 [210]. The calculated values of $\Delta G_{\text{ads}}$ from 30°C to 60°C for the various systems studied are presented in Table 6.10. The values of $\Delta G_{\text{ads}}$ are negative in all cases indicating that the PVA is strongly adsorbed on the mild steel surface [150]. It is an established fact that values of $\Delta G_{\text{ads}}$ around -20 kJmol$^{-1}$ or less indicates physiosorption. The adsorption is attributed to the electrostatic attraction between the charged organic molecules and charged metal surface. The values of $\Delta G_{\text{ads}}$ around -40
kJmol$^{-1}$ or more are considered as chemisorptions. However, the values of $\Delta G_{ads}$ between -20 and -40 kJmol$^{-1}$ gives a disputed judgment about the type of adsorption [211, 216, and 232]. In the present investigation the values of $\Delta G_{ads}$ are in the range of -32.32 to -37.65 kJmol$^{-1}$ suggesting a mixed type of adsorption involving both physisorption and chemisorption. However, the variation in the values of %IE with temperature and higher values of $E_a$ in presence of additives compared to blank suggest major contribution of physisorption in the adsorption process.

6.6 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDAX) Analysis

The SEM images were obtained to establish the fact that corrosion inhibition of mild steel in acid solution is due to the formation of a protective film by the adsorbed inhibitor molecules. The SEM photomicrographs of the blank mild steel surface and steel surface exposed to 0.1M H$_2$SO$_4$ in absence and presence of PEG and PEG-surfactants mixtures has been depicted in Figures 6.10-6.14. The surface morphology of the sample before immersion in 0.1M H$_2$SO$_4$ solution (Figure 6.10) shows a characteristic freshly polished mild steel surface which is free from any noticeable defects such as cracks and pits. The marks on the surface are the scratches which had arisen during polishing with emery papers. Figure 6.11 shows the photomicrograph of mild steel surface obtained after immersion in uninhibited 0.1M H$_2$SO$_4$. A damaged and heterogeneous surface is observed as a result of severe corrosion of mild steel by the aggressive acid solution. Figure 6.13-6.14 shows the photomicrographs of the mild steel surface immersed for the same period of time in 0.1M H$_2$SO$_4$ containing 25 ppm of PEG, PEG (25 ppm)+SDBS (5 ppm) and PEG (25 ppm)+CTAB (1 ppm), respectively. The surface heterogeneity is considerably
decreased in the presence of PEG which is further decreased in presence of surfactant additives. The decrease in the surface heterogeneity would have been caused by the deposition of the additives molecules on the mild steel surface which protected the steel surface from the attack of corrosive medium. The scratches formed during the polishing were also covered well by the additives molecules.

The EDAX spectrum of the blank mild steel surface and steel surface exposed to 0.1M H₂SO₄ in absence and presence of PEG and PEG-surfactants mixtures were obtained and the results are shown in Figures 6.15-6.19. The EDAX spectrum was recorded in order to determine the iron and sulfur content on the steel surface in absence and presence of additives. Figure 6.15 represents the EDAX profile of blank mild steel, which revealed that the surface was free from any corrosion product in the absence of immersion in acid solution. In case of mild steel exposed to 0.1M H₂SO₄ the iron content on the surface was appreciably reduced in comparison to the blank mild steel due to formation of corrosion products; presence of sulfur was also revealed on the surface (Figure 6.16). Figures 6.17-6.19 show EDAX profile of mild steel specimen immersed for the same period of time in 0.1M H₂SO₄ containing 25 ppm of PEG, PEG (25 ppm)+SDBS (5 ppm) and PEG (25 ppm)+CTAB (1 ppm), respectively. The spectra showed higher concentration of iron presumably due to lowering in the extent of corrosion in presence of inhibitors but did not show the presence of sulfur. This indicates that PEG alone and PEG-surfactant mixtures adequately protected the mild steel from corrosive attack of acid.
6.7 Atomic Force Microscopy (AFM) Analysis

The 2D/3D AFM images of the blank mild steel surface and steel surface exposed to 0.1M H₂SO₄ in absence and presence of PEG and PEG-surfactants mixtures taken at room temperature in the range of 0-50 μm are shown in Figures 6.20-6.24. The AFM results further support the results of SEM and EDAX studies. The surface roughness parameters of steel samples as obtained by AFM photographs are also shown along with the AFM photographs. The average surface roughness of mild steel specimen before subjecting to corrosion inhibition studies is 44.8 nm (Figure 6.20). When the steel specimen was exposed to uninhibited 0.1M H₂SO₄ the average roughness increased to 511 nm due to excessive corrosive action of the H₂SO₄ (Figure 6.21). However, when the steel was exposed to PEG inhibited H₂SO₄ solution the average roughness is considerably reduced to 162 nm (Figure 6.22); which is further reduced to a value of 160 and 102 nm in presence of PEG-SDBS (Figure 6.23) and PEG-CTAB (Figure 6.24) mixture, respectively. A smoother layer in case of PEG and PEG-surfactant mixture in comparison to uninhibited acid solution is as a result of the formation of a protective layer by the adsorbed inhibitors.

6.8 Conclusions

- Polyethylene glycol was found to be an efficient corrosion inhibitor for mild steel in 0.1M H₂SO₄. The inhibition efficiency increased with an increase in inhibitor concentration but decreased with rise in temperature.
- The corrosion process is inhibited by adsorption of the polyethylene glycol on the mild steel surface following the Langmuir adsorption isotherm.
• Addition of SDBS and CTAB synergistically increased the inhibition efficiency of polyethylene glycol.

• The negative free energy of adsorption $\Delta G_{ad}^*$ indicates strong and spontaneous adsorption of polyethylene glycol on the mild steel surface.

• The results obtained from chemical analysis of solution are highly consistent with the results of weight loss measurements.

• SEM, EDAX and AFM studies further confirmed the inhibitive character of the PEG and PEG-surfactant additives.
Table 6.1

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H$_2$SO$_4$ in the absence and the presence of PEG at 30-60°C from weight loss measurements

<table>
<thead>
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<th>PEG conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
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<td>30°C</td>
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<tr>
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Table 6.2

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1M H$_2$SO$_4$ in the absence and the presence of SDBS and CTAB at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>Surfactant conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
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<td>40°C</td>
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Table 6.3

Calculated values of corrosion rate (mpy) and inhibition efficiency (%IE) for mild steel in 0.1 M H₂SO₄ in the absence and the presence of varying concentration of PEG with SDBS and CTAB at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>PEG conc. (ppm)</th>
<th>Surfactant conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%IE)</th>
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166
Table 6.4

Calculated values of corrosion rate (gm⁻²h⁻¹) and inhibition efficiency (%IE) for mild steel in 0.1M H₂SO₄ in the absence and the presence of PEG at 30-60°C from chemical analysis of solution.

<table>
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<tr>
<th>PEG conc. (ppm)</th>
<th>Corrosion rate (gm⁻²h⁻¹)</th>
<th>Inhibition efficiency (%IE)</th>
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Table 6.5

Calculated values of corrosion rate (gm$^{-2}$h$^{-1}$) and inhibition efficiency (%IE) for mild steel in 0.1M H$_2$SO$_4$ in the absence and the presence of SDBS and CTAB at 30-60°C from chemical analysis of solution

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Table 6.6
Calculated values of corrosion rate (gm⁻²h⁻¹) and inhibition efficiency (%IE) for mild steel in 0.1M H₂SO₄ in the absence and the presence of varying concentration of PEG with SDBS and CTAB at 30-60°C from chemical analysis of solution

<table>
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<tr>
<th>PEG conc. (ppm)</th>
<th>Surfactant conc. (ppm)</th>
<th>Corrosion rate (gm⁻²h⁻¹)</th>
<th>Inhibition efficiency (%IE)</th>
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<td>2.59</td>
<td>7.31</td>
</tr>
<tr>
<td></td>
<td>CTAB</td>
<td>12.02</td>
<td>24.35</td>
</tr>
<tr>
<td>---</td>
<td>1</td>
<td>1.98</td>
<td>6.69</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1.67</td>
<td>5.17</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>1.14</td>
<td>3.96</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>1.33</td>
<td>4.57</td>
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<td>1</td>
<td>1.45</td>
<td>4.87</td>
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<td>150</td>
<td>1</td>
<td>1.98</td>
<td>5.78</td>
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<tr>
<td>200</td>
<td>1</td>
<td>2.21</td>
<td>6.39</td>
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</tbody>
</table>

169
Table 6.7

Calculated values of synergism parameter ($S_i$) for mild steel in 0.1M H$_2$SO$_4$ in the absence and the presence of varying concentration of PEG with SDBS and CTAB at 30-60°C.

<table>
<thead>
<tr>
<th>PEG conc. (ppm)</th>
<th>Surfactant conc. (ppm)</th>
<th>Synergism parameter ($S_i$) obtained by weight loss measurements</th>
<th>Synergism parameter ($S_i$) obtained by chemical analysis of solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td>---</td>
<td>SDBS</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>1.165</td>
<td>1.080</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>1.159</td>
<td>1.071</td>
</tr>
<tr>
<td>25</td>
<td>5</td>
<td>1.135</td>
<td>1.071</td>
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<tr>
<td>50</td>
<td>5</td>
<td>1.159</td>
<td>1.090</td>
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<td>100</td>
<td>5</td>
<td>1.169</td>
<td>1.100</td>
</tr>
<tr>
<td>150</td>
<td>5</td>
<td>1.171</td>
<td>1.108</td>
</tr>
<tr>
<td>200</td>
<td>5</td>
<td>1.176</td>
<td>1.102</td>
</tr>
<tr>
<td>---</td>
<td>CTAB</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.283</td>
<td>1.167</td>
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<td>5</td>
<td>1</td>
<td>1.311</td>
<td>1.177</td>
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<tr>
<td>25</td>
<td>1</td>
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<td>1.183</td>
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<td>50</td>
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<tr>
<td>100</td>
<td>1</td>
<td>1.327</td>
<td>1.209</td>
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<tr>
<td>150</td>
<td>1</td>
<td>1.346</td>
<td>1.218</td>
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<tr>
<td>200</td>
<td>1</td>
<td>1.370</td>
<td>1.225</td>
</tr>
</tbody>
</table>
Table 6.8

The values of linear regression coefficient ($R^2$) and adsorptive equilibrium constant ($K$) for mild steel in 0.1M H$_2$SO$_4$ in the presence of PEG and PEG-surfactants mixtures at 30-60°C from weight loss measurements

<table>
<thead>
<tr>
<th>Additives</th>
<th>Linear regression coefficient ($R^2$)</th>
<th>Adsorptive equilibrium constant ($K$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td>PEG</td>
<td>0.9998</td>
<td>0.9998</td>
</tr>
<tr>
<td>PEG+SDBS</td>
<td>0.9998</td>
<td>0.9998</td>
</tr>
<tr>
<td>PEG+CTAB</td>
<td>0.9994</td>
<td>0.9994</td>
</tr>
</tbody>
</table>

