Synthesis of Water Soluble Copolymer in Sulphamic Acid Medium for Corrosion Inhibition of Mild Steel and Stainless Steel in Acid Medium

BY

KARTHIKA. J
(Reg. No. 04MP52)

A Dissertation Submitted to the
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in partial fulfilment of the requirements for the degree of
Master of Philosophy in Applied Chemistry

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CERTIFICATE

This is to certify that the dissertation entitled **"Synthesis of Water Soluble Copolymer in Sulphamic Acid Medium for Corrosion Inhibition of Mild Steel and Stainless Steel in Acid Medium"** submitted to the Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore, in partial fulfilment of the requirements for the award of the **Degree of Master of Philosophy in Applied Chemistry** is a record of original research work done by **Ms. Karthika. J** during the period of her study in the Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women - Deemed University, Coimbatore, under my supervision and guidance and the dissertation has not formed the basis for the award of any Degree / Diploma / Associateship / fellowship or similar title to any candidate of any other University.

S. Subhashini
Signature of the Guide

Place: Coimbatore

Date: 30.11.2005

S. Sivakamasundari
30/11/05
Signature of the Head of the Department

DECLARATION

I hereby declare that the dissertation entitled **"Synthesis of Water Soluble Copolymer in Sulphamic Acid Medium for Corrosion Inhibition of Mild Steel and Stainless Steel in Acid Medium"** submitted to the Avinashilingam Institute for Home Science and Higher Education for Women Deemed University, Coimbatore, in partial fulfilment of the requirement for the award of the **Degree of Master of Philosophy in Applied Chemistry** is a record of original research work done by me under the supervision and guidance of **Dr.S.Subhashini, Reader,** Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women – Deemed University, Coimbatore, and it has not formed the basis for the award of any Degree / Diploma / Associateship / Fellowship or similar title to any candidate of any other university.

Place: Coimbatore

Date: 30.11.2005

Karthika.J

Signature of the Candidate

S. Subhashini

Signature of the Guide

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"You are the supreme indestructible worthy of being known. You are the ultimate refuge of this universe. You are again the protector of ageless Dharma; I consider you to be the eternal imperishable being".

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KARTHIKA. J

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θ	-	Surface Coverage
b_a	-	Anodic Tafel slope
b_c	-	Cathodic Tafel Slope
C.R.	-	Corrosion Rate
C_{dl}	-	Double layer capacitance
Conc.	-	Concentration
E_{corr}	-	Corrosion Potential
HCl	-	Hydrochloric acid
I.E	-	Inhibitor Efficiency
I_{corr}	-	Corrosion Current
mpy	-	Mills per year
MS	-	Mild Steel
PANI	-	Polyaniline
ppm	-	Parts per million
PVA	-	Polyvinyl alcohol
R_{ct}	-	Charge transfer resistance
SS	-	Stainless Steel
VAANI Copolymer	-	Vinyl Alcohol Aniline copolymer

Introduction

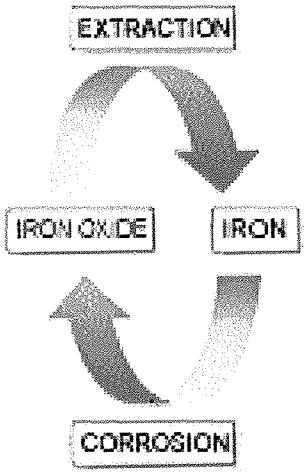
1. INTRODUCTION

It is now-a-days necessary to pay more attention to metallic corrosion than the one done earlier due to

- Increasing use of metals in all fields of technology
- Use of rare and expensive metals
- Use of new high strength alloys which are usually more susceptible to certain types of corrosion attack
- Increasing pollution of air and water resulting in a more corrosive environment
- Strict safety standards of operating equipment, which may fail in a catastrophic manner due to corrosion.

The term 'corrosion' derives from the Latin, rodere, meaning 'to gnaw' in the context of rats, and 'corrodere' means 'to gnaw to pieces'.

To the great majority of people, corrosion means rust, an almost universal object of hatred. Rust has more recently referred specifically to the corrosion of iron. But corrosion is a destructive phenomenon that affect almost all the metals. Although iron was not the first metal used by humans, it has certainly been the most used, and must have been one of the first with which serious corrosion problems were noticed.



The cycle of corrosion

FIGURE - 1

Metals tend to return to their natural ores, owing to corrosion. It is also defined as an extractive metallurgy in reverse, which is illustrated in figure (1).

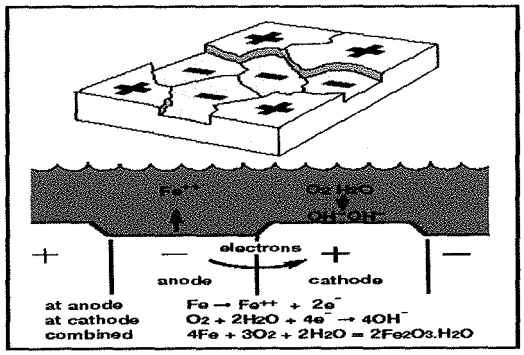
"Corrosion involves loss of electrons from the metal to the environment and formation of corrosion product such as oxides".

ISO 8044 defines corrosion as "physico-chemical interaction, which is usually of an electrochemical nature, between a metal and its environment, which results changes in the properties of the metal and which may often lead to impairment of the function of the metal in the environment, or the technical system of which, these form a part" **(Mattson, 1989)**.

Principle of Corrosion

Nearly all metallic corrosion processes involve transfer of electronic charge in aqueous solutions. Hence it is necessary to discuss electrochemical nature of corrosion, which can be illustrated by the attack of iron by hydrochloric acid. When iron is placed in dilute hydrochloric acid, a vigorous reaction occurs, as a result of which hydrogen gas is evolved and iron is dissolved.

The chemical changes that happen during corrosion can be shown as follows:



A Schematic representation of Corrosion Mechanism

FIGURE – 2

$$2Fe \rightarrow 4e^- + 2Fe^{2+} \quad \text{oxidation}$$

$$4e^- + O_2 + 2H_2O \rightarrow 4OH^- \quad \text{reduction}$$

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

$$Fe(OH)_2 \rightarrow Fe_2O_3.xH_2O \quad \text{rust}$$

hydrated iron (III) oxide

These partial reactions occur simultaneously and at the same rate on the metal surface. If this were not true, the metal would spontaneously become electrically charged which is clearly impossible. Thus during metallic corrosion the rate of oxidation is equal to the rate of reduction. Corrosion occurs through the formation of electrochemical cells in which the anode corrodes and the cathode is protected.

Forms of Corrosion

The more common forms of corrosion which affects all metals and alloys are

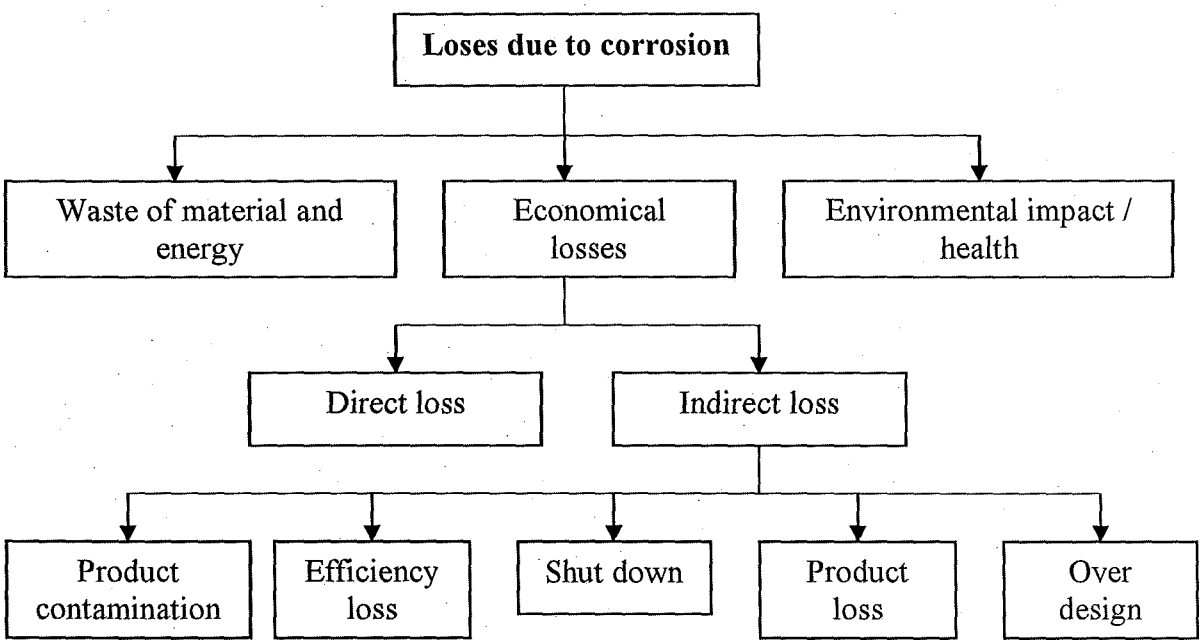
- **General / uniform corrosion**
  - Atmospheric corrosion
  - Galvanic corrosion
- **Localized corrosion**
  - Pitting corrosion
  - Crevice corrosion
- **Metallurgically influenced corrosion**
  - Intergranular corrosion
  - Dealloying corrosion
  - Erosion corrosion
- **Mechanically assisted degradation**
  - Erosion corrosion
  - Fretting corrosion
- **Environmentally induced cracking**
  - Stress cracking corrosion
  - Solid metal embrittlement

Expense of Corrosion

In the history of the use of materials, the past 150 years have been closely associated with alloys of metals such as iron, aluminium and copper. The developed civilization could not exist without them. Corrosion is their Achilles heel. The collasal loses due to corrosion are huge. The losses due to corrosion can be divided into

℘ Waste of Material and Energy

Internationally, one tonne of steel turns into rust for every 90 seconds. On the other hand, the energy required to make one tonne of steel is approximately equal to the energy an average family consumes over three months. From every tonne of steel from the world's production, approximately 50 percent is required to replace rusted steel **(Uhlig, 1971 and DCE, 1988)**.



Schematic representation of corrosion and its losses

FIGURE - 3

℘ Economical Losses

The cost of corrosion has been reported to be in the order of 1 – 5 percent of GNP (grand net profit) for any country. In India, the annual losses are estimated to be Rs.40 x 10^9 in 1988. The indirect losses result due to deterioration in quality of product, loss of efficiency, plant shut down, over design of the system etc.,

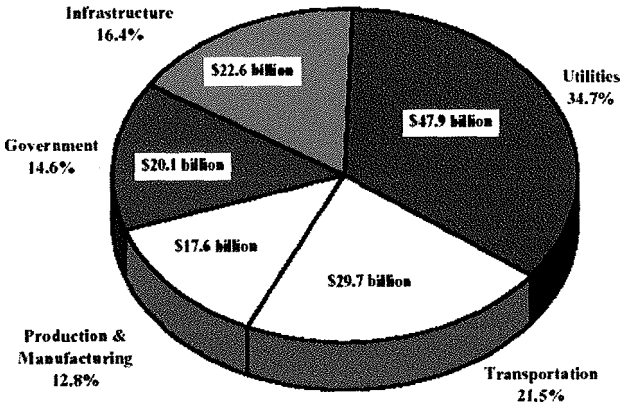
℘Environmental and Health Impact

Huge life, material losses and large scale environmental pollution are some of the results due to corrosion. Recent years have seen an increasing use of metal prosthetic

devices in the body, such as pins, plates, hip joints, pace makers and other implants. New alloys and better techniques of implantation have been developed, but corrosion continues to create problems. Examples include failures through broken connections in pace makers, inflammation caused by corroded products in the tissue around implants and fracture of weight bearing prosthetic devices due to corrosion.

Cost of Corrosion in India

"The cost of corrosion is estimated to be around $364 billion as of 2004. his does not include the indirect cost and other consequential damages. If this is taken into account, it would go up several times from the present level of 3.1% of GDP," said Houston-based NACE International president George Hays during his presentation at the NACE International India Section conclave in Mumbai.



Cost of corrosion in sector categories

FIGURE - 4

"As for the cost of corrosion in India alone, it is estimated to touch Rs. 36,000 crore," said Mr. Hays. "We can only be proud that we have enough money to lose like this! Yet another fact is that we are not in bad company as the cost of corrosion in US is over $360 billion."

Corrosion monitoring – What is it?

"If you do not measure (monitor) corrosion, you can't understand it ... if you can't understand corrosion, you can't control it or improve your corrosion control methods."

Some definitions assigned to corrosion monitoring have been wide ranging, essentially including any type of corrosion-related measurement or observation. For example, a glossary published by the National Corrosion Service of the National Physical Laboratory (NPL, UK) has defined corrosion monitoring as: **"Any method used to observe or measure the progress of corrosion."**

Such broad definitions highlight the **multi-disciplinary** nature of corrosion monitoring, covering a wide range of materials, measurement techniques, instrumentation, rules and regulations, standards, logistical support, data analysis, communication and information management.

Corrosion Monitoring Techniques

Some of the important corrosion monitoring techniques are

- Corrosion Coupons
- Electrical Resistance (ER)
- Linear Polarization Resistance (LPR)
- Electrochemical Impedance Spetroscopy (EIS)
- Potentiodynamic Polarization

(www.prginc.com)

Importance of Corrosion

Virtually all metals suffer corrosion, so its effect permeate nearly every aspect of human endeavour and this fact alone should make the study of corrosion more important. Resources and many important metals are exhausted as time passes and their prices will become exorbitant. Rapidly diminishing metal resources will have far more profound effect on civilization than many publicized energy crisis. However as yet there exists no practical substitutes to many commonly used metals and alloys whose scientific engineering properties make them indispensable. Evidently more concern must be shown for conservation of metals by minimizing losses due to corrosion.

Protection against Corrosion

Corrosion phenomena, their prevention and control have become a perpetual struggle between man and nature particularly in view of modern age of technological

developments and the increasing need and use of metallic materials in all facets of technology.

The practical control methods available for the production of metals against corrosion are diverse. Some of the corrosion control methods are:

- Proper designing
- Using pure metal
- Using metal alloys
- Cathodic / anodic protection
- Modifying the environment
- Use of inhibitors
- Application of protective coatings

➢ **Proper Design**

The design of the material should be such that corrosion even if it occurs, is uniform and does not result in intense and localized corrosion. Some of the designing principles involve avoiding the contact of dissimilar metals in the presence of corroding solution, preventing the occurrence of inhomogeneties etc.

➢ **Using Pure Metal**

Impurities in a metal causes heterogeneity which decreases corrosion – resistance of the metal. Thus the corrosion resistance of a given metal may be improved by increasing its purity.

➢ **Using Metal Alloys**

Corrosion resistance of most metals are best increased by alloying them with suitable elements but for maximum corrosion – resistance, alloy should be completely homogenous.

➢ **Cathodic / Anodic Protection**

The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. There are two types of cathodic protections.

- ☞ Sacrificial anodic production method.
- ☞ Impressed current cathodic protection

➢ **Modifying the Environment**

The corrosive nature of the environment can be reduced either

- ☞ by the removal of harmful constituent or
- ☞ by the addition of specific substances, which neutralize the effect of corrosive constituents of the environment. This includes deaeration, deactivation, dehumidification, alkaline neutralizations, etc.,

➢ **Application of Protective Coatings**

It is probably the oldest of the common procedures for corrosion prevention. A coated surface isolates the underlying metal from the corroding environment. The coating applied must be chemically inert and must prevent the penetration of the environment to the metal.

➢ **Use of Inhibitors**

A corrosion inhibitor is a substance which when added in small quantities to the aqueous corrosive environment, effectively decreases the corrosion of a metal.

Required properties of Inhibitors

The required properties of inhibitors for acid pickling are

- Effective inhibition of metal dissolution
- No over pickling in the presence of higher iron salt contents
- No delay of the pickling process
- Effective at low concentration
- Effective also at high temperatures
- Thermally and chemically stable
- Effective inhibition of hydrogen up-take by the metal
- Good surfactant characteristics
- Good foaming characteristics

Classification of Inhibitors

- Inhibitors which retard the cathodic process are termed as cathodic inhibitors. Eg: Organic amines.
- Chemical substances which influence the anodic process are called anodic inhibitors Eg: Molybdates, Phosphates, Chromates etc.

- Those substances that influences both cathodic and anodic process are called mixed inhibitors, Inhibitors are also classified as organic and inorganic inhibitors.
- Inorganic inhibitors

  Inorganic compounds such as AS_2O_3 and Sb_2O_3 have been reported as inhibitors in acid media. The action of these compounds have been attributed to the deposition of the metal on iron and steel surface and raises the hydrogen over voltage there by reducing corrosion. Recently it is shown that the addition of heavy metal ions such as Pb^{2+}, Te^{2+}, Mn^{2+}, Cd^{2+} inhibit the corrosion of iron in acids. Eg. Silicates, Chromates etc.

Selection of Inhibitor

The selection of appropriate inhibitor depends mainly on the type of acid, concentration, temperature, the extent of dissolved organic or inorganic substances in solution and chiefly the type of metallic material exposed to acid corrosion. The use of organic inhibitors in acid solution is very common, particularly in view of the high corrosion rate. Nitrogen containing organic compounds have been widely used as effective and efficient metallic corrosion inhibitors.

The inhibitive action of these organic compounds has been explained in terms of number of mobile electron pairs, π-orbital character of free electrons and electron density around nitrogen atoms. The efficiency of an organic compound as an inhibitor is largely dependent on its adsorption on the metal surface which consists of replacement of water by the organic inhibitor at the interface and can be represented as

$$Org_{(sol)} + nH_2O \leftrightarrows Org_{(ads)} + nH_2$$

The adsorption of these materials is influenced by the presence of functional groups such as = NH, -N = N-, -CHO, R-OH, R = R etc in the inhibitor molecule.

Nature of Adsorption of Inhibitors

In formulating organic inhibitor system, it is necessary to know the inhibition mechanism and the application field of the molecules concerned. It is generally accepted

that organic molecules inhibit corrosion by adsorption at the metal / solution interface and that the degree of adsorption are dependent upon

- The chemical structure of the molecule
- The chemical composition of the Solution
- The nature of the metal surface and
- The electrochemical potential at the metal / solution interface **(Riggs, 1973)**.

The utility of organic corrosion inhibitors in industries has considerably increased in recent years due to increased awareness of corrosion worldwide. Inhibitors effective in the corrosion prevention of iron and steel on treatment with acid solutions mainly belongs to the group of nitrogen containing organic compounds, such as alkyl and aryl amines, saturated and unsaturated nitrogen compounds, condensation products of amines with aldehydes and ketones, ethoxylated amines, nitrites, aldoxime, ketoxime and imidazoline derivatives.

The inhibitive action of these organic compounds containing N, S or O is due to the formation of a co-ordinate type of bond between the metal and the lone pair of electrons present in the additive. The tendency to co-ordinate bond formation and the extent of inhibition can be enhanced by increasing the effective electron density at the functional group of the additive.

Hackerman (1962), demonstrated that the inhibition efficiency increases with increase in the electron densities on the nitrogen atom. In aromatic or heterocyclic ring compounds the effective electron density at the functional group can be varied by introducing different substituents in the ring leading to variations of the molecular structure.

Effectiveness of organic inhibitors

The effectiveness of organic inhibitors depends upon

- The size of the organic molecules
- Aromaticity or conjugate bonding
- Chain length
- Strength of bonding to the metal substrates
- Type and number of bonding atoms or groups in the molecule
- The ability to become cross-linked

- The ability to complex with the metal atoms as a solid with in the metal lattice.
- Adequate solubility in the environment.

Conducting polymers

Polymers are known to have good insulating properties. Polymers are one of the most used materials in the modern world. Their uses and application range from containers to clothing. They are used to coat metal wires to prevent electric shocks. However it is now recognized that there are some polymers which have conducting properties.

Conducting polymers have been widely studied during the last ten years because their interesting mechanical and electrical properties allowed their use in a large field of applications. Recently, they have been studied for corrosion protection purposes.

Conducting Polymers as Active Protectors

Industrial treatment of mild steel / stainless steel or other oxidizable metals before painting uses conversion steps such as phosphatation and chromatation, that improve the corrosion resistance of the substrates. In the automobile industry, for instance, the painted metals resist corrosion for a period that exceeds the car's life time. Unfortunately, these conversion treatments have a strong environmental impact, and international antipollution regulations may restrict their use in the near future. The electro deposition of conducting polymers on oxidizable metals might be a cheap alternative treatment, since it could take advantage of the electrodeposition baths already used in industry and could reduce the overall pollution.

This process presents several advantages:

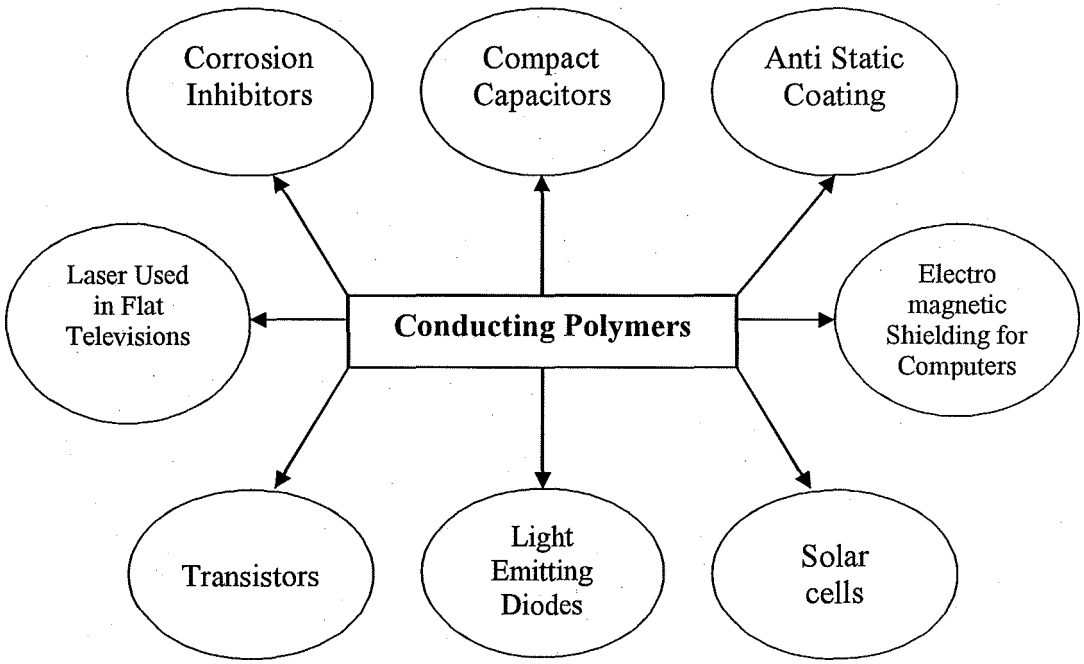
- Owing to the conductive properties of the material, thick layers can be generated in a short time and can constitute a physical barrier towards corrosive reagents.
- Further more, as the polymers carry polar groups or can be doped with specific anions.
- They may act as inhibitors and shift the potential of the coated material to a value. Where the rate of corrosion of the underlying metal is reduced.

Importance of Conducting Polymers

Indeed, they constitute a physical barrier towards aggressive chemical reagents and, as they carry polar groups, they may act as polymeric inhibitors and shift the potential of the coated material to a value where the kinetics of corrosion of the underlying metal are lowered.

The electrodeposition of conducting polymers might be a cheap alternative treatment since it can turn to advantage the electrodeposition baths already in use in the automotive industry.

Conducting polymers have many uses. The most documented as follows:



Uses of conducting polymers

FIGURE - 5

Water Soluble Polyaniline

Among all conducting polymers, polyaniline has a special representation due to

- Easy synthesis
- Environmental stability
- Simple – non redox doping by protonic acids
- Low cost.

Polyaniline (PANI) is a conducting polymer which attracts the greatest interest interms of applications. The most advantageous property of polyaniline is a possibility of gaining its conductivity in a proton doping mechanism as well as in a charge transfer process. This opens a broad gate for easy modifications of properties, such as solubility in organic solvents, plasticity etc., by doping PANI with an appropriate compound. Recently the interest was aimed towards water-processable polyaniline. Considerable progress was made in preparation of polyaniline in the form of aqueous colloidal dispersions.

Literature studies revealed that in copolymers electron transfer is always faster than in pure polymer which may be due to the difference is charge density on substituted and unsubstituted constituents of the polymer chain as a result of the electronic effect of substituents which may facilitate faster electron transfer.

In particular the polymers derived from aniline present some kind of interactions involving dopants which are responsible for the solubility of the polyanilines.

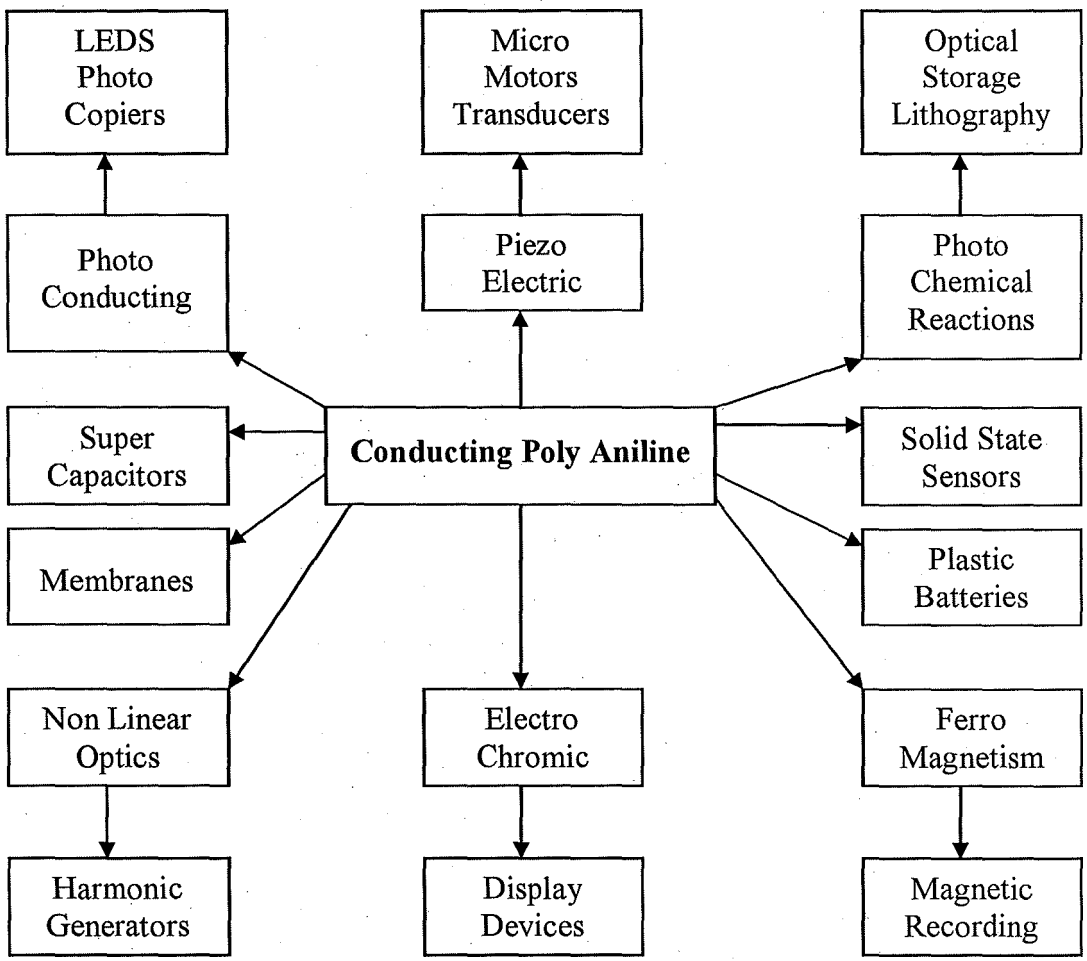
These soluble polyanilines, besides their application in advanced technologies, can have a big impact in corrosion control by being used as inhibitors as well as for covering metals as a very thin protection layer.

Electro chemical synthesis of conducting PANI is an efficient technique to obtain protective polyaniline coatings on metals and alloys. However, to form a film of conducting polyaniline on reactive metals such as iron and steel is difficult because of its preferred dissolution at a potential lower than the oxidation potential of the monomer key to the deposition is to design electro chemical conditions which lead to partial passivation of the metal and decrease its dissolution rate without precluding electro polymerization.

Efforts are presently underway to develop methods of corrosion protection of steel that are more effective and also more environmentally friendly than the present techniques.

Application of Conducting Polyanilines

Let us now consider some of the important applications of conducting poly aniline from the scientific view point.



Applications of conducting polyaniline

FIGURE - 6

Electrodeposition of Conducting Polymers

The electrodeposition of conducting polymers on electrode surfaces has been a very active research area in electrochemistry for almost two decades.

The great deal of interest in this area is due to the large number of potential applications of the conducting polymers themselves as well as of the modified electrode surfaces.

One very promising application of conducting polymers is the protection of metals against corrosion, although the vast majority of studies are referred to the

electropolymerization of inert anodes such as Pt, Au or various forms of carbon. Because of the electrochemical nature of the metal corrosion in various corrosive media.

Electro polymerization on oxidizable metals with high corrosion rates is not an easy task. This is due primarily to the fact that the metal substrate is dissolved is most of the solutions from which polymerization can be carried out. However, if deposition of conducting polymers on the metal surface could be possible, then the electrochemical reactions leading to the metals electro dissolution may occur at the surface of the conducting film avoiding corrosion of the metal substrate. There are also evidences that if a redox reaction can occur in the coating then it appears to be capable of maintaining the native passive film on the metal. **(Deberry, 1985).**

OBJECTIVES

The main objective of this work was to obtain a polymer layer able to efficiently protect stainless steel and mild steel against corrosion. The investigator is keen to prepare a water soluble polymer and to utilize the same for corrosion studies.

Present work is undertaken with following objectives:

- To obtain water soluble polymer, attempts are made to copolymerize aniline and polyvinyl alcohol.
- To select a medium from which the copolymerization of aniline/ PVA to be carried out.
- To examine the protection of MS and SS against corrosion by using the obtained copolymer.
- To investigate the effect of VAANI Copolymer by varying its concentration and the period of immersion at room temperature.
- To assess the stability of the VAANI Copolymer at higher temperatures.
- To fit the experimental results into the various adsorption isotherms.
- To calculate the energy of activation from temperature studies.
- To calculate thermodynamic parameters – change in free energy, change in enthalpy, change in entropy.
- To understand the roll of VAANI Copolymer on metal surface, electrochemical measurements were carried out.
- To employ cyclic voltammetry technique to obtain well-adhering layers of VAANI Copolymer on iron / SS surface.
- To obtain information regarding the nature of polymerization substrate, the surface analysis technique was carried out. To study the surface morphology of the Fe substrate and polymer layer by optical electron micrograph.
- To suggest a possible mechanism for inhibition process.

Review of Literature

2. REVIEW OF LITERATURE

It is really very interesting to go through the literature and learn the important concepts of corrosion and how researchers and scientists struggled to bring competitive results in the field of corrosion science and Engineering.

The present study on **"Synthesis of Water Soluble Copolymer in Sulphamic Acid Medium for Corrosion Inhibition of Mild Steel and Stainless Steel in Acid Medium"** is reviewed under the following topics:

- Corrosion of Metals
- Corrosion Inhibitors
- Inhibitors for Ferrous Materials in Acidic Medium
- Polymer Film Forming Inhibitors
- Polymeric Materials
- Polymeric Inhibitors for Non Ferrous Metals in Acidic Medium
- Polymeric Inhibitors for Non-Ferrous Materials in Neutral Media
- Electrochemical Deposition of Polymers for Corrosion Inhibition

Corrosion of Metals

- **Lomonosov (1743 – 1756),** was the first to make broad systematic experiments on the study of the action of acids on metals.
- **Davy (1826),** proposed an electrochemical method using sacrificial anode for the protection of copper sheathed ocean, going ships.
- **De La Rive (1830),** attributed the pronounced corrosion of impure zinc metal to the operation of short-circuited micro cells on the metal surface.
- **Faraday's** research **(1830 – 1840),** established a very important relationship between chemical action and the generation of electric current.
- **Wagner (1938),** proposed a mixed potential theory. This theory proclaims that (i) any electro chemical reaction comprises two or more partial oxidation and reduction reactions (ii) there can be no net accumulation of electrical charges during an electrochemical reaction and (iii) The potential at the entire surface of an isolated electrode should be the same.

- The ancient Greek historian Herodotus (fifth century BC) and the ancient Roman naturalist. Pliny the Elder (first century BC) mentions the adoption of tin for the protection of iron from corrosion. Alchemists through centuries made fertile attempts to transform base metals into noble once. Early attempts to mitigate corrosion of metals were empirical and centered largely around the use of organic and metallic coatings. Inhibitors for acid corrosion of metals were known from middle ages. There were obvious measures to product metallic structures constructed by early artisans, often at the expense of much time and very hard labour **(Herbet H Uhlig, 1971)**.

Corrosion Inhibitors

- Organic corrosion inhibitors may function by
  (i) Chemisorption of the molecule on a metallic surface
  (ii) Complexing of the molecule with the metal ion which remains in a solid state
  (iii) Neutralizing the corrodant and
  (iv) Adsorbing the corrodant **(Hausler, 1983)**.
- In Situ polymerization of heterocyclic compounds, such as pyrrole and thiophene and aniline, produces homogenous, adhesive films on the metal surface. These films were electronically conducting. These conducting polymers were used as inhibitors for metal corrosion **(Skotheim, 1986)**.
- **Santos et al., (1998),** describe the inhibitor action as involving the displacement of adsorbed water from the metal surface by soluble organic species (org),

$$Org_{sol} + nH_2O_{ads} \rightarrow Org_{ads} + nH_2O_{sol}$$

Polymers

Polymers are very large molecules that are formed by the combination of a number of relatively small molecules called monomers. Polymers can be made from inorganic or organic molecules. They may have different forms eg. They may be chain like as in polyethylene or sheets like as in quartz. The synthetic polymers are long chain organic molecules whose dimensions could approach 10^5A^0 as compared to simple

molecules having dimensions of 10A°. In the last two decades, there has been an increase in the use of polymeric compounds as corrosion inhibitors.

Inhibitors for Ferrous Materials in Acidic Medium:

Polymer Film Forming Inhibitors

- The molecule with –C ≡ C bond found to be effective inhibitor. In the middle 1940's acetylenic compounds were discovered to be effective inhibitors **(Funhouser, 1961)**.
- **Duwell et al., (1964),** reported the mechanism of ethylcyclohexanol polymerization using iron powder in 2M H_2SO_4 under nitrogen atmosphere.
- A postulation came in 1961 which described the affinity of the triple bond of alcohols for the metal'd' electrons lead to the chemisorption at the anodic sites with a consequent sharing of electrons. After adsorption of these species, polymerization ensures which was responsible for the corrosion inhibition, it was put forward by **Poutilsva, I.N., (1965)**.
- Propargyl alcohols and other alkynols were investigated in detail by IR – reflectance spectroscopy which confirmed the formation of polymers on the metal surface **(Poling, G.W., 1967)**.
- **Wessling (1994),** observed that the corrosion current of polyaniline (PANI) coated steel was lower than bare steel and that the reduction in current was greater when thicker PANI coatings were applied to the metal.
- **Back et al., (1996),** used electrochemical impedance spectroscopy (EIS) to investigate the effect on corrosion rate of electrochemically formed PANI, polypyrrole and polythiophene layers on iron. An inhibition of corrosion was only observed for coatings greater than 1μm thick and this effect was attributed to a barrier effect.
- **Aramaki (1997)**, investigated the mechanism of propargyl alcohol (PA) for iron corrosion in 0.5M HCl at elevated temperature using surface enhanced Raman Scattering XPS and FTIR techniques. A high inhibitor efficiency of PA at 343K was attributed to the coverage of the surface with a protective film of PA polymer

and partly to adsorption of allyl alcohol formed by cathodic reduction of PA. Electro initiated polymerization of PANI theory was proposed.

- **Pud et al., (1999),** investigated the nature of the oxide layer formed between PANI and steel when the PANI was applied in different ways. These workers found that the passive layer forms when the PANI-Emaraldine Base was that onto the steel and was further modified when the PANI-Emaraldine Base was converted to PANI-Emaraldine Salt by immersing in acid.
- **Mariusz (2004),** proposed a novel composite organic, inorganic coating in the form of a redox polymer film for protection of stainless steel against general corrosion in strong acid medium (2M H_2SO_4). They utilized poly (4-vinyl pyridine) polymer. By analogy to a conducting polymer (e.g. poly aniline, poly pyrrole), introduction of the redox polymer composite film leads to stabilization of the steel substrate's potential within the passive range.

Polymeric Materials

Conducting polymers have recently attracted a deal of attention from chemists, physicists and material scientists due to their wide spread technological applications.

- **Ghosh et al., (1857),** have reported Amido polyamines were found to be inhibitors in 5N HCl at 333K offering more than 95% inhibition. The amido poly amines (APA) form an ionisable salt in acid medium. The positive nitrogen centres of these compounds ensured that they could not be discharged at the cathode sites and adsorbed through the nitrogen atom. They prevent hydrogen discharge and thereby corrosion.
- **Mann, C.A., (1936),** evaluated polyamide resin. It contributed towards good inhibitive properties. The amide cations were adsorbed on the cathodic area of the metal surface through nitrogen atoms thereby forming a monomolecular layer over the metal surface.
- Detailed investigations carried out on polyamide epoxy systems in acidic solutions revealed that the presence of amino group, a fatty cyclic dimerised acid and an imidazoline ring in the polyamide resin contributed towards good inhibitive properties **(Baldmin et al., 1970)**.

- Polyglycol and polyethyleneglycol were tested as inhibitors in 0.05N HCl solutions at 343K by **Abdel Fattah et al., (1986)**. These compounds adsorbed on the surface obeying Langmuir isotherm. They offered large coverage due to the long hydrocarbon chain and by the presence of OH groups. Being hydrophilic in nature, the OH groups counter acted the effect of chain length and ensured higher solubilities.
- **Joshi et al., (1989),** proved that polyvinyl pyrrolidone having a molecular weight of the order of 10,000 to 40,000 was an effective inhibitor for iron in 5N H_2SO_4 solutions.
- **Karpagam et al., (1996),** reported that polymers of acrylamide with specific polar end group namely thio-malic acid for their corrosion inhibition property for mild steel in acids. The inhibition efficiency found to depend on polyacrylamide back bone length.
- The corrosion of mild steel in H_2SO_4 and 1N HCl solutions were inhibited by polyamide macro cyclic compounds. 3, 4: 11, 12 di benzo- 2, 5 : 10, 13 tctraoxo – 1, 6, 9, 14 – tetra azocyctohexa decane acted as mixed inhibitors **(Mohammed Ajmel et al., 1998)**.
- **Abed (1999),** investigated poly (4-vinyl pyridine poly-3-oxide ethylene) as inhibitor for Armco iron in H_2SO_4. The observed 99% inhibition was due to adsorption and adsorbed molecules obeyed Frumkin isotherm.
- The use of radical polymerization in a solution of acrylamide (AA) and oligo (oxy ethylene) methacrylate (OEGMA) for corrosion and protection of steel in highly acidic solutions. At moderately elevated temperature, OEGMA provided higher inhibition compared to AA **(Elmorsi, 1999)**.
- The influence of poly (4-vinyl pyridine-poly(3-oxide-ethylene) tosyle, on the corrosion inhibition of iron in molar sulphuric acid solution was studied using weight-loss, polarization resistance, potentiodynamic and EIS measurements. This polymer was an excellent inhibitor and its inhibition efficiency increases with the increase of concentration to attain 100% since 2.5 x 10^{-8}m. Potentiodynamic polarization studies clearly reveal that it acts as a mixed type inhibitor.