Table 6.9

Calculated values of kinetic/thermodynamic parameters for mild steel in 0.1M H$_2$SO$_4$ in the absence and the presence of PEG, surfactants and PEG-surfactant mixtures from weight loss measurements

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conc. (ppm)</th>
<th>$E_a$ (kJmol$^{-1}$)</th>
<th>$\Delta H$ (kJmol$^{-1}$)</th>
<th>$\Delta S$ (Jmol$^{-1}$K$^{-1}$)</th>
<th>$\Delta Q$ (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>---</td>
<td>43.39</td>
<td>40.82</td>
<td>-54.41</td>
<td>---</td>
</tr>
<tr>
<td>SDBS</td>
<td>5</td>
<td>47.81</td>
<td>45.10</td>
<td>-41.72</td>
<td>-52.77</td>
</tr>
<tr>
<td>CTAB</td>
<td>1</td>
<td>53.63</td>
<td>50.99</td>
<td>-24.33</td>
<td>-51.52</td>
</tr>
<tr>
<td>PEG</td>
<td>5</td>
<td>69.34</td>
<td>66.70</td>
<td>15.78</td>
<td>-35.64</td>
</tr>
<tr>
<td>PEG+SDBS</td>
<td>5+5</td>
<td>74.96</td>
<td>72.23</td>
<td>31.96</td>
<td>-41.66</td>
</tr>
<tr>
<td>PEG+CTAB</td>
<td>5+1</td>
<td>84.40</td>
<td>81.69</td>
<td>59.74</td>
<td>-50.45</td>
</tr>
</tbody>
</table>
Table 6.10

Calculated values of $\Delta G_{ads}$ for mild steel in 0.1M H$_2$SO$_4$ in the presence of PEG and PEG-surfactants mixtures at 30-60°C from Weight loss Measurements

<table>
<thead>
<tr>
<th>Additives</th>
<th>$\Delta G_{ads}$ (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
</tr>
<tr>
<td>PEG</td>
<td>-36.61</td>
</tr>
<tr>
<td>PEG+SDBS</td>
<td>-37.00</td>
</tr>
<tr>
<td>PEG+CTAB</td>
<td>-37.65</td>
</tr>
</tbody>
</table>
Figure 6.1  Plots of inhibition efficiency (%IE) against PEG concentration for mild steel in 0.1M H₂SO₄ at different temperatures

Figure 6.2  Plots of inhibition efficiency (%IE) against (PEG+5 ppm SDBS) concentration for mild steel in 0.1M H₂SO₄ at different temperatures
Figure 6.3  Plots of inhibition efficiency (%IE) against (PEG+1 ppm CTAB) concentration for mild steel in 0.1 M H₂SO₄ at different temperatures

Figure 6.4  Langmuir adsorption isotherm for PEG adsorbed on mild steel surface in 0.1 M H₂SO₄ at different temperatures
Figure 6.5  Langmuir adsorption isotherm for (PEG+5 ppm SDBS) adsorbed on mild steel surface in 0.1M H₂SO₄ at different temperatures

Figure 6.6  Langmuir adsorption isotherm for (PEG+1 ppm CTAB) adsorbed on mild steel surface in 0.1M H₂SO₄ at different temperatures
Figure 6.7  Adsorption isotherm plots for log CR versus 1/T in the absence and presence of PEG, SDBS, CTAB and PEG in combination with SDBS/CTAB

Figure 6.8  Adsorption isotherm plots for log (CR/T) versus 1/T in the absence and presence of PEG, SDBS, CTAB and PEG in combination with SDBS/CTAB
Figure 6.9  Adsorption isotherm plots for log (θ/1-θ) versus 1/T in the absence and presence of PEG, SDBS, CTAB and PEG in combination with SDBS/CTAB
Figure 6.10  SEM photomicrograph of the surface of mild steel before immersion in 0.1M H₂SO₄ solution

Figure 6.11  SEM photomicrograph of the surface of mild steel after immersion in 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 6.12  SEM photomicrograph of the surface of mild steel after immersion in PEG (25 ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C

Figure 6.13  SEM photomicrograph of the surface of mild steel after immersion in PEG (25 ppm)-SDBS (5 ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 6.14  SEM photomicrograph of the surface of mild steel after immersion in PEG (25 ppm)-CTAB (1 ppm) inhibited 0.1 M H₂SO₄ solution for 6 h at 30°C
Figure 6.16 EDAX profile of the surface of mild steel before immersion in 0.1M H₂SO₄ solution
Figure 6.17 EDAX profile of the surface of mild steel after immersion in 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 6.18 EDAX profile of the surface of mild steel after immersion in PEG (25 ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C.
Figure 6.19 EDAX profile of the surface of mild steel after immersion in PEG (25 ppm)-SDBS (5ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C
Figure 6.20 EDAX profile of the surface of mild steel after immersion in PEG (25 ppm)-CTAB (1 ppm) inhibited 0.1M H$_2$SO$_4$ solution for 6 h at 30°C.
2D (Height) and 3D AFM image (50 um x 50 um)

Roughness of the whole image:
Average roughness, $Ra = 44.8$ nm
Root mean square roughness, $Rq = 59.6$ nm

Figure 6.20  AFM image of the surface of mild steel before immersion in 0.1M H$_2$SO$_4$ solution
Roughness of the whole image:
Average roughness, \( Ra = 511 \) nm
Root mean square roughness, \( Rq = 663 \) nm

Figure 6.21  AFM image of the surface of mild steel after immersion in 0.1M \( \text{H}_2\text{SO}_4 \) solution for 6 h at 30°C
Roughness of the whole image:
Average roughness, Ra = 162 nm
Root mean square roughness, Rq = 204 nm

Figure 6.22  AFM image of the surface of mild steel after immersion in PEG (25 ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C
Roughness of the whole image:
Average roughness, $Ra = 160$ nm
Root mean square roughness, $Rq = 203$ nm

**Figure 6.23** AFM image of the surface of mild steel after immersion in PEG (25 ppm)-SDBS (5 ppm) inhibited 0.1M $H_2SO_4$ solution for 6 h at 30°C
2D (Height) and 3D AFM image (50 μm x 50 μm)

Roughness of the whole image:
Average roughness, Ra = 102 nm
Root mean square roughness, Rq = 130 nm

Figure 6.24 AFM image of the surface of mild steel after immersion in PEG (25 ppm)-CTAB (1 ppm) inhibited 0.1M H₂SO₄ solution for 6 h at 30°C
References
REFERENCES


List of Publications


Published Papers
Inhibition of Mild Steel Corrosion in Acidic Medium Using Starch and Surfactants Additives

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Corrosion Research Laboratory, Department of Applied Chemistry, Aligarh Muslim University, Aligarh 202 002, India

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ABSTRACT: The corrosion inhibition of mild steel in 0.1M H2SO4 in presence of starch (polysaccharide) was studied using weight loss and potentiodynamic polarization measurements in the temperature range of 30-60°C. Starch inhibits the corrosion rates of mild steel to a considerable extent; the maximum inhibition efficiency (%IE) being 66.2% at 30°C in presence of starch concentration of 200 ppm. The effect of the addition of very small concentration of sodium dodecyl sulfate and cetyl trimethyl ammonium bromide on the corrosion inhibition behavior of starch was also studied. The IE of starch significantly improved in presence of both the surfactants. The effect of surfactants on the corrosion inhibition behavior of starch appears to be synergistic in nature. Starch alone and in combination with surfactants is found to obey Langmuir adsorption isotherm from the fit of the experimental data of all concentration and temperature studied. Phenomenon of physical adsorption is proposed from the trend of IE with temperature and also the values E_g, ΔG^ads, and Q^ads obtained. The results obtained by potentiodynamic polarization measurements are consistent with the results of the weight loss measurement. © 2011 Wiley Periodicals, Inc.

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Key words: corrosion inhibition; mild steel; polysaccharide; surfactant; adsorption isotherm

INTRODUCTION

The corrosion of iron and steel is a subject of fundamental, academic, and industrial concern and has received a considerable amount of attention. The use of corrosion inhibitors is one of the most practical methods for the protection against corrosion, especially in acid media. The corrosion inhibitors are generally used to protect metals against the attack of the acid solutions, which are widely used in acid pickling, industrial cleaning, acid descaling, and oil-well acidizing, etc. The acid pickling of steel in various industries is generally carried out at temperatures up to 60°C. Corrosion inhibitors are added to the solution during pickling to reduce the degree of metal attack and rate of acid consumption. The inhibitors prevent corrosion either by being adsorbed on the surface of metals or by forming a protective layer, or by causing the formation of insoluble complex. Most of the inhibitors used in industry are organic compounds containing multiple bonds in their molecules that mainly contain nitrogen, sulphur, and/or oxygen atoms through which they get adsorbed on the metal surface. However, most of these substances are toxic and using them is harmful for both human health and environment.

In recent times, a number of polymers have been exploited as corrosion inhibitors due to their inherent stability and cost effectiveness. The functional groups of the polymers form complexes with metal ions, which occupy a large surface area and thus protecting the metals from corrosive agents present in solution. The polymer inhibitors which have been widely examined include: polyethylene glycol, polyvinyl alcohol, polyvinyl pyridine, polyvinyl pyrrolidone, polyethyleneimine, polyacrylic acid, and poly acrylamide. A survey of literature shows that a number of naturally occurring materials such as natural honey, henna, guar gum, opuntia extract, and jojoba oil have shown promising results as corrosion inhibitors for iron and steel in acidic solutions. Recently, inhibition of mild steel corrosion in H2SO4 using synthetic (polyethylene glycol) and naturally occurring (gum arabic) polymer was studied in the temperature range of 30-60°C. Both the polymers were found to act as inhibitors but synthetic polymer was more effective than natural polymer.

Starch is a natural polymer, available in abundance at low cost, renewable, and biodegradable. Chemically it is a polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. Starch is produced by all green plants as an energy store. It contains two
structurally different components namely, amylose (15-20%), and amyllopectin (80-85%). The amylose is composed of large linear chain of \( \gamma (1-4) \) linked \( \alpha-D - \text{glucopyranosyl} \) residue, whereas amyllopectin is a branching form of \( \alpha \)-glycon linked by \( \gamma (1-6) \) linkages. The molecular structure of the starch suggests that it has strong potential to become an effective corrosion inhibitor. A survey of literature indicates that only few references are available dealing with the corrosion inhibition effect of starch on aluminum\(^{21,22}\) and steel.\(^{23}\) More recently, modified cassava starches were evaluated as corrosion inhibitor for carbon steel under alkaline conditions in 200 mg/L NaCl solutions.\(^{24}\) The inhibitive properties were studied by means of electrochemical impedance spectroscopy. The starches were found to show corrosion inhibitive properties; their protection level depended on the type and amount of active groups present in the molecules. Surfactants have been used as corrosion inhibitors either alone or in combination with other compounds to improve their performance as inhibitors. The surfactant molecules possess strong adsorption ability to the metallic surfaces. The adsorb molecules form a monolayer or bilayer hemimicelles or admicelles, depending upon the surfactant concentration and prevent the acid to attack the surface, and thus reduce the corrosion attack.\(^{25-28}\) The surfactant can be used either alone or in mixtures with other compounds.