Adsorption of this compound on iron surface had an S-shaped adsorption isotherm **(Chetouant et al., 2004)**.

Polymeric Inhibitors for Non Ferrous Metals in Acidic Medium

- **Frignani et al., (1995)** analyzed the inhibition of nickel corrosion in 1N HCl and H_2SO_4 solutions by means of 3-methyl-1-butyne-3-ol (H), its halo derivatives and 1-octyn-3-ol (OCT). They revealed these compounds formed polymeric films. OCT was more efficient than H but efficiency of the latter can be improved by replacing the H in C ≡ CH by halogen, especially iodine.
- Silver and copper were protected by the use of spin applied conjugated polymers such as PANI and the addition of KI and PA offered synergistic effects. The presence of iodide ions in the solutions stabilized the adsorption of PA molecules and improved the inhibition efficiency of PA **(Brusia., 1997)**.
- **Zhu et al., (1998),** investigated the corrosion of inhibition of copper by PMTA (1-phenyl 1-5 mercapto tetrazole). The polymer film was found to superior to those formed tetrazole, benzotriazole, hydroxyl benzotriazole, 2-mercapto benzothiazole, 2-mercapto benzomidazole, imialazole and chromates.
- **Kim et al., (1998)**, conducted at elevated temperatures the copolymer of vinyl imidazole and vinyl trimethoxy silane offered inhibition for copper corrosion.
- The adsorption and inhibitive effects of polyvinylpyrrolidone (PVP) and polyethylenimine (PEI) on copper in 2M H_2SO_4 at 30°C have been investigated by means of weight loss, potentiodynamic and in situ surface-enhanced Raman Scattering (SERS) techniques. Both polymers reduce the rate of anodic (metal dissolution) and cathodic (O_2 reduction) corrosion reaction. At all concentration studied, PVP was found to be an able inhibitor **(D.P.Schweinsberg, 1998)**.
- The corrosion inhibition of nickel in 0.5M H_2SO_4 solution by 2-(tri phenyl phosphoanylidine) succinic anhydride , 1, 4, 8, 11 tetra azocyclo tetradecane were studied by **Mahgouband et al., (1998)**. They proved the inhibition efficiency varied with chemical structure.

- The corrosion protection properties of the poly (O-anisidine) POA coatings in aqueous 3% NaCl were examined by potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS). POA exhibits the excellent corrosion protection properties and reduces the corrosion of copper **(Sudeshan Chaudari et al., 2000)**.

Polymeric Inhibitors for Non-Ferrous Materials in Neutral Media

- The effect of adding carboxymethylcellulose drag reducing polymer on the rate of corrosion of aluminium tube by a weight loss technique. The variables studied were solution flow rate and polymer concentration. Polymer addition was found to decrease the rate of corrosion by a maximum of 63% depending on polymer concentration. These results were reported by **Sedahmed et al., (1984)**.
- The effect of polyvinylpyrrolidine (PVP) of various average molecular weights ($M=1x10^4$, $2.45x10^4$ and $4x10^4$), poly-2-vinylpyridine ($M=2.85 \times 10^5$) and poly-4-vinylpyridine as inhibitors of the corrosion behaviour of zinc metal in 1M H_2SO_4 solutions has been studied by **Abo El-Khair et al., (1990)**. It was shown using the weight loss technique that the polymers studied import a significant inhibiting effect on the corrosion rate of zinc metal. The protection efficiency in the presence of such polymers reached about 87% at an inhibitor concentration of 0.1M.
- **Kim et al., (1997)**, stated that vinylsilane modified imidazole copolymer was found to be an inhibitor for copper corrosion. The free radical copolymerization of vinyl imidazole (VI) and vinyl trimethoxy silane (VTS) was carried out in benzene at 341K using azobis isocyanate butylonitrile as initiator. The copolymer of vinyl imidazole (VI) and vinyl trimethoxy silane (VTS) was synthesized in benzene at 68°C as a novel corrosion inhibitor for copper. The effect of the copolymer composition on copper corrosion protection at elevated temperatures were investigated by Fourier transform infrared reflection, and scanning electron microscopy (SEM).Corrosion protection capabilities of the copolymer at 360^0C in air was improved via increasing the mole ratio of VTS in the feed due to the improved thermal stability and the reactivity of the copolymer with copper.

- **Beccaria et al., (1999)**, evaluated the inhibitory action with meta acryloxy propyl methoxy silane (MAOS) on the corrosion of aluminium in 3.5% NaCl solutions revealed that the siloxane polymeric film formed by MAOS acted as a good corrosion inhibitor.
- 3-Mercapto propyl trimethoxy silane (MPS) had been used as a copper corrosion inhibitor in 0.1M KCl solution. In the presence of oxygen, it acted as a mixed inhibitor. The polymer film formation on the surface was confirmed by polarized grazing angle and Fourier transform–infra red (FTIR) analysis **(Tremont et al., 2000)**.

Polymeric Inhibitors for Ferrous Materials in Neutral Media

- In cooling water systems, various cationic and anionic polymers were studied. Polyethylene oxide (PEO) and poly dimethyl sulphoxide (PDMS) were found to be effective inhibitors for ferrous and non-ferrous materials in fresh water systems **(Ahamad et al., 1988)**.
- **Sekine et al., (1992)**, examined polyethyleneimine and its derivatives, polyacrylamine (PAAM) and polydicyanodiamide derivative as cationic polymers and polymaleic acid and its derivatives poly acrylic acid and its derivatives as anionic polymers. These were found to be antiscaling and corrosion inhibiting.
- The inhibiting action of 3-(trimethoxy silyl) propane thiol-1 polymer film on steel corrosion in 3% NaCl solutions were studied by **Baccaria et al., (1995)**. The formation of a chemisorbed methoxy silane compound which modified the surface shifted the free corrosion potentials to nobler values. The inhibitor acted as passivating cathodic and anodic inhibitors.
- **Santos et al., (1998)**, investigated poly aniline coated mild steel and stainless steel specimens exhibited enhanced corrosion protection in 3% NaCl.
- **Dominis et al., (1998),** reported polarization resistance values for Emaraldine Salt(ES) and Emraldine Base(EB) coated steel tested in 500 ppm NaCl solution. The polarization resistance of ES was more than an order of magnitude lower than that obtained for EB-coated steel.

Electrochemical Deposition of Polymers for Corrosion Inhibition

- Polyaniline (PANI) films electro synthesized on mild steel were studied in acidic (HCl) and alkaline (3% NaCl) media.The mechanism of protection of conducting polymer coating was investigated by **Jain et al., (1986)**. He showed that the doped conducting polymer generated an electric field which restricted the flow of electrons from the metal to an outside oxidizing species thus preventing corrosion.
- Aniline was electropolymerized in acidic aqueous solutions (HCl, H_2SO_4) on noble metal electrodes (Pt, Au). The growth of the polyaniline (PANI) film depends on the nature of the anions. The PANI may be found in different forms, depending on the pH of the solution and the oxidation potential **(M.C. Diarmid et al., 1990)**. The application of EIS as a new tool for the investigation of methods of corrosion protection was illustrated for corrosion inhibitors, conversion coatings, polymer coatings and oxide layers as well as for cathodic protection of stainless steels in sea water. It was pointed out that it is essential for all these cases to develop the appropriate models for the impedance which can be used to fit the experimental data and extract the parameters which characterize the corrosion inhibition.
- **Sathiyanarayanan et al., (1992),** investigated the corrosion inhibition of iron in acid chloride solution offered by a new class of polymer ortho-substituted poly ethoxy aniline, a conducting polymer. Preparation of polymer by electrochemical and chemical methods has been described. Characterization of this polymer has been done by infrared and UV-vis absorption studies. Its corrosion inhibitive action was examined by the Tafel extrapolation method, linear polarization resistance method, impedance method and direct weight loss method. All these methods confirmed the effectiveness of the inhibitor, indicating also the possibility of monitoring its effectiveness by electrochemical techniques. Double layer capacitance studies indicated strong adsorption of polymer which followed the Temkin isotherm.

- **Lacroix et al., (1996),** reported the electrodeposition of protective polyaniline films on mild steel from aqueous oxalic acid. He stated that the electro polymerization of aniline occurs on a surface passivated by the precipitation of an Fe(II) – oxalate layer and leads to strongly adherent films. When they dipped in an acidic solution (0.4M NaCl + 0.1 M HCl) the PANI – coated iron samples exhibit very good protection against corrosion and are much effective.
- Potentiodynamic polarization curves were obtained for carbon and stainless steel in contact with aqueous sodium chloride solution (3% NaCl) saturated with air in order to evaluate the capacity of polyaniline in the emeraldine oxidation state to protect the surface against corrosion process **(Santos, 1997)**. From the experiments it was concluded that corrosion of steel could be prevented using the conducting polymers as a protective layer.
- The emeraldine base form of polyaniline (PANI), has been used as a corrosion protecting undercoat on steel and iron samples in hydrochloric acid medium. By using X-ray photoelectron spectroscopy the anti-corrosion performance of emeraldine base PANI was studied. It was found to offer corrosion protection for both the cold rolled steel and iron samples **(Fahlman et al., 1997)**.
- **Dimitra Sazou et al., (1997)**, reported the electropolymerization of aniline on an iron disc electrode in aqueous solutions, by using various inorganic acids and organic acids. Under potentiodynamic, potentiostatic and galvanostatic conditions, smooth well adhering polyaniline coatings were obtained in oxalic acid solutions. The coatings obtained on iron appear to be promising anodic protection in corrosive aqueous media.
- **Talo et al., (1997),** studied the polyaniline / epoxy blend coatings on mild steel in 0.6M NaCl and 0.1M HCl aqueous solutions by electrochemical methods. The corrosion protective performance was characterized by a permanent shift of corrosion potential.

- PANI films can be electrosynthesized by oxidation of aniline on iron and mild steel in a one-step process from an aqueous oxalic acid medium which passivates substrates **(Camalet et al., 1998)**. These films were characterized by techniques such as IR, X-ray photoelectron spectroscopy (XPS), gel permeation chromatography (GPC) and matrix-assisted UV-laser desorption ionization (MALDI) and have a structure similar to that of PANI deposited on platinum. Iron samples coated with PANI exhibit much better protection against corrosion in an acidic solution (0.4M NaCl + 0.1M HCl) compared to the poly pyrrole coated ones.
- Aqueous p-toluensulfonicacid solution was used to electrosynthesize a polyaniline film on mild steel, examined by **Camalet et al., (1998)**. Polarization of the substrate in this medium leads to passivation of the surface mainly via the formation of an iron oxide layer. When aniline was added to the solution, electro polymerization was not hindered and a dark green deposit was obtained in high yield(80%). Spectrochemical techniques (IR, XPS and UV) and mass determination indicate that it has the same properties as reported for PANI. This polymer coating could be used for corrosion protection.
- **Zagorska et al., (1999),** studied the application of PANI as the post rinse treatment in a typical steel phospating process. The comparison with Cr (VI) post treatment based on impedance measurements showed that PANI effectively stabilizes coating system in an aggressive environment.
- **Bernard, M.C., (1999),** studied the chemically prepared PANI coatings on iron electrodes by testing them in chloride and sulphate solutions at neutral or slightly acidic pH for which only the emeraldine base moiety exists. The impedance results indicated the efficient anticorrosive properties of PANI films.
- Polyaniline (PANI) epoxy blend coatings on mild steel have been studied **(Talo et al., 1999)** in neutral, acidic and alkaline solutions with various electrochemical methods. It has been found that coatings containing emeraldine base provide better corrosion protection in NaCl solution than coatings based on conducting polyaniline.

- Polyaniline (PANI) has been electrodeposited on platinum from neutral $LiClO_4$ aqueous electrolyte **(Dung Nguyen et al., 1999)**. It was found that this electrolytic medium allows the deposition of PANI films with properties similar to those obtained with acidic aqueous media. From the results it was found that neutral electrolytic media can be used to generate PANI films on mild steel with little dissolution of the electrode.
- **Wessling et al., (1999)**, stated that nano-particulate dispersions of the organic metal polyaniline in various paints at low concentrations cause tremendous effects in corrosion protection. It was studied by scanningvoltapotential and EIS measurements.
- **Marcin A. Malik (1999),** investigated the ability of a polyaniline film into highly dispersed platinum microparticulates were introduced to protect stainless steel against corrosion in strong acid solution and found that the electrolytic reduction of oxygen on the platinized polyaniline film can be coupled to the self-passivation of steel.
- **Camalet et al., (2000),** stated that aniline has been electropolymerized on platinum from neutral aqueous electrolytes. The properties of the resulting polyaniline films were similar to those obtained in acidic media. PANI films were generated using multiple cyclic voltammetry or galvanostatically. The films were generated with less method dissolution compared to acid electrolytes and exhibit similar anticorrosion properties.
- **Abdolreza mirmohseni et al., (2000),** has synthesized polyaniline (PANI) chemically and cast from 1-methyl-2-pyrrolidine (NMP) solution over iron samples. A series of electrochemical measurements including corrosion potential and corrosion current has been made on polyaniline coated iron samples in various environments. Protective properties of the conducting polymer were compared with a conventional polymer such as polyvinyl chloride (PVC). Comparative experiments revealed that emeraldine base form of polyaniline has better protective properties.

- Electrochemical polymerization of several ring substituted anilines namely Ortho-Toluidine, Meta-Toluidine, Ortho-anisidine and Ortho-chloroaniline were carried out on passivated Fe surfaces. Thin polymeric films deposited by cyclic voltammetry, potentiostatic or galvanostatic techniques on the Fe-disc electrode from aqueous oxalic acid solutions showed protective properties against corrosion of Fe in sulfuric acid solutions **(Dimitra Sazou, 2001)**.
- A novel route has been designed to prepare water soluble polyaniline which is crystalline in nature compound to parent polymer polyaniline which was amorphous as revealed by XRD analysis. The water soluble polyaniline can be used as a corrosion inhibitor for iron in HCl medium **(Sarswat Koul et al., 2001)**.
- Polyaniline (PANI) was able to protect mild steel against corrosion owing to the stabilization of the iron oxide passive layer **(Bernard et al., 2001)**. The electropolymerization conditions on iron samples must be carefully selected, leading to the choice of phosphoric acid solution. The protection lasts during a period from several hours in pH 0.5. A simple electrochemical test characterizes the passivation breakdown, the increase of polarans delocalization does not allow the oxidized PANI from to be regenerated.
- **ShahKunal (2001),** reported the deposition of the substituted polyaniline and polypyrrole. Polypyrrole composite coatings on aluminium alloy (AI– 2024). The coatings were electrodeposited using galvanostatic and cyclic voltammetry techniques by using oxalic acid as an electrolyte. The coatings were characterized by using IR, SEM, UV / VIS spectra and cyclic voltammetry. The corrosion resistance of polyaniline – polypyrrole composite coatings was evaluated by DC polarization (Tafel) technique. It was shown that the composite coatings having higher concentration of aniline and formed at higher current densities were much more uniform and denser as compared with the ones with higher pyrrole concentration.
- The poly (N-ethylaniline) and poly (O-anisidine) coatings were successfully deposited on AI-2024 in oxalic acid medium. These coatings were formed at much lower oxidation potential than the aniline. The mechanism for formation of

the polymers was found to be similar to that of aniline. They found to exhibit very good protection against corrosion **(Shahkunal, 2001)**.

- Cyclic polarization measurements made on steel, iron-oxalate coated steel and polyaniline coated steel in a high pH solution **(Nicholar M. Martyak et al., 2002)**. Polyaniline (PANI) coated steel showed good anticorrosive properties, when compared with iron oxalate coated steel and bare steel in the chloride containing alkaline solution.
- Corrosion protection of mild steel was investigated **(Samui, 2003)** by coating it with paint containing polyaniline – hydrochloride (PANI – HCl) as pigment. Painted panels were exposed in weatherometer chamber, humidity cabinet, saltspray chamber, sea water. Potentiodynamic measurement were also made for finding corrosion current, potential, polarization resistance etc., Lower loading of PANI – HCl was found to be more effective in corrosion protection compared to others.
- **Anton J. Dominis (2003),** found the effect of the dopant with polyaniline (PANI) emeraldine salt affected the corrosion rate of coated steel. The polyaniline (PANI) was used as a primer with a polyurethane or epoxy topcoat. The results showed that epoxy top coated systems showed adequate corrosion protection for upto 2 years during immersion in 3.5% saliva solution.
- **Lu et al., (2003),** proposed a mechanism for the corrosion protection of steel by PANI films in HCl and NaCl media. They concluded that the PANI film can protect the steel surface following a mechanism where the steel passivation occurs with the formation of layers Fe_2O_3 and Fe_3O_4.
- Multilayered coatings, consisting of combinations of the conducting polymers PANI and polypyrrole (PPY) were galvanostatically deposited on to both carbon steel and stainless steel. Potentiodynamic polarization was used to asses the ability of these copolymers to provide and effective barrier to corrosion in chloride environment. It was found that the degree of protection was a function of the deposition order of the copolymer, with films consisting of a PANI layer over the top of a polypyrrole (PPY) layer yielding the best results **(Tan et al., 2003)**.

- **Kraljic et al., (2003),** obtained the electrosynthesised PANI steel samples using sulphuric and phosphoric acids as supporting electrolytes. Polymer deposited from the phosphate solution appears to have better. Protective properties than the layer deposited in the sulphate solution when they were tested in acidic solution of 0.1M dm^{-3} HCl.
- The electrochemical synthesis of PANI was achieved on stainless steel (316L) electrode using cyclic voltammetry technique in a monomer containing oxalic acid solution. The polymer films exhibited significant barrier property against the attack of corrosive agents **(Ozyilmaz, 2004)**.
- PANI with excellent adherence was electrosynthesised on stainless steel from aniline containing phosphate buffer solutions. The electropolymerizations were carried out by cyclic voltammetry at $50mVs^{1}$ from phosphate buffer solutions at different pH values (1.7 – 2.2). The most uniform thin film was formed from 1.0M phosphate buffer solution containing 0.1M aniline. The corrosion behaviour of stainless steel covered by these films was investigated by potentiodynamic polarization in 3% NaCl solution **(Sandra R. Moraes, 2004)**.
- Polyaniline (PANI), poly (2-iodoaniline) (PIANI) and poly (aniline-10-2-iodoaniline) (10-PIANI) were synthesized using cyclic voltammetry on 304-stainless steel electrodes. The corrosion performance of PANI, PIANI and 10-PIANI coated electrodes were investigated in 0.5M HCl by potentiodynamic polarization technique, open circuit potential – time curves and electrochemical impedance spectroscopy (EIS). It was found that the PANI film have barrier property as well as passivator. EIS measurement shows that every coating gives protection efficiency of greater than 75% after 48h of immersion time in corrosive test solution. **(Gozen Bereket etal., 2005)**.