The majority of the acidic inhibitors have been known for their specificity of inhibition action. A combination of inhibitors is likely to provide multiple effects required for effective corrosion inhibition. The addition of halide ions to organic compounds has shown synergistic effect and resulted in improved inhibition efficiency (IE) of many organic compounds and reported in the literature.\(^{29-31}\) However, the influence of surfactants on the corrosion inhibition behavior of organic compounds is very scanty.\(^{32}\) This work was undertaken to investigate the inhibition of mild steel corrosion in acidic medium using starch for which no reference is available in the literature. Further, the effect of the addition of very small concentration of sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) on the corrosion inhibition behavior of starch has also been investigated.

**EXPERIMENTAL**

**Material preparation**

The mild steel coupons having composition 0.19% C, 0.055% Si, 0.366% Mn, 0.069% P, 0.087% S, 0.074% Ni, 0.075% Cr, 0.11% Mo and balance Fe were used for corrosion inhibition studies. The mild steel sheets were mechanically press-cut into coupons of dimension 2.5 x 2 x 0.03 cm. The coupons were machined and abraded on different grades emery papers, washed with double distilled water, degreased with absolute ethanol and finally dried in acetone. A hole of 1 mm dia was made near the edge of the specimen for hooking. The treated coupons were then stored in moisture-free desiccators before their use in corrosion studies. Starch and surfactants SDS and CTAB (MERCK, India) were used as received. The starch selected for the investigation is soluble extra pure having solubility of 50 g/L (90°C), bulk density 300 kg/cm\(^3\) and the pH value 6.0-7.5 (20 g/L H\(_2\)O, 25°C). The concentration of starch prepared and used for the study ranges from 1 to 500 ppm. The concentration of H\(_2\)SO\(_4\) prepared and used was 0.1M. All solutions were made using double distilled water. The study was carried out at 30-60°C maintaining the temperatures using a thermostated water bath.

**Weight loss measurements**

The weight loss experiments were performed for duration of 8 h as per ASTM designation G1-90. The cleaned mild steel coupons were suspended in 250-mL beakers containing 200 mL of test solutions maintained at 30-60°C in a thermostated bath with the aid of glass rods and hooks. The concentration of inhibitor (starch) in H\(_2\)SO\(_4\) was kept between 1 and 500 ppm. The weight loss taken was the difference between the weight at a given time and the original weight of the coupons. The measurements were carried out for the uninhibited solution (blank) and solutions containing starch and starch-surfactant mixtures. The corrosion rates were determined using the equation:

\[
\text{Corrosion rate (mpy)} = \frac{534 \times W}{\rho \times A \times t}
\]  \hspace{1cm} (1)

where, \( W \) is weight loss in mg; \( \rho \) is the density of specimen in g/cm\(^3\); \( A \) is the area of specimen in sq. inch and \( t \) is exposure time in hours.

The %IE of starch, surfactants and starch-surfactant mixtures was evaluated using the following equation:

\[
\%\text{IE} = \left( \frac{C_{Ro} - C_{Ri}}{C_{Ro}} \right) \times 100
\]  \hspace{1cm} (2)

where, \( C_{Ro} \) is the corrosion rate of mild steel in absence of inhibitor and \( C_{Ri} \) is corrosion rate of mild steel in presence of inhibitor.

**Potentiodynamic polarization measurements**

Experiments were performed using a conventional three electrode cell assembly, using an EG&G potentiostat/Galvanostat, model 263A. The experiments were carried out using a corrosion cell from EG&G, Journal of Applied Polymer Science DOI 10.1002/app
TABLE I
Calculated Values of Corrosion Rate (mpy) and Inhibition Efficiency (%IE) for Mild Steel in 0.1M H2SO4 in the Absence and the Presence of Starch at 30-60°C from Weight Loss Measurement

<table>
<thead>
<tr>
<th>Starch cone (ppm)</th>
<th>Blank</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>203.88</td>
<td>7.22</td>
<td>7.12</td>
<td>69.66</td>
<td>68.58</td>
<td>70.74</td>
<td>70.74</td>
<td>70.74</td>
</tr>
<tr>
<td>40°C</td>
<td>522.74</td>
<td>227.75</td>
<td>217.18</td>
<td>207.64</td>
<td>209.53</td>
<td>201.39</td>
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</tr>
<tr>
<td>50°C</td>
<td>1132.70</td>
<td>536.51</td>
<td>521.41</td>
<td>502.42</td>
<td>502.36</td>
<td>500.49</td>
<td>500.49</td>
<td>500.49</td>
</tr>
<tr>
<td>60°C</td>
<td>2087.66</td>
<td>1144.50</td>
<td>1081.31</td>
<td>1002.36</td>
<td>1002.36</td>
<td>1000.49</td>
<td>1000.49</td>
<td>1000.49</td>
</tr>
</tbody>
</table>

- **Blank**
- **1**: 5.99 ppm
- **5**: 7.22 ppm
- **10**: 7.12 ppm
- **50**: 69.66 ppm
- **100**: 68.58 ppm
- **200**: 70.74 ppm
- **500**: 70.74 ppm

The model K0047 with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and mild steel coupons as working electrode. The working electrode was polished with 320, 600, 800 grade emery papers, washed with distilled water, and degreased with acetone. Before starting the measurements, the specimen was left into the solution for 30 min to attain the steady state. The experiments were performed with the potential of -250 to 250 mV at a scan rate of 0.166 mV/s. All the experiments were carried out at room temperature (30 ± 1°C). The electrochemical experiments data were collected and analyzed by electrochemical software PowrSuit ver. 2.58. The IE was calculated from the measured \( i_{corr} \) values using the relationship:

\[
\%\text{IE} = \left( \frac{i_{corr}}{i_{corr}} \right) \times 100
\]

where, \( i_{corr} \) is corrosion current density in the absence of inhibitor and \( i_{corr} \) is corrosion current density in the presence of inhibitor.

**RESULTS AND DISCUSSION**

Weight loss measurements

The corrosion of mild steel in 0.1M H2SO4 in the absence and presence of starch as inhibitor was studied using weight loss technique at temperature range of 30-60°C. The calculated value of corrosion rates and IE for the starch at different concentrations and temperatures is shown in Table I. From the table, it is clearly seen that the corrosion rates are reduced in presence of starch as compared to the free acid solution. Also, the corrosion rate increased with increase in temperature at all concentrations. The plot of IE as a function of starch concentrations at 30-60°C (Fig. 1) reveals that IE increases with increase in starch concentration showing a maximum efficiency of 66.21% at 30°C temperature in presence of starch concentration of 200 ppm: further addition of starch does not significantly influence the IE. The inhibition of mild steel corrosion in the presence of starch could be attributed to the adsorption of the compound on to mild steel surface, which blocks the metal and thus do not permit the corrosion process to take place. Starch can be adsorbed by the interaction between the lone pair of electrons of the oxygen atom and the steel surface. The presence of \( \pi \) vacant orbital of low energy in the iron atom, as observed in transition group metals, facilitates the adsorption process. In acid, medium starch may be partially hydrolyzed into simpler carbohydrates but the products with higher hydrophilicity than starch is likely to go into the bulk water. As the hydrolysis is quite slow, only negligible starch molecules are expected to hydrolyze and desorbs from the steel surface. Also, the starch in bulk water may occupy the steel surface as the molecules are in dynamic equilibrium. So, even after slow hydrolysis, inhibition by starch is effective.

The increased IE with increasing starch concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film. A decrease in IE with increasing temperature suggests possible desorption...
of some of the adsorbed starch molecules from the metal surface at higher temperatures. This behavior shows that the starch was physically adsorbed on the metal surface. As the temperature increases, the quantity of equilibrium of adsorption decreases and as a result, the plot of higher temperatures is below the lower ones. This is clearly demonstrated in Figure 1, which shows that starch is physically adsorbed on the steel surface since the plots of higher temperatures are under that of lower ones. The decrease in IE with increasing temperature may be due to the fact that most of the effects at elevated temperatures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the starch to be adsorbed on the steel surface.

To observe the effect of SDS and CTAB on the corrosion inhibition behavior of starch, the corrosion of mild steel in 0.1M H2SO4 in absence and presence of varying concentration of starch in combination with SDS (5 ppm) and CTAB (1 ppm) was separately studied in the temperature range of 30-60°C by weight loss technique. The results are shown in Tables II and III. It is observed that the corrosion rates of mild steel in 0.1M H2SO4 in presence of starch in combination with surfactants is further reduced in comparison to starch alone. Plots of IE versus concentration of starch in combination with surfactants at 30–60°C are shown in Figures 2 and 3. The anionic SDS binds with starch through electrostatic interaction, thus helps to adsorb at the metal surface more firmly and display higher IE. The IE of starch in presence of 1 ppm of CTAB is also higher than the starch alone. It may be due to the adsorption of starch to the metal surface by binding with CTAB as co-ions or through hydrophobic interaction. The effect of surfactants on the IE of starch in 0.1M H2SO4 appears to be synergistic in nature.

Synergism considerations

The synergism parameter, S, was evaluated using the relationship,

\[ S = \frac{1 - S_1}{1 - S_2} \]

where, \( S_1 \) is IE of starch and \( S_2 \) is IE of surfactant, SDS/CTAB and \( S_{1+2} \) is IE of starch in combination with surfactant. \( S_1 \) approaches 1 when

| TABLE II | Calculated Values of Corrosion Rate (mpy), Inhibition Efficiency (%IE) and Synergism Parameter (S_i) for Mild Steel in 0.1M H2SO4 in the Absence and the Presence of Varying Concentration of Starch with SDS at 30-60°C from Weight Loss Measurement |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|          | SDS conc. (ppm) | Corrosion rate (mpy) | Inhibition efficiency (%ie) | Synergism parameter (S_i) |
|          |                 | 30°C | 40°C | 50°C | 60°C | 30°C | 40°C | 50°C | 60°C | 30°C | 40°C | 50°C | 60°C |
| Blank   | Blank           | 210.88 | 522.74 | 1132.70 | 2087.66 | 30.82 | 26.70 | 12.54 | 7.12 | –    | –    | –    | –    | –    |
|         | 1               | 5    | 138.96 | 383.16 | 949.67 | 1939.00 | 65.35 | 51.35 | 43.97 | 35.22 | 1.313 | 1.377 | 1.125 | 0.948 |
|         | 5               | 5    | 69.61 | 254.31 | 634.62 | 1352.33 | 68.17 | 65.02 | 59.74 | 50.82 | 1.360 | 1.283 | 1.092 | 1.029 |
|         | 10              | 5    | 63.93 | 182.83 | 456.04 | 1026.65 | 69.36 | 65.33 | 57.56 | 52.73 | 1.379 | 1.308 | 1.158 | 1.050 |
|         | 50              | 5    | 61.54 | 181.21 | 480.73 | 986.83 | 69.43 | 65.64 | 63.09 | 54.94 | 1.390 | 1.330 | 1.110 | 1.077 |
|         | 100             | 5    | 61.40 | 179.60 | 417.99 | 940.75 | 69.28 | 66.02 | 63.38 | 55.70 | 1.401 | 1.317 | 1.123 | 1.091 |
|         | 200             | 5    | 61.71 | 177.60 | 414.73 | 924.77 | 68.75 | 65.61 | 63.82 | 56.73 | 1.417 | 1.352 | 1.125 | 1.088 |
|         | 500             | 5    | 65.46 | 176.14 | 421.79 | 903.27 | 67.41 | 65.92 | 62.76 | 56.73 | 1.424 | 1.343 | 1.147 | 1.080 |

| TABLE III | Calculated Values of Corrosion Rate (mpy), Inhibition Efficiency (%IE) and Synergism Parameter (S_i) for Mild Steel in 0.1M H2SO4 in the Absence and the Presence of Varying Concentration of Starch with CTAB at 30-60°C from Weight Loss Measurement |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|          | CTAB conc. (ppm) | Corrosion rate (mpy) | Inhibition efficiency (%ie) | Synergism parameter (S_i) |
|          |                 | 30°C | 40°C | 50°C | 60°C | 30°C | 40°C | 50°C | 60°C | 30°C | 40°C | 50°C | 60°C |
| Blank   | Blank           | 200.88 | 522.74 | 1132.70 | 2087.66 | 33.12 | 22.07 | 14.88 | 11.41 | –    | –    | –    | –    | –    |
|         | 1               | 1    | 134.34 | 407.38 | 964.18 | 1849.42 | 70.55 | 62.44 | 48.84 | 37.16 | 1.248 | 1.053 | 1.080 | 1.044 |
|         | 5               | 1    | 59.15 | 196.32 | 579.43 | 1311.80 | 72.78 | 65.25 | 58.54 | 49.53 | 1.305 | 1.206 | 1.156 | 1.145 |
|         | 10              | 1    | 54.68 | 181.66 | 469.55 | 1053.54 | 71.29 | 63.79 | 60.38 | 51.10 | 1.394 | 1.266 | 1.143 | 1.170 |
|         | 50              | 1    | 59.67 | 189.26 | 448.78 | 1020.80 | 68.84 | 62.08 | 59.95 | 53.33 | 1.436 | 1.332 | 1.209 | 1.192 |
|         | 100             | 1    | 62.00 | 198.24 | 453.68 | 974.23 | 68.18 | 61.53 | 59.47 | 54.17 | 1.458 | 1.338 | 1.238 | 1.203 |
|         | 200             | 1    | 63.91 | 201.07 | 459.12 | 956.83 | 66.62 | 61.97 | 59.11 | 54.08 | 1.498 | 1.357 | 1.257 | 1.224 |
|         | 500             | 1    | 68.19 | 199.94 | 465.30 | 960.39 | 66.05 | 61.75 | 58.92 | 53.99 | 1.489 | 1.359 | 1.263 | 1.226 |

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no interaction between inhibitor (starch) and the surfactant exist, whereas $S_1 > 1$ indicate a synergistic effect. In the case of $S_1 < 1$, antagonistic behavior prevails which may be attributed to competitive adsorption.

The values of the synergism parameter for the various concentrations of starch studied were calculated from the gravimetric data at 30–60°C, and the results are presented in Tables II and III. The synergism parameter $S_1$ is found to be greater than unity indicating that the enhanced IE caused by the addition of surfactants is only due to synergism. The addition of a very small amount of surfactant can improve the adsorption of starch on the mild steel.

### Adsorption considerations

The adsorption of organic compounds on metal surfaces can be described by two main types of interactions namely, physical adsorption and chemical adsorption. These adsorptions are dependent on the electronic structure of the metal, the nature of the electrolyte and the chemical structure of the organic compounds. The character of adsorption of starch alone and starch in combination with SDS and CTAB was elucidated from the values of degree of surface coverage ($\theta$) calculated from the weight loss data. Attempts were made to fit the $\theta$ values to various adsorption isotherms but best results were obtained for Langmuir adsorption isotherm.

The plots of $C/\theta$ against $C$ are drawn which is characteristics of Langmuir adsorption isotherm given by equation:

$$\frac{C}{\theta} = \frac{1}{K} + C$$

where $\theta$ is the degree of surface coverage, $K$ is the equilibrium constant of the adsorption process and $C$ is the starch concentration. The plots of $C/\theta$ versus $C$ for mild steel corrosion in 0.1M H$_2$SO$_4$ for starch alone and starch in combination with SDS and CTAB at temperature 30–60°C is shown in Figures 4–6. A linear correlation of slope close to unity suggests that adsorption of starch alone and starch in combination with SDS and CTAB on mild steel...
Effect of temperature

The corrosion of mild steel was studied in the temperature range of 30-60°C in the absence and presence of starch, surfactants and starch in combination with the surfactants. The logarithm of corrosion rate (log CR) versus reciprocal of absolute temperature (1/T) for 0.1 M H2SO4 is presented in Figure 7 for blank, starch, surfactants and starch-surfactant mixtures. Linear plot was obtained which indicates that it follows Arrhenius equation\(^\text{39}\) given by relationship:

\[
\log CR = \log A - \frac{E_a}{2.303 RT}
\]

where CR is the corrosion rate, A is the Arrhenius constant, \(E_a\) is the apparent activation energy, \(R\) is the molar gas constant and \(T\) is the absolute temperature. The values of \(E_a\) obtained from the slope of the linear plot are presented in Table IV. The increases in \(E_a\) values in presence of the additives compared to the blank indicate the decrease in adsorption process of the inhibitor on the mild steel surface with rise in temperature and a corresponding increase in reaction rate of greater area of metal that is exposed to acid.\(^\text{38}\) This shows physical adsorption.\(^\text{39}\)

Enthalpy of adsorption, \(\Delta H\) and entropy of adsorption, \(\Delta S\) for the corrosion of mild steel in 0.1 M H2SO4 in the presence of starch, surfactants and starch-surfactant mixtures was obtained by the equation:

\[
CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right)
\]

where \(N\) is the Avogadro’s number, \(h\) is the Planck’s constant, \(R\) is the molar gas constant, and \(T\) is the absolute temperature. Figure 8 shows the plot of log (CR/T) versus 1/T for blank, starch and starch in combination with surfactants. Linear plot was obtained and from the slope \(-\frac{\Delta H}{RT}\) and intercept \([\log(\frac{R}{h}) + \left(\frac{\Delta S}{RT}\right)]\) of the linear plot, the values of \(\Delta H\) and \(\Delta S\), respectively were obtained. The calculated values are presented in Table IV. The enthalpy of adsorption increases in presence of the additives compared to the free acid solution; this indicates physical adsorption. The values of \(\Delta S\) are positive which indicates a decrease in the system order in the presence of additives.\(^\text{40}\) Figure 9 shows the plot of log \((\frac{Q}{R})\) versus 1/T for starch and starch in combination with the surfactants. Linear plot was obtained and from the slope \(-\frac{Q}{R}\) of the linear plot, heat of adsorption, \(Q_{\text{ads}}\) was obtained. The

### Table IV

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conc. 5ppm</th>
<th>(E_a) (kJ/mol(^{-1}))</th>
<th>(\Delta H) (kJ/mol(^{-1}))</th>
<th>(\Delta S) (kJmol(^{-1})K(^{-1}))</th>
<th>(Q) (kJmol(^{-1}))</th>
<th>(\Delta G_{\text{ads}}) (kJmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
<td>64.96</td>
<td>62.36</td>
<td>5.19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SDS</td>
<td>5</td>
<td>72.76</td>
<td>70.19</td>
<td>27.79</td>
<td>51.20</td>
<td>-22.76</td>
</tr>
<tr>
<td>CTAB</td>
<td>1</td>
<td>72.76</td>
<td>70.19</td>
<td>27.79</td>
<td>-37.74</td>
<td>-32.57</td>
</tr>
<tr>
<td>Starch</td>
<td>5</td>
<td>74.51</td>
<td>71.90</td>
<td>28.55</td>
<td>-17.73</td>
<td>-33.54</td>
</tr>
<tr>
<td>Starch - SDS</td>
<td>5 + 5</td>
<td>76.89</td>
<td>74.27</td>
<td>34.68</td>
<td>-19.84</td>
<td>-34.87</td>
</tr>
<tr>
<td>Starch - CTAB</td>
<td>5 + 1</td>
<td>81.85</td>
<td>79.23</td>
<td>50.00</td>
<td>-27.30</td>
<td>-35.54</td>
</tr>
</tbody>
</table>

\(\Delta G_{\text{ads}}\) values are calculated from the weight loss measurements.

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calculated values of $Q_{ads}$ were negative (Table IV) indicating that the adsorption of starch, SDS, CTAB, and starch-surfactant mixture on mild steel surface is exothermic.\(^{45}\) In general, the values are less than $-40$ kJ mol\(^{-1}\) suggesting the physical adsorption of the compounds.\(^{45}\)

Free energy of adsorption, $\Delta G_{ads}$, was obtained from the intercept of plot of log (\% IE) versus log inhibitor concentration (log C) and evaluated using the following equation.

$$\log C = \log \left( \frac{\theta}{1 - \theta} \right) - \log B$$  \hspace{1cm} (8)

where, $\log B = -1.74 - (\frac{\Delta G_{ads}}{2.303 \times 8.314})$ and C, is the concentration of the system studied. The calculated values of $\Delta G_{ads}$ from 30 to 60°C for the various systems studied are presented in Table IV. The $\Delta G_{ads}$ values obtained are negative, which indicate the spontaneous adsorption of the starch and starch in combination with surfactants on the mild steel surface. The value of $\Delta G_{ads}$ of $-40$ kJ/mol is usually accepted as a threshold value between chemisorptions and physisorption. The values of $\Delta G_{ads}$ obtained in this study are below $-40$ kJ/mol (between $-9.96$ and $-35.54$ kJ/mol). This is consistent with electrostatic interactions between the charged molecules and the charge metals, which are indicative of physical adsorption.