- **Herrasti et al., (2005),** revealed that electroactive polymer films of polyaniline, poly-o-toluidine and a composite of both were deposited on stainless steel and their performance as protective coatings against corrosion was evaluated. Open circuit potential and potentiodynamic studies of the polymer-coated stainless steel in a corrosive medium showed a significant shift in the corrosion potential towards more positive values. The best results were obtained in the case of the polyaniline-o-toluidine composite corrosion protection – microhardness – poly pyrrole and polyaniline composite by potentiodynanmic curves.
- Stable and adherent polymer films of polyaniline and of poly (2-anisidine) were gown on 304-stainless steel by cyclic voltammetry in tetrabutylammonium perchlorate / acetonitrile solution containing perchloric acid. The anti-corrosion behaviour of polyaniline poly (2-anisidine) and poly (aniline-10-2-anisidine) coated electrodes were investigated in 0.5M HCl by potentiodynamic polarization technique, open circuit potential-time curves and electrochemical impedance spectroscopy. Poly (2-anisidine) film shows protection against corrosion 304-stainless steel in 0.5M HCl by passivating steel substrate in similar manner as has been observed for polyaniline **(Gozen Bereket et al., 2005)**.

From the literature survey, it is clearly understood that the role of PANI in corrosion studies is less undertaken and the capacity of PANI is found to be remarkable in various fields. The water soluble polymers have an enormous role to play in corrosion studies viewing all these in mind, the present study is carried out to prepare polyaniline in polyvinyl alcohol and this copolymer (VAANI) is water soluble and hence this current studies and conducted using PANI and PVA as corrosion inhibitor.

Materials and Methods

3. MATERIALS AND METHODS

Design of the present investigation consisted of the following steps:

- Selection of samples
- Selection of medium
- Preparation of inhibitors
- Different parameters studied
- Different techniques used

The study of the corrosion inhibition by polyaniline uniformly dispersed in 5% solution of PVA (VAANI Copolymer) was carried out using mild steel / stainless steel specimens in 1M HCl/6M HCl medium using efficient methods namely, weight loss methods, polarization and impedance methods. These methods are used to study corrosion behaviour of mild steel.

Selection of Samples

Mild steel / stainless steel has been extensively used under different conditions in chemical and allied industries in handling alkalies, acid and salt solutions. In such cases mild steel / stainless steel undergoes corrosion. The life of mild steel / stainless steel in acidic conditions is very minimum as it undergoes severe corrosion. Hence the need to mitigate the corrosion of mild steel / stainless steel arises.

Preparation of Specimens

Mild steel / stainless steel coupons of area 5 x 1cm^2 were sheared from commercially available sheet of mild steel and stainless steel. These coupons were polished, degreased, cleaned successively with deionised water and stored in a dessicator. The mild steel / stainless steel specimens had the following percentage, nominal composition.

Composition of Mild Steel/SS

Cold rolled MS and SS coupons were polished mechanically degreased, cleaned successively in deionized water, dried, stored in a dessicator and used for all studies.

TABLE - 1

Composition of mild steel and stainless steel

S.No	Elements	Percentage of elemental composition	
		MS	SS
1.	Carbon	0.048	0.049
2.	Manganese	0.238	1.867
3.	Silicon	1.081	0.444
4.	Phosphorus	0.031	0.030
5.	Sulphur	0.030	0.014
6.	Chromium	0.016	19.188
7.	Molybdenum	0.018	0.147
8.	Nickel	0.023	8.485
9.	Lead	0.005	-
10.	Iron	98.55	69.776

Selection of Test Media

Among the commercially available acids the most frequently used acid is hydrochloric acid. At the present time hydrochloric acid is the most important pickling acid. Large scale continuous treatment such as metal strip and wire pickling, as well as economic advantages in the regeneration of depleted pickling solutions – a factor of increasing economic and ecological importance–were the main reasons why hydrochloric acid gradually replaced sulphuric acid. It is used for the removal of oxide from the metallic parts, before coatings (acid pickling), removal of undesirable scales and rust (acid cleaning) and several other industrial processes. The present experiments were carried out in 1M HCl/6M HCl.

Selection of Inhibitors

Considering the technical process of pickling, good inhibitors must meet quite a number of requirements.

Required properties of inhibitors for acid pickling:

- Effective inhibition of metal dissolution.
- No over-pickling in the presence of higher iron salt contents
- No delay of the pickling process
- Effective at low concentrations
- Effective at higher temperature
- Thermally and chemically stable
- Good surfactant characteristics

Most of the nitrogen, oxygen and sulphur containing organic compounds are found to effectively inhibit the corrosion of mild steel and stainless steel.

In this connection, the present study is undertaken to find out the efficacy of polyaniline homogenously dispersed in 5% PVA solution (VAANI Copolymer) on the corrosion inhibition of mild steel / stainless steel in 1M HCl / 6M HCl medium.

Synthesis of VAANI Copolymer

2ml of vacuum distilled aniline is mixed with 40ml of 5% PVA solution. The chemical oxidative polymerization of aniline was carried out in a medium containing organic acid like sulphamic acid. The oxidant ammonium persulphate was added slowly to the reaction vessel kept at 5°C – 10°C by constant stirring. At the end of the reaction period, the reaction mixture was filtered. The water soluble polyaniline homogeneously dispersed in PVA (VAANI Copolymer) thus obtained was used for the studies.

Selection of VAANI Copolymer as Inhibitor

Due to its ease of synthesis, environmental stability and low synthetic cost, VAANI Copolymer is selected for corrosion studies.

Equipments used

The following equipments were used for this study

- **Thermostat**
- **Denver-220D digital balance**
- **Solartron 1284Z**

Techniques used

The efficiency of the inhibitor under study are evaluated using the following techniques:

- **Weightloss method**
- **Cyclic voltammetry**
- **Electrochemical measurements – Potentiodynamic polarization studies.**
- **Impedance measurements**
- **Optical electron micrograph**

Selection of Media and Polymer

Although polyaniline is the most widely studied conducting polymer and is readily formed in aqueous solutions on various substrate (mainly inert metals and semi conductors), it is used less for the formation of protective coatings on oxidisable metals.

Certainly, aniline electropolymerisation is more feasible in acidic aqueous solutions on metals, where these metals are highly corroded. From the earlier attempts showed that, polyaniline adhesive coatings are not obtained on these metals by electro polymerization of aniline either in sulphuric acid solutions or in the solutions of other inorganic acids, unlike stainless steel where polyaniline films are formed in sulphuric acid solutions using cyclicvoltammetry.

Polymerization Medium

The important aspect of polyaniline synthesis is the acid dissociation constant (pK_a) of the acid, because in polyaniline protonation equilibria involves exclusively the quinine diamine segment, having two imine nitrogen with pK_{a1}=1.05 and pK_{a2}=2.55 **(Huang et al., 1987)**. Therefore any acid whose pK_a value falls within that range would be suitable as a dopant. (Table 2)

TABLE - 2
DISSOCIATION CONSTANTS OF VARIOUS ACIDS

ACID	pK_a			
	K_1	K_2	K_3	K_4
α-Amino acetic acid (glycine)	2.35	9.78		
Arsenic acid	2.22	6.98	11.4	
Trichloroacetic acid	0.89			
Dichloroacetic acid	1.26			
Oxalic acid	1.27	4.27		
Phorphoric acid	2.15	7.21	12.36	
Trifluroacetic acid	0			
Pyrophosphoric acid	0.96	1.86	6.68	9.40
Sulphamic acid	1.0			
Sulphuric acid	-4	1.92		
Sulphurous acid	1.76	7.19		
Hydrochloric acid	-7.0			
Hydrofluoric acid	3.17			
Benzene sulphonic acid	0.2			
p-Toluene sulphonic acid	0.3			
5-Sulphosalicylic acid	-.75	2.42	11.4	
Perchloric acid	-10			

In the present study the polymerization / electro polymerization of aniline was carried out in acidic media with the aim of obtaining well adherent VAANI Copolymer. Trials in several inorganic acids like sulphuric acid were proved to be unsuccessful also in terms of the formation of stable coatings on Fe, with the exception of nitric acid **(Troch-Nagels1992).** This exception is probably associated with the property of Fe to be more easily passivated in nitric acid solution. However, part of this coating was readily removed by washing with water.

Then our focus was turned to the organic acids where the results were more promising.

Different Parameters Studied

The different parameters taken into consideration for the present investigation are: Determination of corrosion rate and inhibition efficiency by weight loss method at

- **Room temperature**
- **Higher Temperature**

Determination of

- **Activation Energy (E_a)**
- **Free energy of Adsorption (ΔG)**
- **Enthalpy Change (ΔH)**
- **Entropy change (ΔS)**

Weight loss Method

It is one of the oldest techniques of monitoring corrosion and is based on exposing the coupons of the metal into the test media for a predetermined period of time when removed. Washed and the weight loss of coupons are measured.

In the present work, weighted test pieces of MS and SS were immersed in triplicate in the test media (100 ml), viz., 1M HCl and 6M HCl with varying concentrations of the inhibitor. They were removed after a particular time of immersion, washed, dried and reweighed. The experiments were performed by varying

- Concentrations of the inhibitor (27ppm to 135ppm)
- Time (0.5hr to 24 hrs), and
- Temperature (308K to 348K)

(for temperature study the time of immersion was 0.5 hour)

Studies were carried out with polymers prepared from sulphamic acid medium.

Determination of Corrosion Rate

The corrosion rate expressed as mills per year was calculated using the formula

$$\text{Corrosion rate (mpy)} = \frac{534\ W}{DAT}$$

Where,

W	-	Weight loss in g
D	-	Density of the specimen in gm / cm^2
A	-	Area of the specimen in cm^2
T	-	Exposure time in hours

Determination of Inhibition Efficiency

Inhibitor efficiency was obtained using the following formula

$$IE = \frac{W_o - W}{W_o} \times 100$$

Where

IE	-	Inhibitor efficiency in (%)
W_o	-	Corrosion rate without inhibitor
W	-	Corrosion rate with inhibitor

Surface Coverage (θ)

The degree of surface coverage (θ) for different concentrations of the inhibitor in acid media have been evaluated from weight loss experiments using the equation.

$$\theta = \frac{W_0 - W}{W_0}$$

θ	-	Surface coverage
W_0	-	Corrosion rate without inhibitor
W	-	Weight loss with inhibitor

Corrosion Dynamics

Determination of Activation Energy (E_a)

$$E_a = -2.303 \times R \times \text{Slope}$$

The slope value is got by plotting **log (corrosion rate) Vs 1/T.**

Change in Free Energy Adsorption

The change in free energy of adsorption for different higher temperatures at various concentrations was calculated using the formula

$$\Delta G = 2.303 \times RT (1.74 + \text{Log}\ \theta / (1 - \theta) - \text{Log}\ C)$$

$$\text{Log}\ (\theta / 1-\theta) = \text{Log}\ C - 1.74 - (\Delta G^0\ ad / 2.303\ RT)$$

R - 8.314 J / mol

T - Temperature in K

θ - Surface coverage

C - Concentration of the inhibitor

Determination of Heat of Adsorption and Entropy Change

The plot of free energy of adsorption as a function of temperature was drawn. According to Gibbs-Helmholtz relation,

$$\Delta G = \Delta H - T\Delta S$$

The slope of these lines were equal to ΔS and the intercepts on free energy axis gave the corresponding heat of adsorption.

Adsorption Isotherm

Since the corrosion inhibition involves the adsorption of the inhibitor on the surface of the metal, the phenomenon of interaction between the metal surface and inhibitor can better be understood interms of adsorption isotherm. The dependence of surface coverage on concentration is studied through the following isotherms.

- Langmuir isotherm
- Temkin isotherm
- Freundlich isotherm
- Flory–Huggins isotherm and
- El-Awady isotherm

A straight line for Langmuir, Temkin, Freundlich and Flory-Huggins indicates the inhibitor molecule is adsorbed on the metal surface.

Potentiodynamic Polarization and Impedance Measurements

Various corrosion monitoring techniques like

- ❖ Potentiodynamic polarization (Tafel polarization) and
- ❖ Electrochemical impedancespectroscopy (EIS) methods

have been used in the present investigation. For all the three techniques, SOLARTRON ELECTROCHEMICAL MEASUREMENT UNIT (1284Z) model was used with a software package of Z PLOT and CORR WARE2. The system includes a potentiostat, personal computer and FRA (Frequency Response Analyser).

For POTENTIODYNAMIC POLARIZATION studies, the experiments were carried out over a potential range of -200mV to +1500mV with respect to open circuit potential and its current response was measured at a scan rate of $1mV\backslash sec^{-1}$.

IMPEDANCE MEASUREMETNS were carried out at corrosion potential. The A.C. amplitude of 10mV was applied and the frequency was varied from 10KHz to 10MHz. The real and imaginary parts of the impedance were plotted in Nyquist plots. From the Nyquist plots and Bode plots, the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were calculated.

The charge transfer resistance values were obtained from the plots of Z' Vs Z". The value of ($R_t + R_s$) corresponds to the point where the plots cuts Z' axis at low frequency and R_s corresponds to the point where the plot cuts Z' axis at high frequency. The difference between R_t and R_s gives the charge transfer resistance (R_{ct}) values. The C_{dl} values were obtained from the relationship.

$$C_{dl} = \frac{1}{2\pi f_{max}} \times R_{ct}$$

where,

C_{dl}	-	Double layer capacitance
R_{ct}	-	Charge transfer resistance
f_{max}	-	Frequency at Z" value maximum

Measurement of Corrosion Current (I_{corr})

Values of corrosion currents were obtained by Tafel extrapolation method. In Tafel extrapolation method, plots of η Vs log current were made and an extrapolation of

linear portion to the corrosion potential gave the corrosion current and the slope of the linear portion of the anodic and cathodic curves gave b_a and b_c respectively.

Determination of Inhibitor Efficiency

The inhibitor efficiency was obtained from the equation

$$IE = \frac{I_{corr(b)} - I_{corr(i)}}{I_{corr(b)}} \times 100$$

$I_{corr(b)}$ - Corrosion current in the absence of inhibitor

$I_{corr(i)}$ - Corrosion current in the presence of inhibitor

Surface Analytical Techniques

a. Optical Electron Micrograph

The surface examination of MS and SS in the absence and presence of VAANI Copolymer under study in the examined media was done using Optical electron microscope (Image analyzer – Nikon EPIPHOT-DX).

Cyclic Voltammetry

Cyclic voltammetry experiments are frequently used to obtain information on the mechanism of polymer growth as well as the redox behaviour and mode of electronic conduction.

Cyclic voltammetry experiments was performed in a typical single compartment three electrode cell using frequency analyzer solartron 1284Z. The composition of stainless steel used was found to be 0.049% C, 1.867% Mn, 8.485% Ni, 19.188% Cr, 0.44% Si, 0.014% S, 0.147% Mo and Fe 69.55% and for mild steel C, 0.048% Mn, 0.238% Si, 1.081% P, 0.031% S, 0.030% Cr, 0.016% Mo, 0.018% Ni, 0.023% Pb, 0.005% and Fe, 98.55 . This SS / MS were used as a working electrode. Prior to deposition they were mechanically polished with abrasive paper, rinsed with water and acetone and air dried. A platinum electrode placed parallel to the working electrode, was used as counter electrode and all the measurements were made against saturated calomel electrode (KCl sat) as reference electrode. The monomer aniline was distilled prior to

use. Sulphamic acid and PVA were used as received. Purified water (obtained by passing house – distilled water through a purifying system) was used to prepare all the solutions.

Synthesis and Characterization of VAANI Copolymer

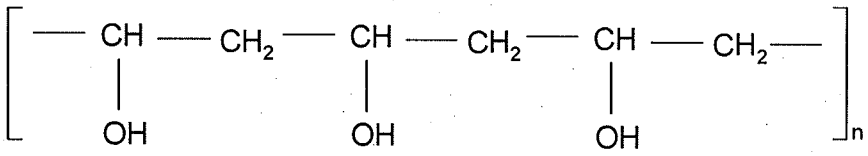
FTIR spectral data are presented in the table (3). In the current study, VAANI Copolymer is chemically and electro chemically synthesized and utilized as corrosion inhibitor for MS and SS surface.

TABLE – 3

IR adsorption data of VAANI Copolymer

S.NO.	PVA	VAANI Copolymer	Assignment
1.	3503	-	-OH stretching
2.	3245	-	-CH stretching
3.	1240	1215	-
4.	-	3420	-NH group
5.	-	1017	-CH stretching
6.	-	1647	Aromatic nucleus
7.	625	608	End group C-H bending
8.	849	849	C-H bending
9.	-	928	Poly conjucated system

To characterize the VAANI Copolymer FTIR spectra are taken for PVA and VAANI Copolymer and depicted in the figure (7, 8). PVA is an addition polymer. Its structure proposed is

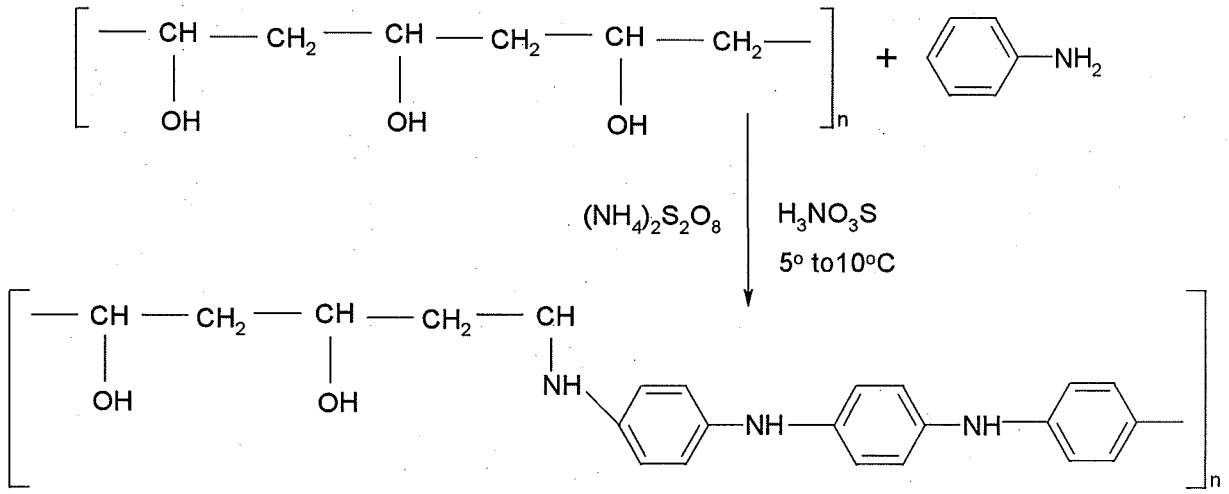


From the structure, we understand that PVA contains free –OH groups and a long alkyl chain. Analysis of FTIR spectrum of PVA reveals an adsorption peak at 3503cm^{-1}. This is due to O – H bond stretching. There are two more peaks corresponds to 1250cm^{-1} and 3000 cm^{-1}. These peaks at 1250cm^{-1} and 3000cm^{-1} are due to C–O stretching and C–H stretching respectively. In this study, the FTIR spectrum of PVA was taken, to confirm the presence of PVA in the formation of water soluble VAANI Copolymer.