**Potentiodynamic polarization measurements**

The potentiodynamic polarization curves for the corrosion of mild steel in 0.1M $\text{H}_2\text{SO}_4$ in absence and presence of varying concentration of starch and starch in combination with 5 ppm of SDS and 1 ppm of CTAB are shown in Figures 10 and 11. The values of electrochemical parameters as deduced from these curves, e.g., corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), the anodic tafel slope ($\beta_a$), the cathodic tafel slope ($\beta_c$), corrosion rate and \% IE are shown in Table V.

The study of electrochemical data (Table V) reveals that the value of $I_{corr}$ continuously decreases in
presence of starch. The maximum IE of about 61.75% was observed at a concentration of 200 ppm indicating that a higher coverage of starch on steel surface is obtained in the solution with highest concentration of inhibitor. The values of $E_{corr}$ shifts to more positive value compared to the blank, indicating that starch acts more anodic than cathodic inhibitor. The addition of 5 ppm of SDS to varying concentration of starch improved the IE of starch significantly. However, the effect of SDS is more pronounced at lower concentrations of starch. The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

CONCLUSIONS

1. Starch showed good performance as corrosion inhibitor for mild steel in 0.1M H2SO4 which is further improved in presence of surfactants SDS and CTAB. The effect of surfactants on corrosion inhibition behavior of starch appears to be synergistic in nature. Phenomenon of physical adsorption is proposed from the trend of IE with temperature.

2. The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir adsorption isotherm at all the concentrations and temperatures studied.

3. The results of potentiodynamic polarization measurements show that starch acts more anodic than cathodic inhibitor. The results are consistent with the results of the weight loss measurements.

References

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Inhibition of mild steel corrosion in HCl solution using amino acid L-tryptophan

M. Mobin*, Mosarrat Parveen and M. Alam Khan

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202002- India.

Abstract
The corrosion inhibition characteristics of nitrogen containing amino acid L-tryptophan on mild steel in 0.1 M HCl solution was studied by weight loss and potentiodynamic polarization measurements. L-tryptophan significantly reduces the corrosion rates of mild steel; the maximum inhibition efficiency being 83% at 50 °C in presence of inhibition concentration of 500 ppm.
The adsorption of inhibitors on mild steel surface obeyed Langmuir’s adsorption isotherm. The calculated thermodynamic parameters for adsorption reveal a strong interaction between the inhibitors and the mild steel surface. The results obtained by electrochemical studies are consistent with the results of the weight loss measurement. L-tryptophan acts more anodic than cathodic inhibitor.

Keywords: Mild steel, Corrosion inhibition, L-Tryptophan, Adsorption, Electrochemical technique.

INTRODUCTION
Organic compounds containing nitrogen, sulfur and oxygen have long been used as potential corrosion inhibitor in acid solutions [1-3]. These compounds get adsorbed, or form a protective layer/insoluble complex on the metal surface and block the active corrosion sites. However, most of these compounds are synthetic chemicals, are expensive and very hazardous to both human beings and the environments and needs to be replaced with nontoxic and eco-friendly compounds. Over the years, numerous classes of organic compounds have been investigated as corrosion inhibitors. However the trend in green chemistry is concentrated towards the replacement of most of these inhibitors with the nontoxic, cheap and eco-friendly compounds.

In recent years, a number of eco-friendly corrosion inhibitors have been exploited as green alternative to toxic and hazardous compound [4-7]. The amino acids which contain carboxyl and amino functionalities bonded to the same carbon atom are non-toxic, relatively cheap and easy to produce in purities greater than 99%. It has been shown by various authors that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds as substitute to conventional corrosion inhibitors that are usually toxic [8-12]. The inhibition effect of three amino acids namely, alanine, glycine and leucine against steel corrosion in HCl solutions has been investigated by potentiodynamic polarization method. The inhibition effect was found to range from 28-91% [13]. The corrosion inhibition of Fe in 1M HCl using twenty two different common amino acids and four related compounds was investigated using potentiodynamic polarization curves [14]. In general, amino acids with longer hydrocarbon chains showed greater inhibition. Additional groups or groups which increased electron density on alpha amino group also increased the inhibition efficiency. The nitrogen containing amino acid L-tryptophan is a derivative of indole. The molecular structure of the compound suggests that it has strong potential to become an effective corrosion inhibitor. Moretti and Guidi [15] reported the corrosion inhibition of L-tryptophan on copper in aerated 0.5M H2SO4 in the temperature range of 20-50°C. The corrosion rate did not rise as temperature increased. Corrosion inhibition behavior of low carbon steel by L-tryptophan was investigated using weight loss experiment and Tafel polarization curves [16]. The adsorption behavior of L-tryptophan at Fe surface was also investigated by the molecule dynamics simulation method and density functional theory. The results indicated that L-tryptophan could adsorb on Fe surface through the indole ring with n-electrons and nitrogen/oxygen atom with the lone pair electrons in its molecule.

A survey of literature indicates that only limited numbers of references are available dealing with the corrosion inhibition effect of L-tryptophan on mild steel. The present work was undertaken to investigate the corrosion inhibition behavior of L-tryptophan on mild steel in 0.1M HCl solution. The techniques used are weight loss measurements and potentiodynamic polarization measurements.

MATERIALS AND METHODS
Material preparation
The mild steel specimens having composition (weight %): 0.20 % C, 0.53 % Mn, 0.11 %S, 0.036 % Si and 0.098 % P and

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balance Fe were used for corrosion inhibition studies. The inhibitor L-tryptophan [(2S)-2-amino-3-(1H-indol-3-yl)propanoic acid, molecular mass 204.23 g mol⁻¹] (CDH, India) was used as received. The stock solutions of 1000 ppm of L-tryptophan in 0.1mol L⁻¹ HCl (MERCK, India) was prepared using double distilled water. The solution was diluted to get inhibitor L-tryptophan solution in the concentration range of 10 ppm to 500 ppm.

Weight loss measurements

The mild steel coupons of dimension 2.5 x 2.0 x 0.03 cm were used for weight loss measurements. The coupons were machined and abraded on different grit silicon carbide papers, washed with double distilled water, degreased with absolute ethanol and finally dried in acetone. To hold the specimens a hole of 1.5 mm diameter was made near the edge. The weight loss studies were carried out in the temperature range of 30-50°C. The concentration of L-tryptophan was kept between 10 to 500 ppm in HCl. The weight loss experiments were performed for duration of 6 hrs, as per ASTM designation G1-90. The cleaned mild steel specimens were weighed on a microbalance (Model: Precisa 205A SOS) and suspended in 250 ml beakers containing 200 ml of test solution and placed in a digitally controlled water bath. The temperature of the water bath is controlled by a microprocessor based PID digital temperature indicator-cum-controller with an accuracy of ± 0.5°C. The beakers were kept covered in order to avoid significant water loss. The inhibition efficiency (%IE) was calculated by using the following equation:

\[ %\text{IE} = \frac{CR_o - CR_i}{CR_o} \times 100 \] (1)

Where, \( CR_o \) = Corrosion rate of mild steel in blank HCl; \( CR_i \) = Corrosion rate of mild steel in presence of inhibitor

Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were carried out using EG and G potentiostat/Galvanostat, model 263A. The experiments were carried out using a corrosion cell from EG and G; model K0047 with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and steel coupons as working electrode. The experiments were performed using a scan rate of 0.186 mV/S commencing at a potential above 250mV more active than the stable open circuit potential. All the measurements were carried out at 30°C. Before starting the measurements the specimens were left to attain a steady state which was indicated by a constant potential. The inhibition efficiency was calculated using the relationship:

\[ IE(\%) = \left(1 - \frac{i_{corr}}{i_{corr}}\right) \times 100 \] (2)

Where \( i_{corr} \) = inhibited current density and \( i_{corr} \) = uninhibited current density

RESULTS

Weight loss measurements

The corrosion of mild steel in 0.1M HCl in absence and presence of varying concentration of amino acid L-tryptophan was studied in the temperature range of 30-50°C using weight loss technique. (Table. 1) shows the calculated values of corrosion rate and IE at different concentrations of L-tryptophan under varying temperature. From the data it is clearly seen that the corrosion rate of mild steel depends upon two factors namely, inhibitor concentration and temperature. The corrosion rates are significantly reduced in presence of L-tryptophan. The maximum increase in IE of 64% was observed at a concentration of 500 ppm at 30°C which further increased to 83% on increasing the temperature from 30 to 50°C. The plots of IE as a function of L-tryptophan concentration at 30-50°C (Fig. 2) reveals that IE increases with increase in concentration. Except at very low concentration of L-tryptophan (up to 10 ppm) IE decreases with increasing temperature.
Inhibition of mild steel corrosion in HCl solution using amino acid L-tryptophan

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A survey of literature indicates that only limited numbers of references are available dealing with the corrosion inhibition effect of L-tryptophan on mild steel. The present work was undertaken to investigate the corrosion inhibition behavior of L-tryptophan on mild steel in 0.1M HCl solution. The techniques used are weight loss measurements and potentiodynamic polarization measurements.

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The potentiodynamic polarization measurements were carried out using EG and G potentiostat/Galvanostat, model 263A. The experiments were carried out using a corrosion cell from EG and G; model K0047 with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and steel coupons as working electrode. The experiments were performed using a scan rate of 0.166 mV/S commencing at a potential above 250mV more active than the stable open circuit potential. All the measurements were carried out at 30°C. Before starting the measurements the specimens were left to attain a steady state which was indicated by a constant potential. The inhibition efficiency was calculated using the relationship:

\[
\text{IE} (\%) = \left( 1 - \frac{i_\text{corr}}{i_\text{corr}^\circ} \right) \times 100
\]

Where \(i_\text{corr}\) = inhibited current density and \(i_\text{corr}^\circ\) = uninhibited current density.

**RESULTS**

**Weight loss measurements**

The corrosion of mild steel in 0.1M HCl in absence and presence of varying concentration of amino acid L-tryptophan was studied in the temperature range of 30-50°C using weight loss technique. (Table. 1) shows the calculated values of corrosion rate and IE at different concentrations of L-tryptophan under varying temperature. From the data it is clearly seen that the corrosion rate of mild steel depends upon two factors namely, inhibitor concentration and temperature. The corrosion rates are significantly reduced in presence of L-tryptophan. The maximum increase in IE of 64% was observed at a concentration of 500 ppm at 30°C which further increased to 83% on increasing the temperature from 30 to 50°C. The plots of IE as a function of L-tryptophan concentration at 30-50°C (Fig. 2) reveals that IE increases with increase in concentration. Except at very low concentration of L-tryptophan (up to 10 ppm) IE increases with increasing temperature.
The inhibition of mild steel corrosion in presence of various 
organic compounds have been attributed to their adsorption on the 
steel surface and are generally confirmed from the fit of the 
experimental data to various adsorption isotherms. The degree of 
surface coverage (θ) for various concentrations of L-tryptophan, in 
0.1M HCl at 30-50 °C for 6 hrs immersion time has been evaluated 
by weight loss measurements. The data were tested graphically by 
fitting to various isotherms and the best result was obtained for 
Langmuir adsorption isotherm.

According to this isotherm, surface coverage (θ) is related to 
the inhibitor concentration C via

\[
\frac{C}{\theta} = \frac{1}{K} + C
\]  

(3)

where \(\theta\) is the degree of surface coverage, \(K\) is the 
equilibrium constant of the adsorption process and \(C\) is the L-
tryptophan concentration.

Enthalpy of adsorption, \(\Delta H\) and entropy of adsorption, \(\Delta S\) for 
the corrosion of mild steel in 0.1 M HCl in the presence of L-
tryptophan was obtained by the equation:

\[
CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right)
\]  

(4)

\[
\Delta G_{ads} = -RT \ln (55.5 K)
\]  

(5)

Where, \(K\) is equilibrium constants and is given by

\[
K = \frac{\theta}{C(1 - \theta)}
\]  

(6)

Where, \(\theta\) is the degree of surface coverage, \(C\) the 
concentration of inhibitors in mol dm\(^{-3}\), \(R\) gas constant and \(T\) is the 
solution temperature.

### Table 2. Thermodynamic parameters for corrosion of mild steel in absence and presence of L-tryptophan.

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>(\Delta H) (kJmol(^{-1}))</th>
<th>(\Delta S) (kJK(^{-1})mol(^{-1}))</th>
<th>(\Delta Q) (kJmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>86.54</td>
<td>78.49</td>
<td>54.95</td>
</tr>
<tr>
<td>500</td>
<td>54.95</td>
<td>33.76</td>
<td>41.8</td>
</tr>
</tbody>
</table>

### Table 3. Thermodynamic parameters for mild steel in 0.1 M HCl in presence of L-tryptophan

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>(\Delta G_{ads}) (kJmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>29.69</td>
</tr>
<tr>
<td>200</td>
<td>28.01</td>
</tr>
<tr>
<td>400</td>
<td>26.70</td>
</tr>
<tr>
<td>500</td>
<td>26.74</td>
</tr>
</tbody>
</table>

Potentiodynamic Polarization Measurements

The potentiodynamic polarization curves for the corrosion of 
mild steel in 0.1M HCl in absence and presence of varying 
concentration of L-tryptophan are shown in (fig.5). The values of 
electrochemical parameters as deduced from these curves e.g., 
corrosion potential \(E_{corr}\), corrosion current density \(i_{corr}\), the cathodic 
tafel slope (bc), the anodic tafel slope (ba) and % inhibition efficiency 
(\% IE) are shown in Table. 4. The IE was calculated using the 
equation:

\[
\% IE = \frac{i_{corr} - i_{corr}}{i_{corr}} \times 100
\]  

(7)

Where, \(i_{corr}\) and \(i_{corr}\) are the corrosion current density in absence 
and presence of inhibitors, respectively.
DISCUSSION

Weight loss measurements

The inhibition behavior of L-tryptophan on mild steel in 0.1 M HCl can be attributed to the adsorption of the molecules on the surface of steel. The effectiveness of the adsorption of L-tryptophan may be attributed to the presence of two nitrogen atoms in the molecule and its large volume [18]. The increased IE with increasing inhibitor concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film [19]. The increase in IE with increasing temperature suggests that at higher concentration L-tryptophan is chemically adsorbed on to the mild steel surface. At lower concentration the adsorbed film is not so stable and gets damaged at higher temperature, thus showing lower IE. The amino acid, L-tryptophan is easily protonated and expected to involve two ways of adsorption. Firstly, it may be adsorbed via donor-acceptor interactions between the π electrons of the indole rings and the unshared electrons pairs of the heteroatom to form a bond with vacant d-orbital of the metal surface [20].

Secondly, the -NH₂ group of amino acid in acid medium is readily protonated and might get adsorbed on the metallic surface via the negatively charged acid anions [21].

The plots of log θ/1-θ versus log C showed a linear correlation of slope close to unity suggesting that adsorption of L-tryptophan on mild steel interface obeys Langmuir adsorption isotherm [16]. The values of heat of adsorption are less than -40 KJ mol⁻¹ suggesting the physical adsorption of the inhibitors [22]. The negative values of ΔG_ads suggest that the adsorption of L-tryptophan on mild steel is spontaneous. It is an established fact that values of ΔG_ads around -20 KJ mol⁻¹ or less indicates physisorption. The adsorption is attributed to the electrostatic attraction between the charged organic molecules and charged metal surface. The values of ΔG_ads around -40 KJ mol⁻¹ or more are considered as chemisorptions. However, the values of ΔG_ads between -20 and -40 KJ mol⁻¹ gives a disputed Judgment about the type of adsorption [23-26]. In the present investigation the values of ΔG_ads are in the range of -26.70 to -34.85 KJ mol⁻¹ suggesting a mixed type of adsorption involving both physisorption and chemisorption.
Potentiodynamic polarization measurements

The study of electrochemical data reveals that the value of $i_{corr}$ continuously decreases in presence of L-tryptophan. The maximum $IE$ of about 75% was observed at a concentration of 500 ppm indicating that a higher coverage of L-tryptophan on steel surface is obtained in the solution with highest concentration of inhibitor. The values of $E_{corr}$ shifts to more positive value compared to the blank, indicating that L-tryptophan acts more anodic than cathodic inhibitor. The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

Table 4. Potentiodynamic Polarization parameters for corrosion of mild steel in 0.1M HCl in absence and presence of various concentrations of L-tryptophan at 30°C.

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (µA)</th>
<th>$\beta_1$ (mV)</th>
<th>$\beta_2$ (mV)</th>
<th>C.R (mpy)</th>
<th>%IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-622.96</td>
<td>666.1</td>
<td>283.19</td>
<td>134.63</td>
<td>58.59</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>-614.41</td>
<td>456.8</td>
<td>263.92</td>
<td>115.64</td>
<td>42.76</td>
<td>29.920</td>
</tr>
<tr>
<td>200</td>
<td>-603.23</td>
<td>435.6</td>
<td>271.522</td>
<td>117.146</td>
<td>39.90</td>
<td>34.69</td>
</tr>
<tr>
<td>500</td>
<td>-573.99</td>
<td>170.1</td>
<td>181.23</td>
<td>121.33</td>
<td>15.59</td>
<td>74.46</td>
</tr>
</tbody>
</table>

Fig 5. Potentiodynamic polarization curves of mild steel in 0.1M HCl in absence and presence of varying concentration of L-tryptophan (1) Blank (2) 100ppm (3) 200ppm (4) 500ppm.

CONCLUSIONS

1. L-tryptophan showed good performance as corrosion inhibitor for mild steel in 0.1 M HCl.
2. The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir adsorption isotherm. The thermodynamic data suggest mixed type of adsorption involving both physisorption and chemisorption.
3. L-tryptophan acts more anodic than cathodic inhibitor.

ACKNOWLEDGEMENT

Financial support from University Grants Commission, New Delhi, is gratefully acknowledged.

REFERENCES


Inhibition of Mild Steel Corrosion Using L-tryptophan and Synergistic Surfactant Additives

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Abstract

The corrosion inhibition characteristics of nitrogen containing amino acid L-tryptophan on mild steel in 0.1 M HCl solution, in the temperature range of 30-50 °C, was studied by weight loss and potentiodynamic polarization measurements. L-tryptophan significantly reduces the corrosion rates of mild steel; the maximum inhibition efficiency being 83% at 50 °C in presence of inhibitor concentration of 500 ppm. The effect of the addition of very small concentrations of anionic surfactant, sodium dodecyl sulfate (SDS), and of cationic surfactant, cetyl trimethyl ammonium bromide (CTAB), on the corrosion inhibition behavior of L-tryptophan was also studied. The inhibition efficiency (IE) of L-tryptophan significantly improved in presence of both surfactants. The effect of SDS and CTAB on the corrosion inhibition behavior of L-tryptophan appears to be synergistic in nature, the values of synergism parameter being greater than unity. The adsorption of inhibitors on mild steel surface obeyed Langmuir’s adsorption isotherm. The calculated thermodynamic parameters for adsorption reveal a strong interaction between the inhibitors and the mild steel surface. The results obtained by electrochemical studies are consistent with the results of the weight loss measurements. L-tryptophan acts more anodic than cathodic inhibitor.

Keywords: L-tryptophan, corrosion inhibitor, adsorption, surfactants, electrochemical technique.

Introduction

Among the several methods to save the metals from corrosion, the use of inhibitors has found wide attention both in academia and industries. The corrosion inhibitors are generally used to protect metals against the attack of the acid solutions, which are widely used in acid pickling, industrial cleaning, acid descaling, oil-well acidizing, etc. Organic compounds containing nitrogen, sulfur
and oxygen have been widely used as potential corrosion inhibitors in acid solutions [1-3]. These compounds prevent corrosion either by getting adsorbed, or by forming a protective layer or an insoluble complex on the metal surface, thus blocking the active corrosion sites. However, most of the organic compounds are synthetic chemicals, expensive and very hazardous to both human beings and the environments, and need to be replaced by non-toxic and environment friendly compounds.

In recent years, a number of eco-friendly compounds such as extract of common plants which contain many organic compounds, e.g., alkaloids, fatty acids, carbohydrates, tannins, pigments and amino acids, have been exploited as green alternative to toxic and hazardous compounds [4]. The amino acids which contain carboxyl and amino functionalities bonded to the same carbon atom are non-toxic, relatively cheap and easy to produce in purities greater than 99%. It has been shown by various authors that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds as substitutes to conventional corrosion inhibitors that are usually toxic [5-9]. The inhibition effect of three amino acids, namely, alanine, glycine and leucine, against steel corrosion in HCl solutions has been investigated by potentiodynamic polarization method. The inhibition effect was found to range from 28-91% [10]. The corrosion inhibition of Fe in 1 M HCl using twenty two different common amino acids and four related compounds has been investigated using potentiodynamic polarization curves [11]. In general, amino acids with longer hydrocarbon chains showed greater inhibition. Additional groups or groups which increased electron density on alpha amino group also increased the inhibition efficiency.

The nitrogen containing amino acid L-tryptophan is a derivative of indole. The molecular structure of the compound suggests that it has strong potential to become an effective corrosion inhibitor. Moretti and Guidi [12] reported the corrosion inhibition of L-tryptophan on copper in aerated 0.5 M H2SO4 in the temperature range of 20-50 °C. The corrosion rate did not rise as temperature increased. Recently, corrosion inhibition behavior of low carbon steel by L-tryptophan was investigated using weight loss experiments and Tafel polarization curves [13]. The adsorption behavior of L-tryptophan at Fe surface was also investigated by the molecule dynamics simulation method and density functional theory. The results indicated that L-tryptophan could adsorb on Fe surface through the indole ring with π-electrons and nitrogen/oxygen atom with the lone pair electrons in its molecule.