The FTIR spectral data of VAANI Copolymer was represented in the figure (8). The perusal of figure shows a deep single adsorption peak at 3420cm^{-1} and it is due to the

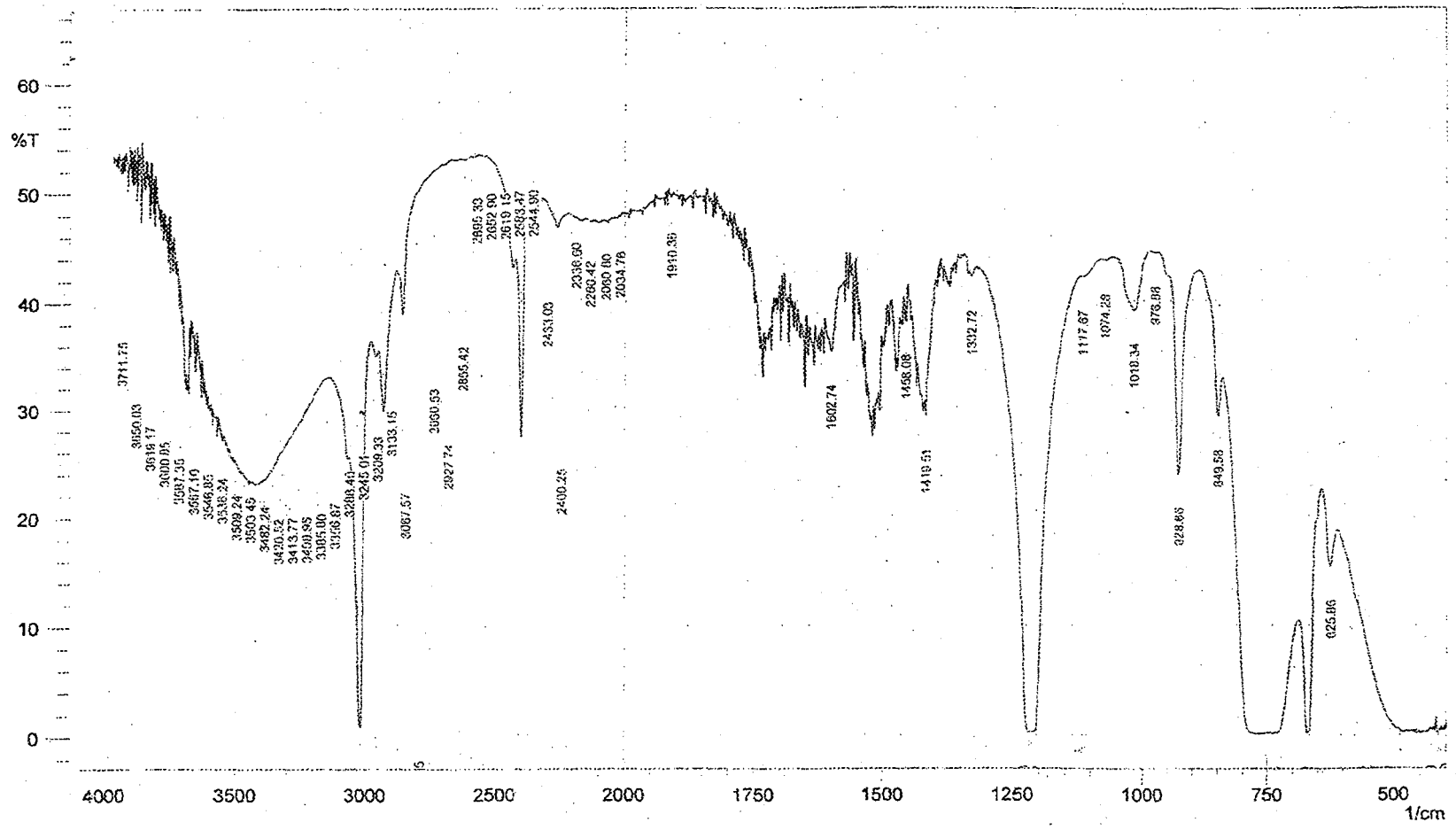
presence of secondary amine group and OH group. The presence of Benzene ring in VAANI Copolymer is confirmed from the peak at finger print region. The presence of alkyl chain in VAANI Copolymer is attributed from the peak at 3000cm^{-1} which is due to – CH stretching.

Assessing the FTIR signals, analyzing the colour of the VAANI Copolymer, and its water soluble nature, the probable structure of VAANI Copolymer is as follows.



The colour of VAANI Copolymer formed during the chemical and electrochemical synthesis was found to be green in colour. Literature survey reveals a green colour for PANI. In the present case, the solubility of VAANI Copolymer was due to the free OH groups present in PVA and the green colour confirms the polymerization of aniline in PVA.

Thus, the efforts are made to synthesis the water soluble VAANI Copolymer using aniline and PVA. Characterisation is also carried out using FTIR spectra, to confirm VAANI Copolymer and its structure and its solubility in water.



No. of Scans; 20
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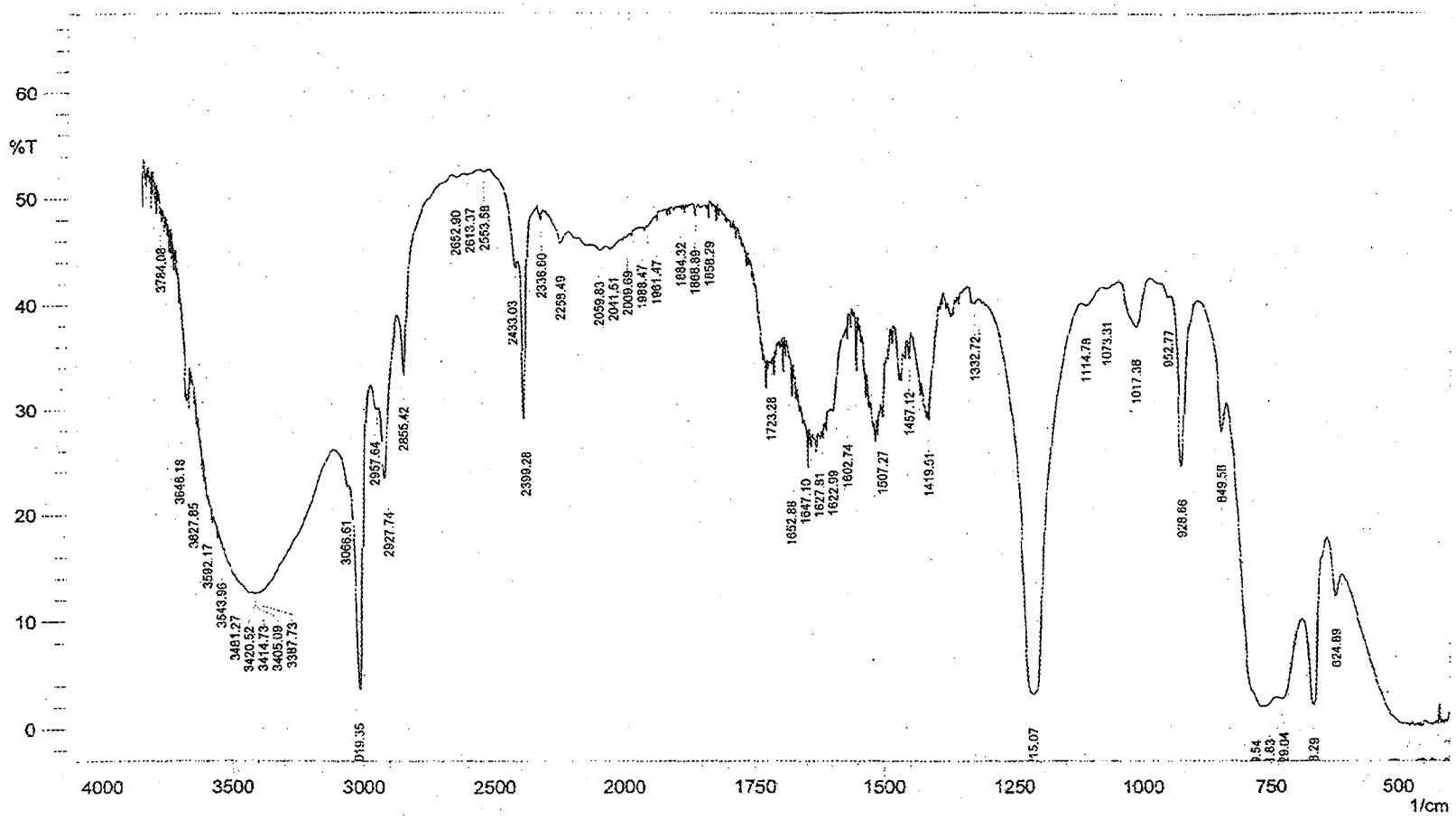
User; Administrator

FTIR Spectra recorded for Polyvinylalcohol
FIGURE - 7



No. of Scans; 20
Resolution; 2 [1/cm]
Apodization; Happ-Genzel

Date/Time; 08/29/2005 09:32:35 AM
User; Administrator

FTIR Spectra recorded for VAANI Copolymer
FIGURE - 8

Results and Discussion

4. RESULTS AND DISCUSSION

The present study has been conducted to explore the inhibition efficiency of VAANI Copolymer for the corrosion of MS and SS in acid medium.

The results pertaining to the present investigation are tabulated and discussed on the light of the objectives set forth under the following headings:

- Effect of concentration of the inhibitor and immersion time.
- Effect of temperature
- Adsorption isotherms and activation parameters
- Thermodynamic parameters
- Electrochemical measurements
- Surface analytical technique
- Mechanism of inhibition and
- Cyclicvoltammetry

Effect of concentration of copolymer on MS in 1M HCl

Data on corrosion rate and inhibitor efficiency during static immersion of MS in 1M HCl with inhibitor are presented in table (4). The results are also represented in figures (9, 10)

The inhibitor efficiency increased with increase in concentration of the inhibitor from 27 ppm to 135 ppm. Maximum inhibitor efficiency was observed at a concentration of 135 ppm.

At all test durations 135 ppm of VAANI Copolymer inhibited corrosion effectively. Maximum inhibitor efficiency of 90% was observed with 135 ppm of VAANI Copolymer at 6 hours.

Effect of time of immersion on inhibitor efficiency of VAANI Copolymer

The inhibitor efficiency of VAANI Copolymer increased with an increase in immersion time up to 6 hours. Further increase in immersion time showed a decline in inhibitor efficiency. For instance with 108 ppm VAANI Copolymer the efficiency increased from 50% to 86% up to 6 hours and then decreased to 66% at 24 hours.

TABLE – 4

INFLUENCE OF TIME ON THE CR AND IE OF VAANI COPOLYMER ON MILD STEEL IN 1M HCl

S. No	Conc. (ppm)	½ hr		3 hrs		6 hrs		24 hrs	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	1814	-	1906	-	2095	-	1648	-
2.	27	1034	43	457	76	796	62	471	71
3.	54	1015	44	419	78	565	73	378	77
4.	81	943	48	324	83	377	82	578	65
5.	108	907	50	324	83	230	89	568	66
6.	135	816	55	343	82	230	89	537	68

TABLE – 5

INFLUENCE OF TIME ON THE INHIBITOR EFFICIENCY AND CORROSION RATE FOR VARIOUS CONCENTRATIONS OF VAANI COPOLYMER (6M HCl)

S.No.	Conc. (ppm)	½ hr		3 hrs		6 hrs		24 hrs	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	244	-	210	-	132	-	345	-
2.	27	113	39	122	42	71	46	140	59
3.	54	95	39	92	56	55	58	118	66
4.	81	87	50	88	58	55	58	105	70
5.	108	69	57	86	59	48	63	84	75
6.	135	78	61	69	67	39	70	74	78

Pictorial Representation of IE Vs Conc of VAANI Copolymer at Various Time Intervals on MS

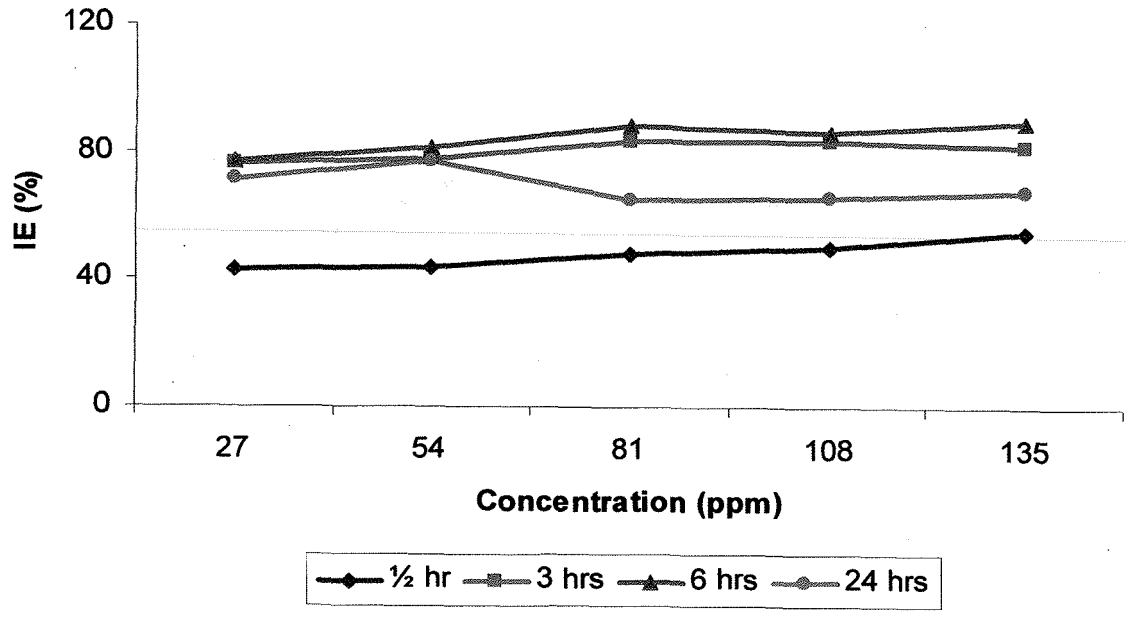


FIGURE – 9

Influence of Concentration on IE of VAANI Copolymer for SS in 6M HCl

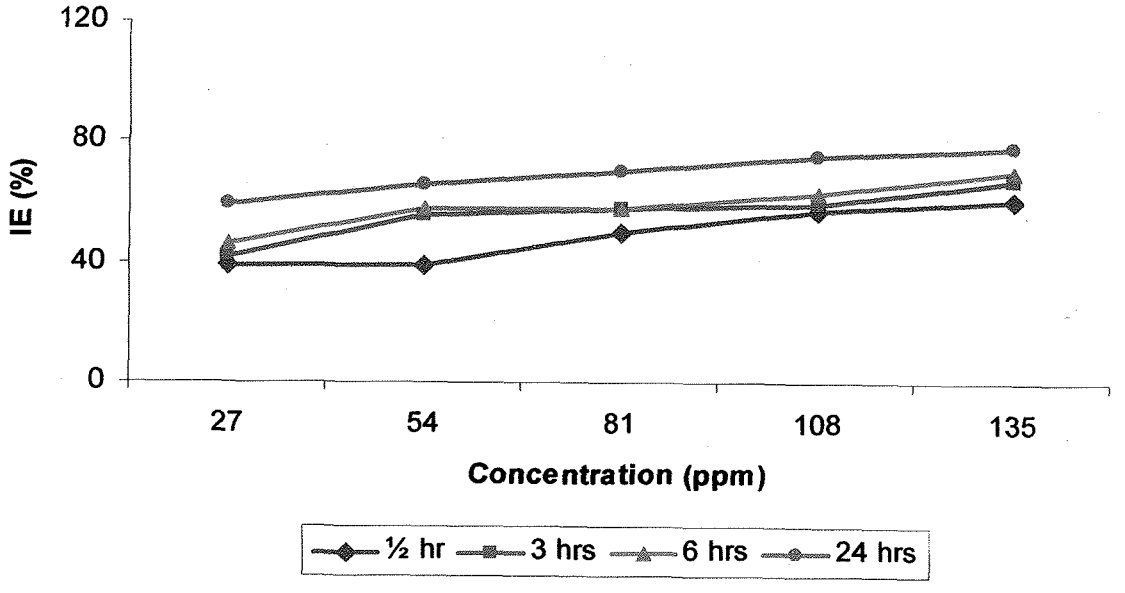


FIGURE - 10

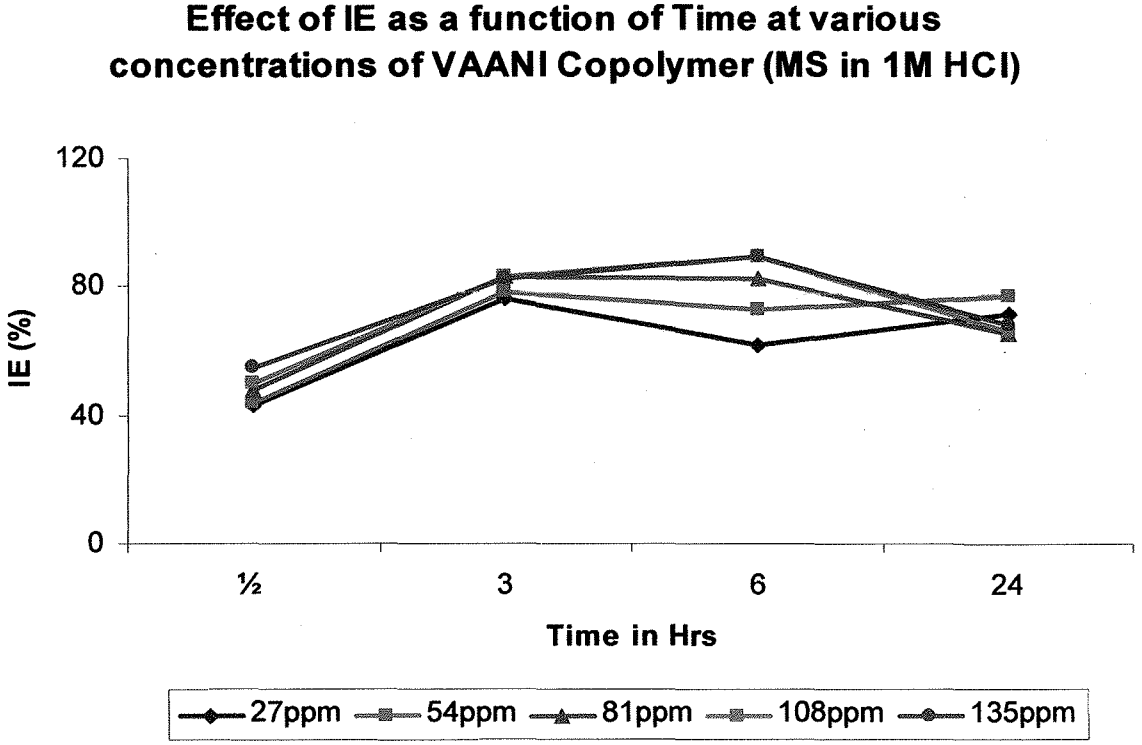


FIGURE – 11

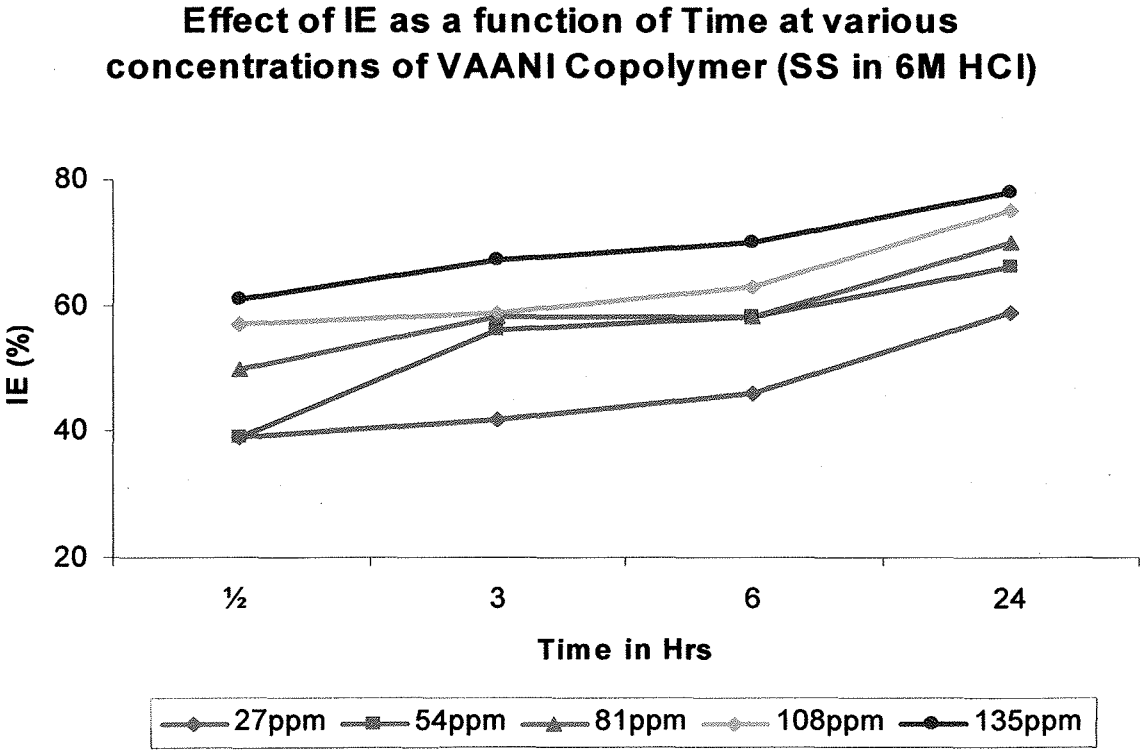


FIGURE – 12

Effect of concentration of copolymer on the corrosion of SS in 6M HCl

Weight-loss experiment showed the effective action of VAANI Copolymer as a corrosion inhibitor for SS in 6M HCl. The data on corrosion rate and inhibitor efficiency during static immersion of SS in 6M hydrochloric acid are depicted in Table (5) and figures (11, 12). The results indicate the successive decrease in corrosion rate and increase in inhibitor efficiency by the addition of VAANI Copolymer. The optimum concentration was found to be 135 ppm, exhibiting 78% efficiency.

Similar results were obtained for all the immersion periods in the presence of 135 ppm VAANI Copolymer, which showed maximum inhibition.

Role of period of immersion on the inhibitor action

In HCl medium the VAANI Copolymer showed an increase in inhibitor efficiency upto 24 hours. Experimental results clearly indicated the consistent behaviour of the copolymer and its effectiveness. The maximum efficiency of 78% was obtained at 24 hours. It could be summarized that the optimum time of immersion is 24 hours and optimum concentration is 135 ppm for VAANI Copolymer in 6M hydrochloric acid medium.

The performance evaluation of VAANI Copolymer as inhibitor for MS in 1M hydrochloric acid and SS in 6M hydrochloric acid with various immersion time and concentration of the copolymer is furnished in Tables (4, 5). The tables clearly inferred the following facts.

- ☞ Inhibitor efficiency increased with the increase in inhibitor concentration.
- ☞ Inhibitor efficiency increased for the first few hours of immersion followed by a slight decrease.

The inhibition effect of this copolymer may be due to the adsorption of the polymer molecules on the metal surface. The adsorbed molecules block the active sites on the metal surface thus preventing the dissolution of the metal. **Taha et al., (1995)** reported that increase in concentration of the polymer causes more blockage of the active sites of the metal. As a result the surface coverage by the polymer increases and the inhibition efficiency also increases. **Muralidharan and Iyer, (1997)** inferred that the maximum inhibition at high concentration can be attributed to the maximum blockage of

TABLE – 6

INFLUENCE OF TEMPERATURE ON THE CR AND IE IN THE PRESENCE OF VAANI COPOLYMER ON MILD STEEL IN 1M HCl

S. No	Conc (ppm)	308K		318K		328K		338K		348K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	1814	-	2747	-	6375	-	9402	-	13536	-
2.	27	1034	43	1308	53	2729	57	3948	58	5721	58
3.	54	1015	44	1168	58	2267	63	3384	64	5206	62
4.	81	943	48	1107	60	2180	68	2820	70	4997	63
5.	108	907	50	994	64	1613	72	2350	75	4500	67
6.	135	816	55	1126	59	2231	65	3290	65	4500	67

TABLE – 7

TEMPERATURE EFFECT ON CORROSION RATE AND INHIBITOR EFFICIENCY FOR VAANI COPOLYMER ON SS IN 6M HCl

S. No.	Conc. (ppm)	308K		318K		328K		338K		348K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	Blank	244	-	819	-	2136	-	7439	-	11242	-
2.	27	148	39	483	41	1068	50	3476	53	5023	56
3.	54	148	39	450	45	940	56	2827	62	3994	65
4.	81	122	50	360	56	918	57	2529	66	3166	72
5.	108	119	57	344	58	769	64	2380	68	3026	73
6.	135	95	61	295	64	662	69	2157	71	2320	79

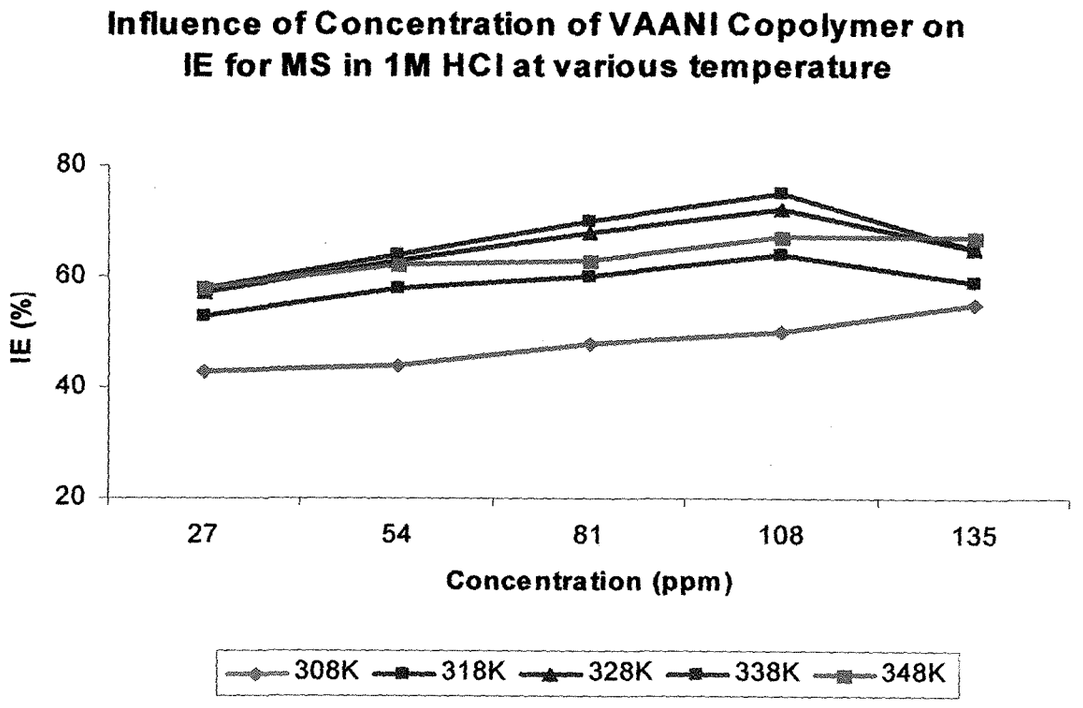


FIGURE – 13

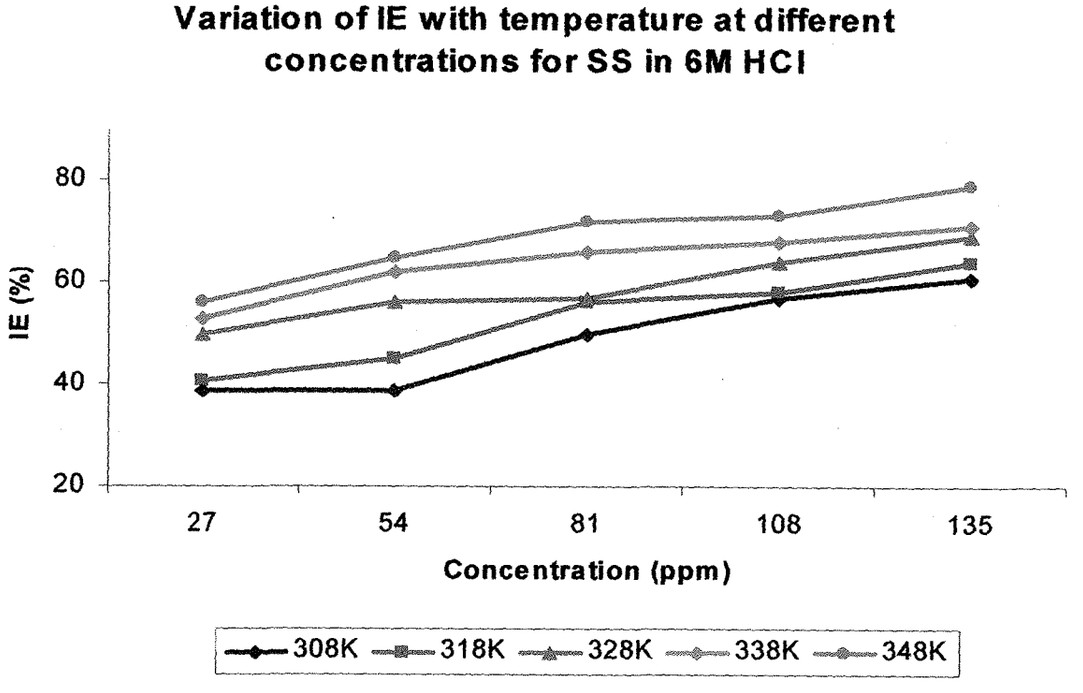


FIGURE - 14

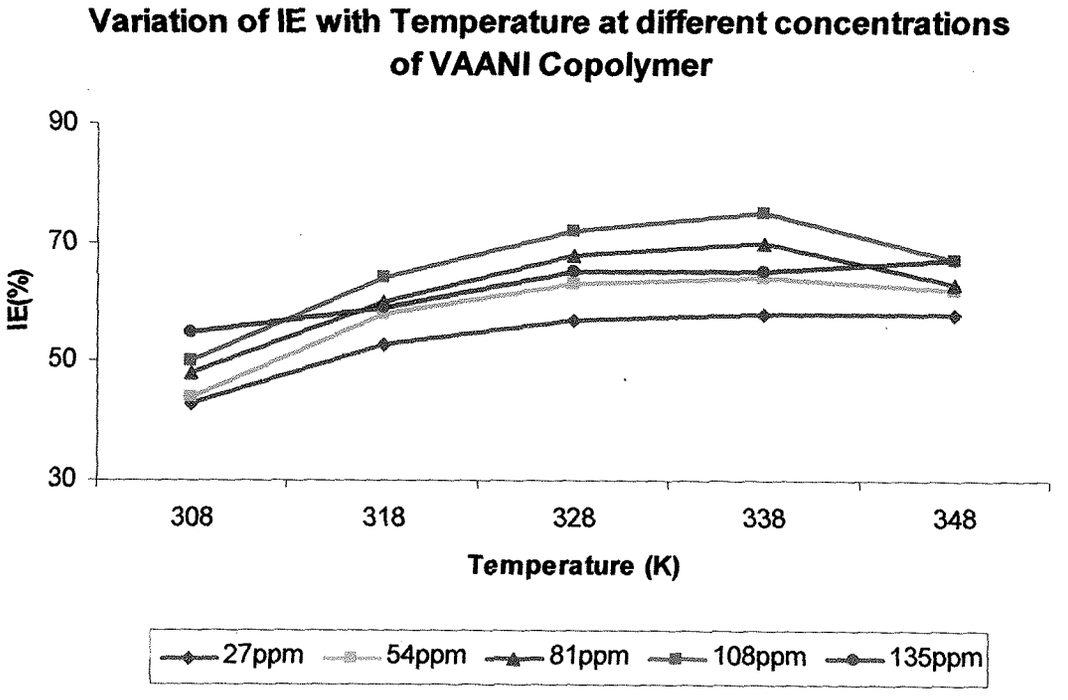


FIGURE - 15

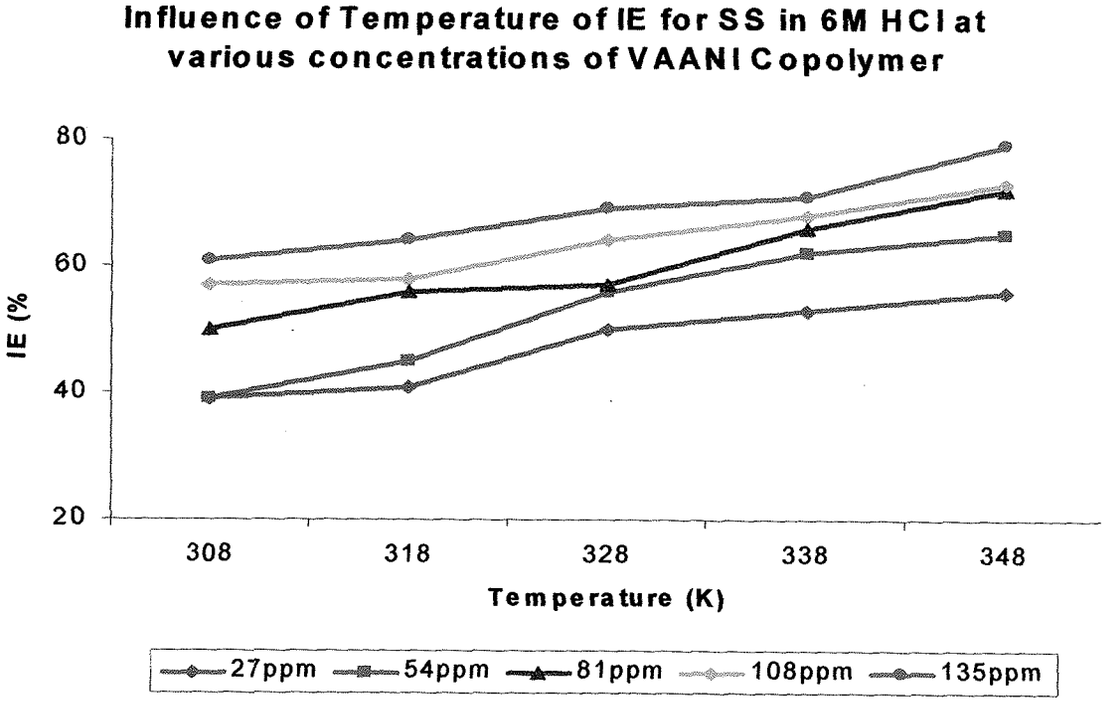


FIGURE – 16

the active sites on the metal surface. Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between these two processes **(Arrora & Choudary, 2002).** At early time of immersion the concentration of the VAANI Copolymer is more and hence the rate of adsorption is greater than the rate of desorption. It may be assumed that due to this greater rate of adsorption during the first few hours of immersion, the inhibitor efficiency increased with time.

Inhibitor Efficiency of VAANI Copolymer generally decreased with prolonged time of immersion. This behaviour can be attributed on the basis that, prolonged immersion of MS and SS in acid solution increases the concentration of ferrous ions, these ions are known to stimulate the corrosive attack of the acid on the metal **(Schmitt, 1984).**

Our experimental results inferred that the performance of VAANI Copolymer on MS and SS was found to be appreciable at room temperature.

Performance of VAANI Copolymer at higher temperature

Temperature can influence the interaction of MS and SS with acid in the absence and presence of the copolymer. To determine the activation energy and free energy of adsorption of corrosion process the weight loss studies were done in the temperature range from 308K to 348K.

The effect of temperature on the inhibition of corrosion of mild steel in 1M HCl by VAANI Copolymer is listed in table (6) and figured in figures (13, 14).

At each temperature the corrosion rate is decreased with increase in concentration of the inhibitor and the inhibitor efficiency is increased. With increase in temperature the corrosion rate is decreased and the inhibitor efficiency is increased. The maximum efficiency of 75% was observed with 108 ppm at 338K.

Effect of temperature on VAANI Copolymer inhibition of SS corrosion

Increase in temperature of test solution from 308K to 348K increased the efficiency of VAANI Copolymer in 6M HCl.The results obtained are shown in table (7) and figures (15, 16). With all the concentrations of the polymer the same trend of inhibitor efficiency with temperature was noticed. At all temperatures the inhibitor

efficiency increased with the increase in concentration. The maximum efficiency of 79% was noticed with 135 ppm concentration of VAANI Copolymer at 348K.

VAANI Copolymer exhibits good inhibition efficiency even at very high temperatures and it can be explained that VAANI Copolymer molecules are strongly adsorbed on the metal surface. It was suggested by **Hoar and Hollyday (1953)** that the enhancement of inhibitor efficiency at higher temperature may be due to the higher activation energy available for adsorption and higher rate of diffusion for inhibitor molecules.

According to **Machu, (1938)** the kinetics of a corrosion process acquires the character of a diffusion process in which, at higher temperature the quantity of the inhibitor present at the metal is greater than that at lower temperature.

Compound which give good inhibitor efficiency even at very high temperature shows that this compound is very strongly adsorbed on the metal surface and its desorption is considerably less **Hariharaputhran et al., (1999)**.

Adsorption isotherms

Five different isotherms are

- Langmuir isotherm (log(θ/1-θ) Vs log C)
- Temkin isotherm (θ Vs log C)
- Freundlich isotherm (log θ Vs log C)
- Flory-Huggins isotherm (log θ/C Vs log (1-θ)) and
- El-Awady isotherm

The experimental results were fitted into various adsorption isotherms and the graphical representation of Langmuir isotherm (log(θ/1-θ) Vs log C), Temkin isotherm (θ Vs log C), Freundlich isotherm (log θ Vs log C), Flory-Huggins isotherm (log θ/C Vs log (1-θ)) and El-Awady isotherm.

Different adsorption isotherms are tested graphically to find a suitable adsorption isotherm for the system studied.

Application of Adsorption Isotherms

Langmuir, Temkin, Flory–Huggins, Freundlich and El-Awady isotherms were tested for their fit to the experimental data.

The Langmuir isotherm is given by

$$\theta / (1 - \theta) = k\, I \qquad \text{---------- (4.1)}$$

Where

k – binding constant of the adsorption reaction, and

I – Inhibitor concentration in the bulk of the solution. A plot of the left side of the equation (4.1) Vs I should give a straight line if Langmuir isotherm is applicable.

The Flory–Huggins isotherm is given by

$$\theta / x\,(1 - \theta)^x = kI \qquad \text{---------- (4.2)}$$

Where,

x is the size parameter and is a measure of the number of adsorbed molecules substituted by a given inhibitor molecules. Rearrangement of equation (4.2) gives

$$\log (\theta/C) = \log xK + x \log (1-\theta) \qquad \text{---------- (4.3)}$$

Where,

θ is the degree of coverage

x is the number of active sites occupied by one inhibitor molecule.