The majority of the acidic inhibitors have been known for their specificity of inhibition action. A combination of inhibitors is likely to provide multiple effects required for effective corrosion inhibition. The addition of halide ions to organic compounds has shown synergistic effect and resulted in improved inhibition efficiency of many organic compounds, and has been reported in the literature [14]. However, the influence of surfactants on the corrosion inhibition behavior of organic compounds is very scanty [15].

Surfactants have effectively been used as corrosion inhibitors as their molecules possess strong adsorption ability to the metallic surfaces. The adsorbed
molecules form monolayer or bilayer hemimicelles or admicelles, depending upon the surfactant concentration, and prevent the acid to attack the surface, and thus reduce the corrosion attack [16-19]. Amino acids interact with the surfactants to form a complex structure and help to adhere to surface, which offers great promise in corrosion inhibition. The binding of surfactants to amino acids depends upon the structure, molecular weights, interaction times and charge densities. A survey of literature indicates that only limited number of references is available dealing with the corrosion inhibition effect of L-tryptophan on mild steel. Further, the corrosion inhibition effect of amino acids in presence of surfactants has not yet been reported to the best of our knowledge. However, the influence of some surfactants on the corrosion inhibition of some oxidiazoles has recently been reported [15]. The adsorption of oxidiazoles on mild steel surface is reported to be significantly enhanced in presence of surfactants.

The present work was undertaken to investigate the corrosion inhibition behavior of L-tryptophan on mild steel in 0.1 M HCl solution. The effect of the addition of very small concentrations of SDS and CTAB on the corrosion inhibition behavior of L-tryptophan, for which no reference is available in the literature, was also studied. The techniques used are weight loss and potentiodynamic polarization measurements.

**Experimental**

**Material preparation**

Mild steel specimens having composition (weight %): 0.20 % C, 0.53 % Mn, 0.11 % S, 0.036 % Si and 0.098 % P, and balance Fe, were used for corrosion inhibition studies. The inhibitor L-tryptophan [(2S)-2-amino-3-(1-H-indol-3-yl) propanoic acid; molecular mass 204.23 g mole$^{-1}$], anionic surfactant, sodium dodecyl sulfate (SDS), cationic surfactant, N-cetyl N,N,N-trimethyl ammonium bromide (CTAB) (CDH, India), were used as received. The other chemicals used were all reagent grade. The stock solution of HCl and inhibitors were prepared using double distilled water.

**Weight loss measurements**

Mild steel coupons of dimension 2.5 x 2.0 x 0.03 cm were used for weight loss measurements. The coupons were machined and abraded on different grit SiC papers and finally washed and degreased using acetone, and dried up. To hold the specimens a hole of 1.5 mm dia was made near the edge. The weight loss studies were carried out in the temperature range of 30-50 °C in 0.1 M HCl. The test solution was made of AR grade 35% HCl using double distilled water. The concentration of L-tryptophan was kept between 1 to 500 ppm in HCl. The weight loss experiments were performed for duration of 6 h, as per ASTM designation G1-90. The inhibition efficiency (%IE) was calculated by using the following equation:
where, \( CR_o \) = corrosion rate of mild steel in blank HCl; \( CR_i \) = corrosion rate of mild steel in presence of the inhibitor.

**Potentiodynamic polarization measurements**

The potentiodynamic polarization measurements were carried out using an EG and G potentiostat/galvanostat, model 263A. The experiments were carried out using a corrosion cell from EG and G; model K0047 with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and steel coupons as working electrode. The experiments were performed using a scan rate of 0.166 mV/S, commencing at a potential above 250 mV more active than the stable open circuit potential. All the measurements were carried out at room temperature (30 ± 1 °C). Before starting the measurements the specimen was left to attain a steady state indicated by a constant potential. The inhibition efficiency was calculated using the relationship:

\[
IE(\%) = \left(1 - \frac{i^\text{corr}}{i^\text{corr}_e}\right) \times 100
\]

where \( i^\text{corr} \) = inhibited current density and \( i^\text{corr}_e \) = uninhibited current density.

<table>
<thead>
<tr>
<th>L-tryptophan Conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (% I)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 °C</td>
<td>40 °C</td>
</tr>
<tr>
<td>Blank</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>102.14</td>
<td>253.62</td>
</tr>
<tr>
<td>50</td>
<td>57.42</td>
<td>131.32</td>
</tr>
<tr>
<td>100</td>
<td>55.03</td>
<td>101.46</td>
</tr>
<tr>
<td>200</td>
<td>47.68</td>
<td>80.25</td>
</tr>
<tr>
<td>400</td>
<td>46.93</td>
<td>78.79</td>
</tr>
<tr>
<td>500</td>
<td>42.53</td>
<td>88.46</td>
</tr>
</tbody>
</table>

**Results and discussion**

**Weight loss measurements**

The corrosion of mild steel in 0.1 M HCl in absence and presence of different concentrations of amino acid L-tryptophan was studied in the temperature range of 30-50 °C using weight loss technique. Table 1 shows the calculated values of weight loss, corrosion rate and IE at different concentrations of L-tryptophan.
under different temperatures. From these data it is clearly seen that the corrosion rate of mild steel depends upon two factors, namely inhibitor concentration and temperature. The corrosion rates are significantly reduced in presence of L-tryptophan. The maximum increase in IE of 64% was observed at a concentration of 500 ppm at 30 °C, which further increased to 83% on increasing the temperature from 30 to 50 °C. The plots of IE as a function of L-tryptophan concentration, at 30-50 °C, reveal that IE increases with increase in concentration (Fig. 1a).

![Graph of IE vs. Concentration](image1)

**Figure 1.** Plots of inhibition efficiency (IE) vs. inhibitor concentration for mild steel in 0.1 M HCl at different temperatures: (a) L-tryptophan; (b) L-tryptophan + SDS; (c) L-tryptophan + CTAB.
Table 2. Calculated values of corrosion rate, inhibition efficiency and synergism parameter for mild steel in 0.1 M HCl in the absence and presence of different concentrations of L-tryptophan with SDS at 30-50 °C, from weight loss measurements.

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (% I)</th>
<th>Synergism parameters (S_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 °C</td>
<td>40 °C</td>
<td>50 °C</td>
</tr>
<tr>
<td>L-tryptophan</td>
<td>SDS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>Blank</td>
<td>102.39</td>
<td>253.62</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>87.55</td>
<td>196.51</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>48.62</td>
<td>97.69</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>44.00</td>
<td>89.82</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
<td>42.53</td>
<td>80.67</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>41.07</td>
<td>88.46</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>36.67</td>
<td>66.00</td>
</tr>
</tbody>
</table>

Except at very low concentration of L-tryptophan (up to 10 ppm), IE increases with increasing temperature. The inhibition behavior of L-tryptophan on mild steel in 0.1 M HCl can be attributed to the adsorption of the molecules on the steel surface. The effectiveness of the adsorption of L-tryptophan may be attributed to the presence of two nitrogen atoms in the molecule and its large volume [20]. The increased IE with increasing the inhibitor concentration indicates that more inhibitor molecules are adsorbed on the steel surface, leading...
to the formation of a protective film [21]. The increase in IE with increasing temperature suggests that at higher concentrations L-tryptophan is chemically adsorbed on to the mild steel surface. At lower concentrations the adsorbed film is not so stable and gets damaged at higher temperature, thus showing lower IE. The amino acid, L-tryptophan is easily protonated and expected to involve two ways of adsorption. Firstly, it may be adsorbed via donor-acceptor interactions between the π electrons of the indole rings and the unshared electron pairs of the heteroatom, to form a bond with vacant d-orbital of the metal surface [22]. Secondly, the –NH₂ group of amino acid in acid medium is readily protonated and might get adsorbed on the metallic surface via the negatively charged acid anions [23].

![Figure 2. Arrhenius plot for log θ/1-θ vs. 1/T (■ L-tryptophan; ▲ L-tryptophan + SDS; ● L-tryptophan + CTAB).](image)

To observe the effect of SDS and CTAB on the corrosion inhibition behavior of L-tryptophan, the corrosion of mild steel in 0.1 M HCl in absence and presence of different concentrations of L-tryptophan, in combination with 1 ppm of SDS and 1 ppm of CTAB, was separately studied in the temperature range of 30-50 °C by weight loss technique. The results are shown in Tables 2 and 3. The corrosion rates of mild steel in 0.1 M HCl in presence of L-tryptophan in combination with surfactants is further reduced in comparison to L-tryptophan alone. Fig. 1b and 1c show the plots of IE as a function of concentration of L-tryptophan in combination with 1 ppm of SDS and CTAB, respectively, at 30-50 °C.

### Table 4. Thermodynamic parameters for corrosion of mild steel in absence and presence of L-tryptophan and surfactants.

<table>
<thead>
<tr>
<th>L-tryptophan conc. (ppm)</th>
<th>Surfactant conc. (ppm)</th>
<th>ΔH (kJmol⁻¹)</th>
<th>-ΔS (jk⁻¹mol⁻¹)</th>
<th>-Q (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>86.54</td>
<td>78.49</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>0.0</td>
<td>54.95</td>
<td>33.76</td>
<td>41.8</td>
</tr>
<tr>
<td>500</td>
<td>1 (SDS)</td>
<td>61.81</td>
<td>11.62</td>
<td>33.51</td>
</tr>
<tr>
<td>500</td>
<td>1 (CTAB)</td>
<td>72.47</td>
<td>20.09</td>
<td>18.19</td>
</tr>
</tbody>
</table>
Considering the effect of surfactants on the corrosion inhibition behavior of L-tryptophan, the anionic SDS binds with L-tryptophan through electrostatic interaction, thus helps to adsorb at the metal surface more firmly and displays higher IE. The IE of L-tryptophan in presence of 1 ppm of CTAB is also higher, but lower in comparison to SDS.

![Figure 3. Arrhenius plot for log CR/T vs. 1/T (● Blank; ■ L-tryptophan; ▲ L-tryptophan + SDS; ● L-tryptophan + CTAB).](image)

It may be due to the adsorption of L-tryptophan to metal surface by binding with CTAB as co-ions or through hydrophobic interaction. The effect of surfactants on the IE of L-tryptophan in 0.1 M HCl appears to be synergistic in nature. The values of the synergism parameter $S_i$ for various concentrations of L-tryptophan in combination with 1 ppm of surfactants were calculated from the gravimetric data at 30 °C using the relationship [14]

$$S_i = \frac{1 - I_{1+2}}{1 - I_{1+2}}$$

where, $I_{1+2} = (I_1 + I_2)$; $I_1$ is IE of L-tryptophan; $I_2$ is IE of the surfactants; and $I'_{1+2}$ being IE of L-tryptophan is in combination with surfactants. The results are given in Tables 2 and 3. The values are all greater than unity. This is an indication that the enhanced IE resulting from the addition of surfactants to L-tryptophan is synergistic in nature and proved that addition of a very small concentration of surfactants can improve the adsorption of L-tryptophan on the mild steel.