Values of 'x' greater than one implies the formation of multi layer of the inhibitors on the metal surface. Values of 'x' less than one, means that a given inhibitor molecule occupies more than one active site.

A plot of log θ Vs I should yield a straight line with a slope x and intercept of log x K.

El – Awady et al equation

$$\log (\theta/1-\theta)) = \log K1 + y \log C \qquad \text{---------- (4.4)}$$

In equation (4.4) the value of (1/y) indicates the number of active sites of the surface occupied by one molecule of the inhibitor. 'K' is the binding constant of the adsorption reaction ($K=k^{1/y}$) and C is the inhibitor concentration in the bulk of the solution.

In the present study, the regression co-efficients were calculated for all the adsorption isotherms studied and the results were tabulated in table (8, 9). Figures (17-24) represents the Langmuir, Temkin, Freundlich and Flory-Huggins adsorption isotherms respectively.

Statistical Analysis of the Best Fit Isotherm Models

The regression co-efficients are obtained for the fitness of the data to various adsorption models are furnished in the tables (8, 9). From this findings it can be inferred that VAANI Copolymer is adsorbed on MS and SS surface obeying Langmuir and Temkin adsorption isotherms. Since the systems under study obey Langmuir adsorption isotherm clearly indicate that VAANI Copolymer is adsorbed on the metal surface and this process of adsorption is responsible for the inhibition of the metal **(El-Shafei, et. al, 2001)**. Adsorption of the inhibitor was found to obey Langmuir isotherm as it is evident from the linear plots of Log θ / 1-θ Vs Log C.

The data obtained give a straight line with the regression coefficient 0.81 to 0.995 at all temperatures. Figures (17, 18) illustrate the Langmuir plots for VAANI Copolymer at various temperatures. It is observed that although these plots are linear, the gradients are never unity, contrary to what is expected for ideal Langmuir adsorption isotherm equation. During the derivation of Langmuir equation it is assumed that there are no inter molecular interactions between the adsorbate molecules. But in practice polymeric molecules having polar atoms (or) groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity.

TABLE – 8

VALUES OF REGRESSION COEFFICIENT (R) OBTAINED USING VARIOUS ADSORPTION ISOTHERMS FOR MS

Isotherms	Regression Values				
	308K	318K	328K	338K	348K
Langmuir	0.9338	0.8130	0.9270	0.9981	0.9742
Temkin	0.9907	0.9726	0.9828	0.9925	0.9984
Flory-Huggins	0.9477	0.3316	0.9260	0.9821	0.9146
Freundlich	0.9365	0.9893	0.9969	0.9916	0.9706
El-awady	0.9338	0.8130	0.9270	0.9981	0.9742

TABLE - 9

VALUES OF REGRESSION COEFFICIENT (R) OBTAINED USING VARIOUS ADSORPTION ISOTHERMS FOR SS

Isotherms	Regression Values				
	308K	318K	328K	338K	348K
Langmuir	0.9189	0.9639	0.9402	0.9968	0.9845
Temkin	0.9745	0.9825	0.9781	0.9845	0.9793
Flory-Huggins	0.9891	0.9513	0.8739	0.9895	0.9414
Freundlich	0.9215	0.9713	0.9586	0.9916	0.9919
El-awady	0.9189	0.9639	0.9402	0.9968	0.9845