The inhibition of mild steel corrosion in presence of various organic compounds has been attributed to their adsorption on the steel surface, being generally confirmed from the fit of the experimental data to various adsorption isotherms. The degree of surface coverage ($\theta$) for various concentrations of L-tryptophan, and L-tryptophan in combination with 1 ppm of SDS and CTAB, in 0.1 M HCl at 30-50 °C, for 6 h immersion time, has been evaluated by weight loss measurements. The data were tested graphically by fitting to various isotherms and the best result was obtained for Langmuir adsorption isotherm.
Table 5. Thermodynamic parameters for mild steel in 0.1 M HCl in presence of L-tryptophan and surfactants.

<table>
<thead>
<tr>
<th>Inhibitor conc. (mol dm$^{-3}$)</th>
<th>$\Delta G^{ads}$ 303 K</th>
<th>$\Delta G^{ads}$ 313 K</th>
<th>$\Delta G^{ads}$ 323 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-tryptophan 0.10</td>
<td>29.69</td>
<td>32.28</td>
<td>34.38</td>
</tr>
<tr>
<td>L-tryptophan 0.20</td>
<td>28.01</td>
<td>30.55</td>
<td>32.61</td>
</tr>
<tr>
<td>L-tryptophan 0.40</td>
<td>26.70</td>
<td>28.33</td>
<td>31.66</td>
</tr>
<tr>
<td>L-tryptophan 0.50</td>
<td>26.74</td>
<td>28.33</td>
<td>31.21</td>
</tr>
<tr>
<td>SDS + L-tryptophan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001 + 0.10</td>
<td>30.20</td>
<td>32.28</td>
<td>34.85</td>
</tr>
<tr>
<td>0.001 + 0.20</td>
<td>28.59</td>
<td>29.31</td>
<td>33.67</td>
</tr>
<tr>
<td>0.001 + 0.40</td>
<td>27.96</td>
<td>28.74</td>
<td>30.48</td>
</tr>
<tr>
<td>0.001 + 0.50</td>
<td>26.75</td>
<td>28.81</td>
<td>30.67</td>
</tr>
<tr>
<td>CTAB + L-tryptophan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001 + 0.10</td>
<td>30.96</td>
<td>33.49</td>
<td>33.15</td>
</tr>
<tr>
<td>0.001 + 0.20</td>
<td>29.29</td>
<td>31.78</td>
<td>33.14</td>
</tr>
<tr>
<td>0.001 + 0.40</td>
<td>28.69</td>
<td>30.25</td>
<td>31.90</td>
</tr>
<tr>
<td>0.001 + 0.50</td>
<td>28.32</td>
<td>29.39</td>
<td>31.37</td>
</tr>
</tbody>
</table>

Figure 4. Potentiodynamic polarization curves of mild steel in 0.1 M HCl in absence and presence of different concentrations of L-tryptophan: (1) Blank; (2) 100 ppm; (3) 200 ppm; (4) 500 ppm.

Figure 5. Potentiodynamic polarization curves for mild steel in 0.1 M HCl in absence and presence of L-tryptophan and SDS: (1) Blank; (2) L-tryp 100 ppm + SDS 1 ppm; (3) L-tryp 200 ppm + SDS 1 ppm; (4) L-tryp 400 ppm + SDS 1 ppm; (5) L-tryp 500 ppm. + SDS 1 ppm.
Figure 6. Potentiodynamic polarization curves for mild steel in 0.1 M HCl in absence and presence of L-tryptophan and CTAB: (1) Blank; (2) L-tryp 100 ppm + CTAB 1 ppm; (3) L-tryp 200 ppm + CTAB 1 ppm; (4) L-tryp 400 ppm + CTAB 1 ppm; (5) L-tryp 500 ppm + CTAB 1 ppm.

Table 6. Potentiodynamic polarization parameters for corrosion of mild steel in 0.1 M HCl in absence and presence of various concentrations of L-tryptophan and of L-tryptophan-surfactant mixtures at 30 °C.

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (μA)</th>
<th>$\beta_a$ (mV)</th>
<th>$\beta_p$ (mV)</th>
<th>C.R (mpy)</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-622.96</td>
<td>666.1</td>
<td>283.19</td>
<td>134.63</td>
<td>58.59</td>
<td>-</td>
</tr>
<tr>
<td>L-trypt 100</td>
<td>-614.41</td>
<td>466.8</td>
<td>263.92</td>
<td>116.64</td>
<td>42.76</td>
<td>29.920</td>
</tr>
<tr>
<td>L-trypt 200</td>
<td>-603.23</td>
<td>435.6</td>
<td>271.522</td>
<td>117.146</td>
<td>39.90</td>
<td>34.60</td>
</tr>
<tr>
<td>L-trypt 500</td>
<td>-573.99</td>
<td>170.1</td>
<td>181.23</td>
<td>121.33</td>
<td>15.59</td>
<td>74.46</td>
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<tr>
<td>SDS 1 + L-trypt 100</td>
<td>-591.88</td>
<td>349.6</td>
<td>255.07</td>
<td>111.37</td>
<td>32.02</td>
<td>47.51</td>
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<td>SDS 1 + L-trypt 200</td>
<td>-582.88</td>
<td>307.1</td>
<td>243.11</td>
<td>106.35</td>
<td>28.13</td>
<td>53.89</td>
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<td>SDS 1 + L-trypt 400</td>
<td>-579.26</td>
<td>204.4</td>
<td>216.94</td>
<td>85.54</td>
<td>18.72</td>
<td>69.31</td>
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<td>SDS 1 + L-trypt 500</td>
<td>-569.54</td>
<td>109.9</td>
<td>206.43</td>
<td>55.75</td>
<td>10.06</td>
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<td>CTAB1 + L-trypt 100</td>
<td>-589.66</td>
<td>438.0</td>
<td>292.43</td>
<td>127.53</td>
<td>40.12</td>
<td>34.24</td>
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<td>264.54</td>
<td>120.69</td>
<td>30.02</td>
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<td>286.99</td>
<td>99.09</td>
<td>15.66</td>
<td>74.328</td>
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<tr>
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<td>130.5</td>
<td>285.87</td>
<td>94.42</td>
<td>11.95</td>
<td>80.408</td>
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</table>

A plot of log $\theta/1-\theta$ vs. $1/T$, where T is the solution temperature, was also obtained for L-tryptophan and for L-tryptophan in combination with 1 ppm of surfactants (Fig. 2). The heat of adsorption ($Q_d$) was calculated from the slope of the plot ($-Q_d/2.303R$) and the values are listed in Table 4. The plot of log (CR/T) vs. $1/T$ in presence of L-tryptophan and surfactants (Fig. 3) gave a straight line with slope of ($-\Delta H/2.303R$) and an intercept of [(log(R/Nh) + ($\Delta S/2.303R$)). The values of $\Delta H$ obtained from the slope and of $\Delta S$ evaluated from the intercept, are
The values of free energy of adsorption ($\Delta G_{ads}$) were calculated using the following equation [24] and are listed in Table 5.

$$\Delta G_{ads} = -RT \ln (55.5 \text{ K})$$ (4)

where $K$ is equilibrium constants and is given by

$$K = \frac{\theta}{C(1-\theta)}$$ (5)

where $\theta$ is the degree of surface coverage, $C$ the concentration of the inhibitors in mol dm$^{-3}$, $R$ is the gas constant and $T$ is the solution temperature. The plots of log $\theta/1-\theta$ vs. log $C$ showed a linear correlation of slope close to unity, suggesting that the adsorption of L-tryptophan on mild steel surface obeys Langmuir adsorption isotherm. The values of heat of adsorption are less than -40 KJ mol$^{-1}$, suggesting the physical adsorption of the inhibitors [25]. The lower values of $\Delta H$ for L-tryptophan in presence of surfactants indicate less energy barrier for the reaction [26]. The negative values of $\Delta G_{ads}$ suggest that the adsorption of L-tryptophan on mild steel is spontaneous. It is an established fact that values of $\Delta G_{ads}$ around -20 KJ mol$^{-1}$ or less indicate physisorption. The adsorption is attributed to the electrostatic attraction between the charged organic molecules and charged metal surface. The values of $\Delta G_{ads}$ around -40 KJ mol$^{-1}$ or more are considered as chemisorptions. However, the values of $\Delta G_{ads}$ between -20 and -40 KJ mol$^{-1}$ give a disputed judgement about the type of adsorption [27-30]. In the present investigation the values of $\Delta G_{ads}$ are in the range of -26.70 to -34.85 KJ mol$^{-1}$, suggesting a mixed type of adsorption involving both physisorption and chemisorption.

**Potentiodynamic polarization measurements**

Potentiodynamic polarization curves for the corrosion of mild steel in 0.1 M HCl in absence and presence of different concentrations of L-tryptophan, and of L-tryptophan in combination with 1 ppm of SDS and CTAB, are shown in Fig. 4-6. The values of electrochemical parameters as deduced from these curves, e.g., corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), cathodic Tafel slope ($b_c$), anodic Tafel slope ($b_a$) and % inhibition efficiency (% IE), are shown in Table 6. The IE was calculated using the equation:

$$\%\text{IE} = \left( \frac{i_{corr}' - i_{corr}}{i_{corr}} \right) \times 100$$ (6)

where $i_{corr}'$ and $i_{corr}$ are the corrosion current density in absence and presence of the inhibitors, respectively. The study of electrochemical data reveals that the value of $i_{corr}$ continuously decreases in presence of L-tryptophan. The maximum IE of about 75% was observed at a concentration of 500 ppm, indicating that a higher coverage of L-tryptophan on steel surface is obtained in the solution with highest concentration of the inhibitor. The values of $E_{corr}$ shift to more positive value compared to the blank, indicating that L-tryptophan acts more as an anodic than a cathodic inhibitor. The addition of 1 ppm of SDS and CTAB to different concentrations of L-tryptophan improved the IE of L-tryptophan significantly.
The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

**Conclusions**

1. L-tryptophan showed good performance as corrosion inhibitor for mild steel in 0.1 M HCl, which is further improved in presence of the surfactants SDS and CTAB. The effect of surfactants on corrosion inhibition behavior of L-tryptophan appears to be synergistic in nature.

2. The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir adsorption isotherm. The thermodynamic data suggest mixed type of adsorption involving both physisorption and chemisorption.

3. L-tryptophan acts more as an anodic than a cathodic inhibitor.

**References**