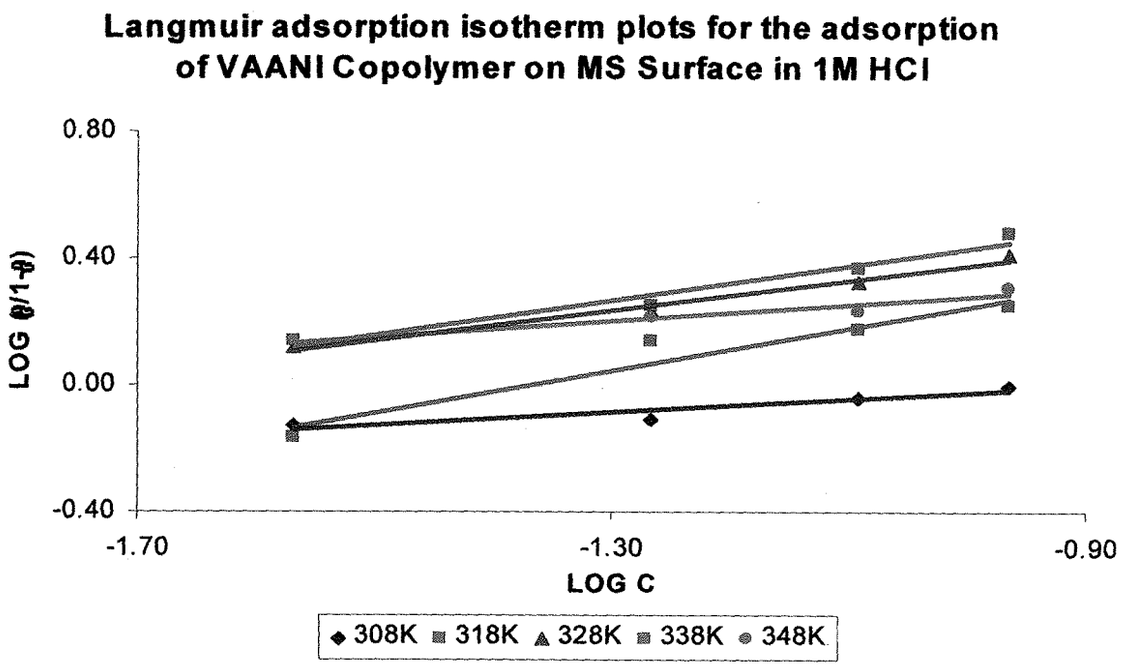


FIGURE – 17

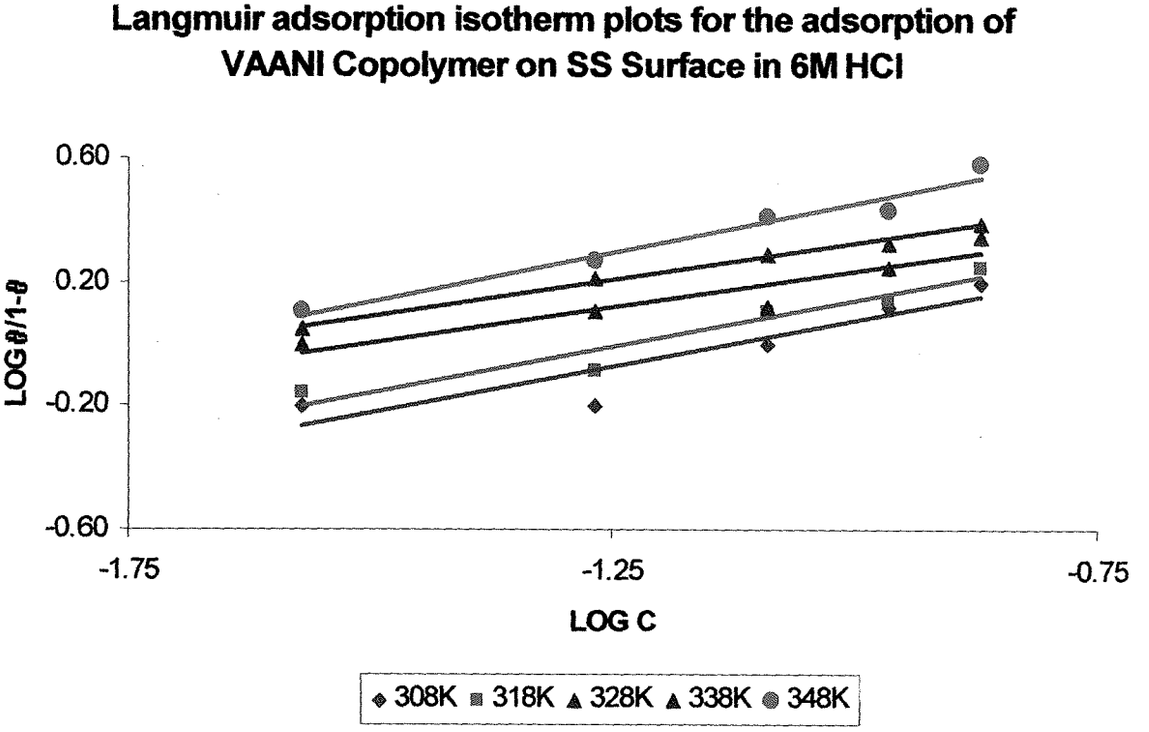


FIGURE-18

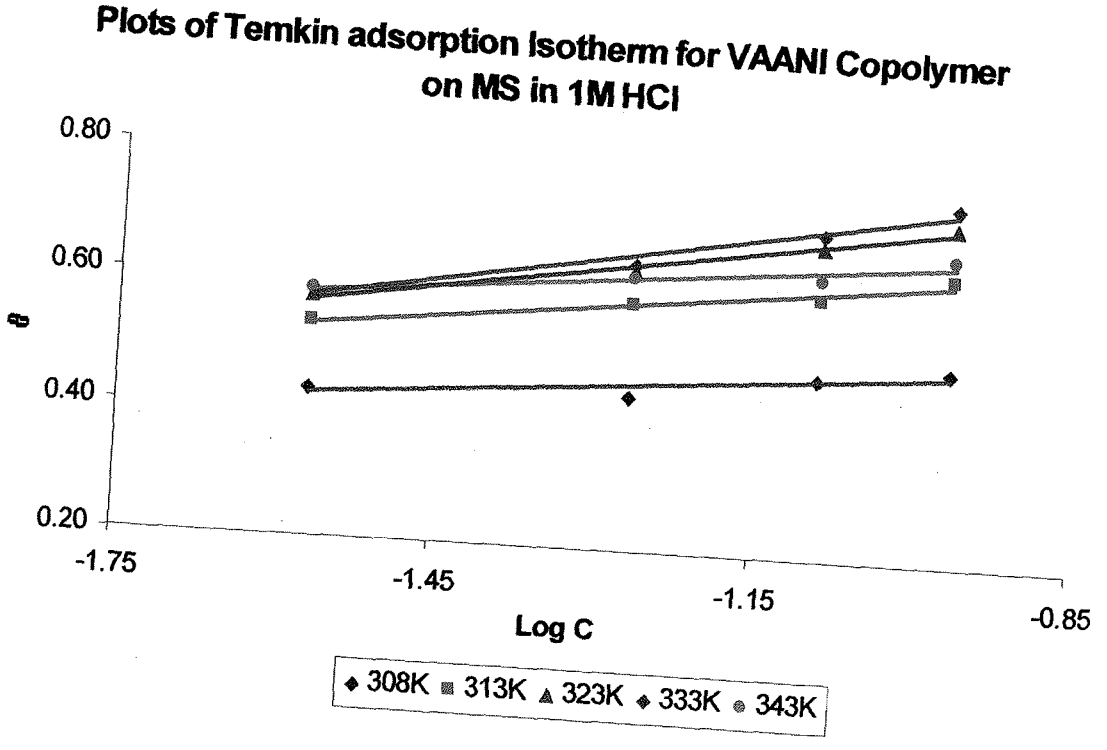


FIGURE – 19

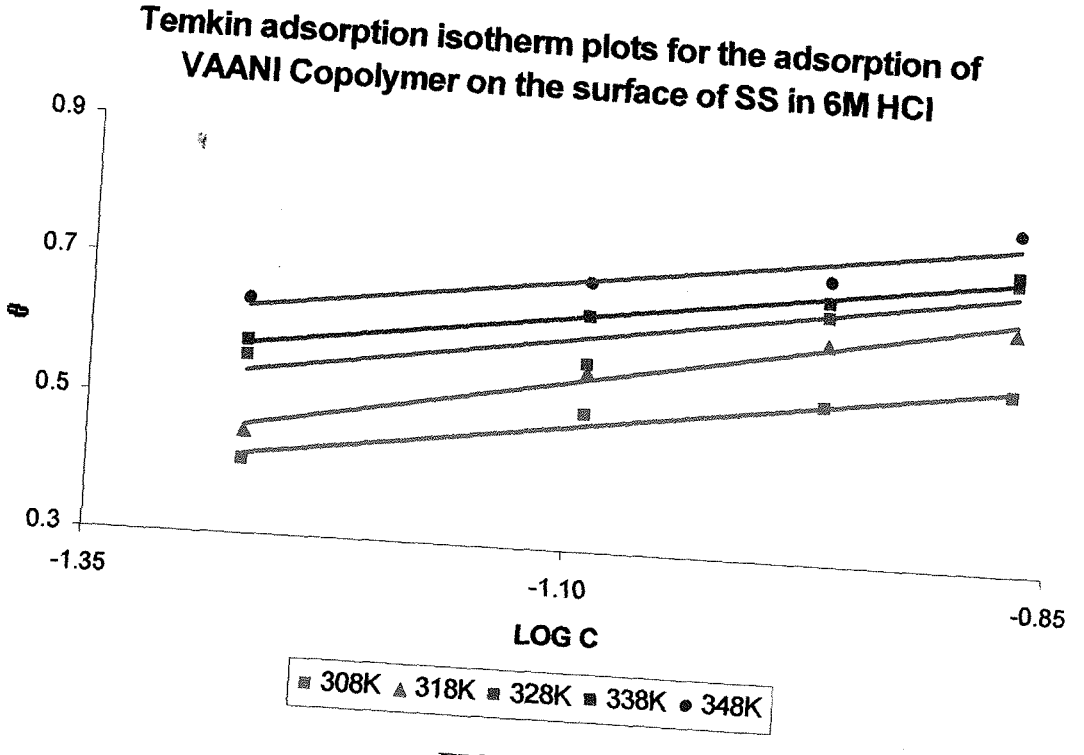


FIGURE - 20

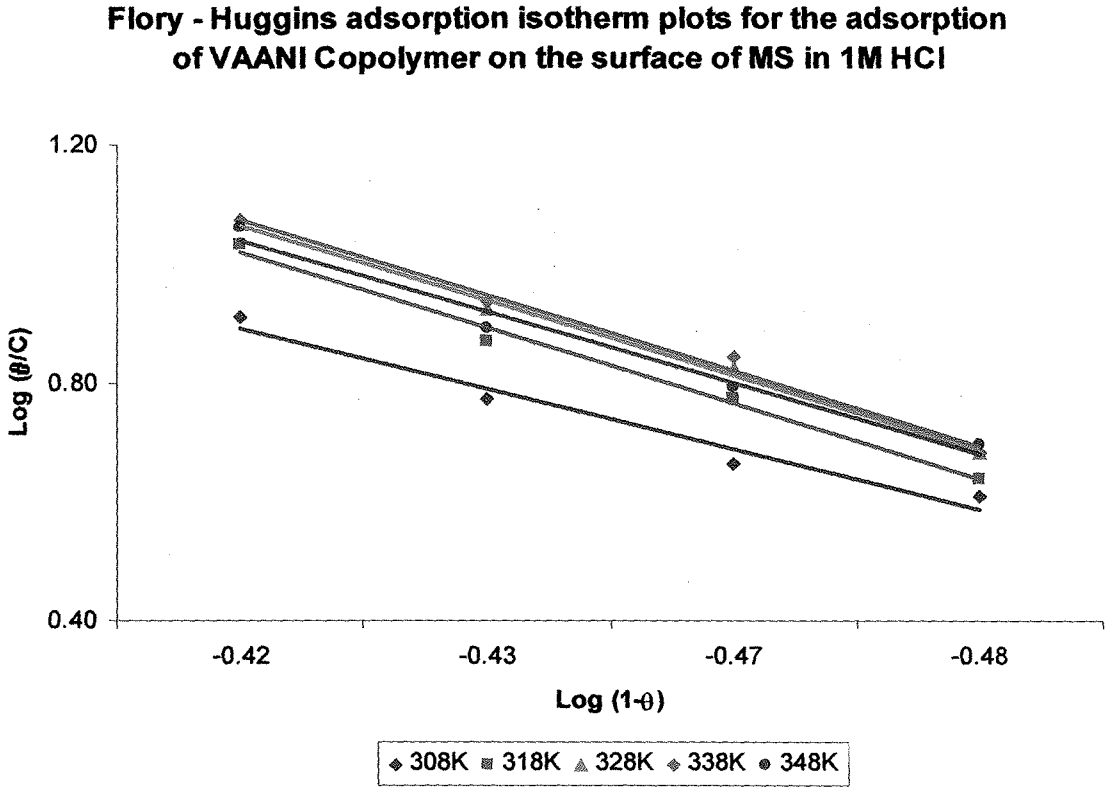


FIGURE - 21

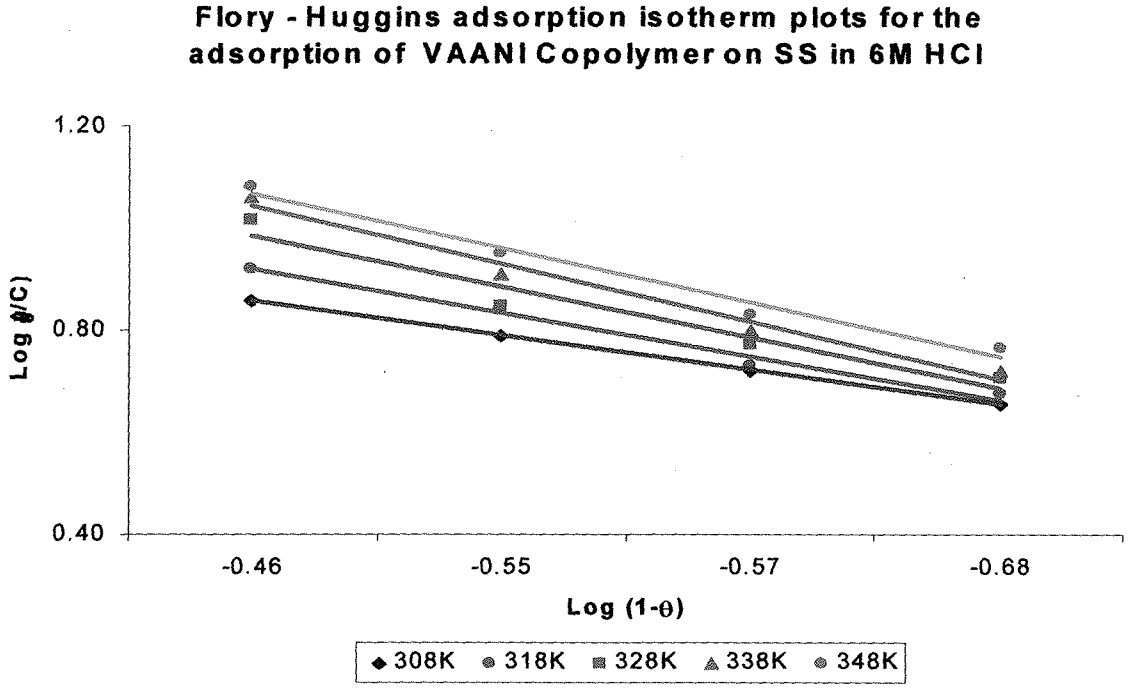


FIGURE - 22

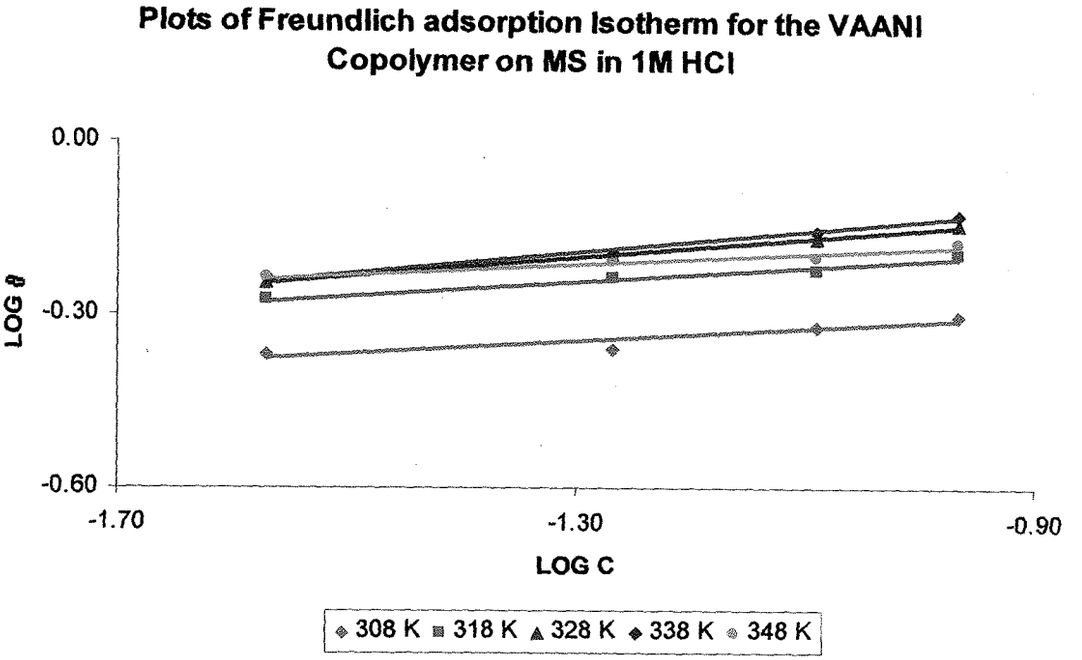


FIGURE – 23

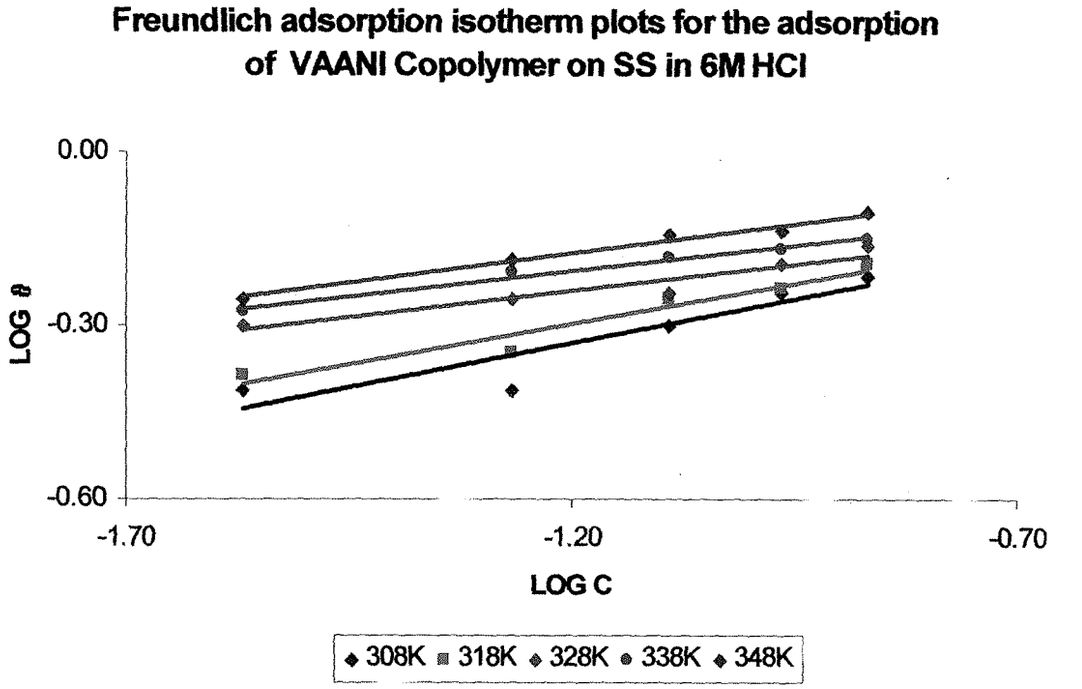


FIGURE – 24

The systems studied also obey Temkin adsorption isotherm indicate that there is molecular interaction among the adsorbed particles and the surface as well as there is heterogeneity of the metal surface. The results presented by **Ibrahim et al., (1987)** reflected similar observations. The data depicted in figures (19, 20) clearly show that excellent fit is obtained with all types of plot. From the temperature study results it was concluded that the IE increases with increase in temperature. θ Vs Log C gave a straight line suggesting that the adsorption of VAANI Copolymer at MS / acidic solution interface and VAANI Copolymer at SS / acidic solution interface obey Temkin isotherm. Hence the inhibitor reduces corrosion by being adsorbed on the metal surface.

Activation energy (E_a)

The values of corrosion rates at different temperatures make it possible to calculate the activation energy (E_a). According to Arrhenius equation

$$\text{Log C.R.} = \frac{-E_a}{2.303\ RT} + \text{Constant}$$

Where, C.R. - Corrosion rate

E_a - Activation energy

T - Temperature

Corrosion rates of MS and SS calculated in the presence and in the absence of the inhibitor by weight loss method are plotted against the temperature (log CR Vs 1/T) figures (25, 26). Activation energies were calculated from the slopes.

The estimated values of E_a for MS in VAANI Copolymer in 1M HCl and SS in VAANI Copolymer in 6M HCl are listed and from the tables (12, 13) it was found that the E_a values of the blank were higher than that of the systems studied in the presence of the inhibitor.

Machu, (1938) in his studies, on the influence of temperature on inhibitor action concluded that with powerful inhibitors, the E_a was lower for the inhibited solution than that of uninhibited solutions. This type of behaviour means that an inhibitor becomes more effective as the temperature increases was explained by **Putilova, (1960)**

TABLE – 10

RELATIONSHIP BETWEEN ΔG, ΔH, ΔS AND ACTIVATION ENERGY WITH VARIOUS CONCENTRATIONS OF VAANI COPOLYMER AT DIFFERENT TEMPERATURES FOR MS IN 1M HCl

Conc. of the Inhibitor (%)	Activation Energy (E_a) KJ / mol	Free energy of adsorption(-ΔG) KJ/mol					Entropy Change ΔS KJ/mol	Heat of Adsorption ΔH KJ/mol
		308K	318K	328K	338K	348K		
Blank	43.66	-	-	-	-	-	-	-
0.027	43.01	18.49	19.50	19.91	20.01	20.01	0.04	7.91
0.054	37.30	16.84	18.26	18.79	18.90	18.68	0.04	4.13
0.081	37.04	16.23	17.45	18.33	18.56	17.77	0.04	3.90
0.108	35.31	15.70	17.15	18.08	18.47	17.49	0.05	1.35
0.135	37.30	15.65	16.06	16.70	16.70	16.92	0.03	5.91

TABLE – 11

TEMPERATURE DEPENDENCE OF THERMODYNAMIC PARAMETERS IN THE PRESENCE OF VAANI COPOLYMER ON SS SURFACE IN 6M HCl

Conc. of the Inhibitor (%)	Activation Energy (E_a) KJ / mol	Free energy of adsorption (-ΔG) KJ/mol					Entropy Change ΔS KJ/mol	Heat of Adsorption ΔH KJ/mol
		308K	318K	328K	338K	348K		
Blank	82.33	-	-	-	-	-	-	-
0.027	74.96	18.07	18.28	19.20	19.49	19.80	0.05	3.59
0.054	69.96	16.32	16.94	18.06	18.68	19.01	0.07	-5.53
0.081	70.34	16.43	17.03	17.14	18.10	18.81	0.06	-1.60
0.108	69.81	16.41	16.52	17.15	17.60	18.21	0.05	1.84
0.135	69.65	16.27	16.59	17.16	17.40	18.48	0.05	0.03

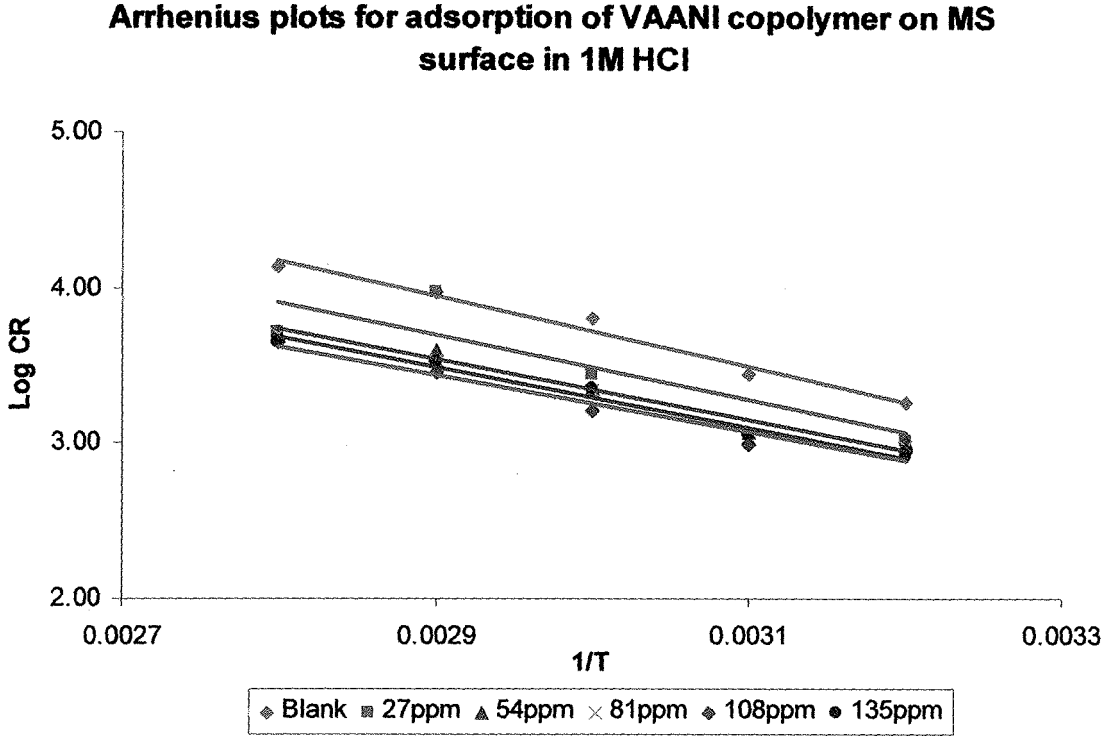


FIGURE - 25

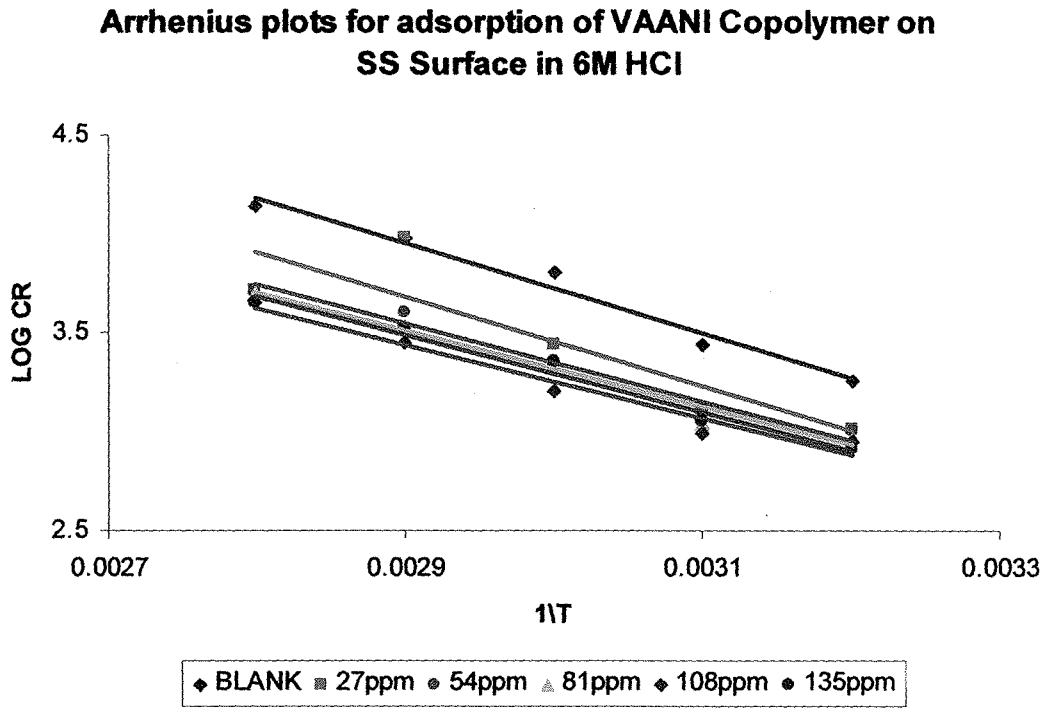


FIGURE - 26

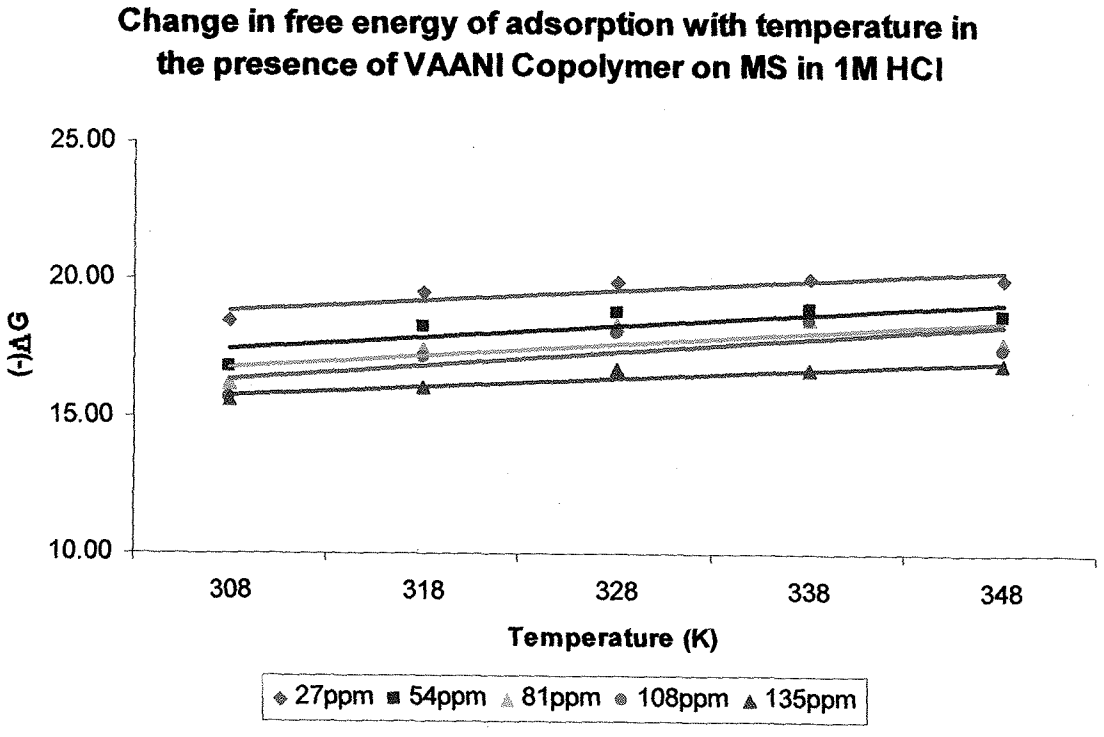


FIGURE - 27

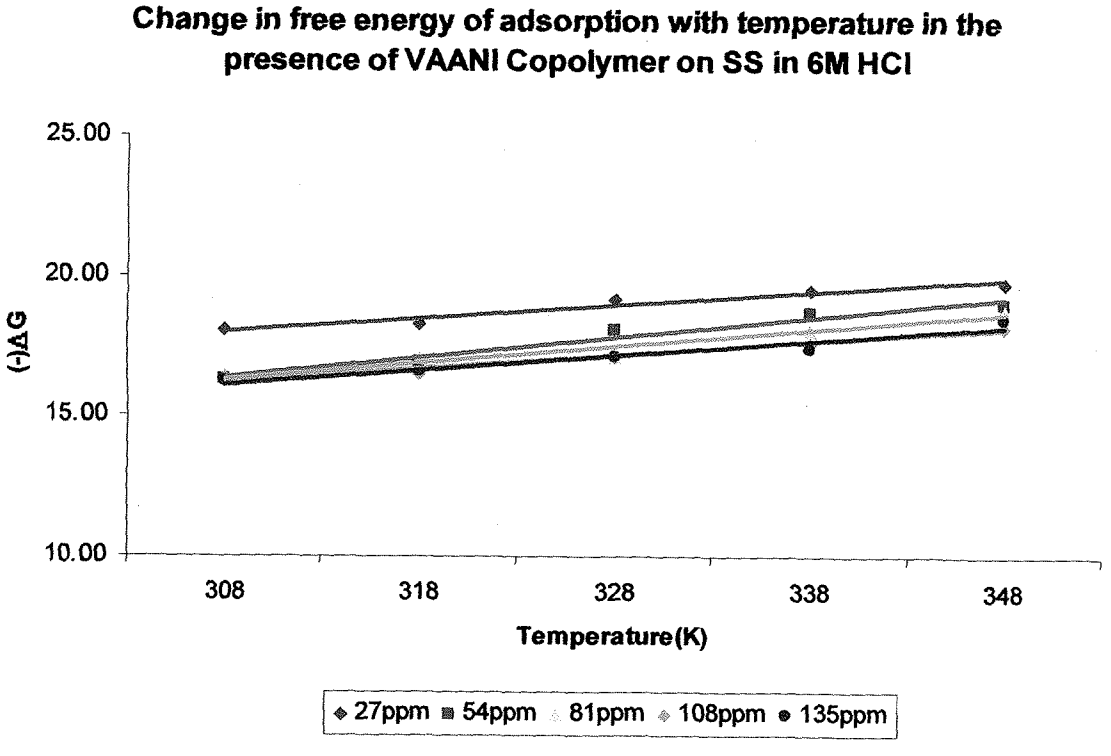


FIGURE – 28

as due to an increase in surface area of the metal covered by the inhibitor molecules as the temperature rises. Experiments conducted by **Bag et al., (1996)** also reflected lower E_a values for the inhibited systems. Studies carried out by **Taha et al., (1995)** revealed that the presence of inhibitors decreased the E_a of the reaction to an extent depending on the nature of inhibitor.

Riggs, (1967) reported that in the presence of adsorbed inhibitor, the dissolution of the metal proceeds with two distinct processes (corresponding to the covered area and the bare metal surface) concluded that at high degree of coverage the dissolution process is not only determined by the reaction of the metal from the bare surface but also involves the adsorbed inhibitor and consequently the E_a can assume values greater or smaller than those calculated in the absence of the inhibitor.

In the present investigation, E_a values were found to be greater or smaller than those calculated in the absence of the inhibitors. This can be explained by the fact that at high degree of coverage, the dissolution process is not only determined by the reaction of the metal from the blank surface but also involves the adsorbed inhibitor.

The estimated E_a in the presence of inhibitors infer that the interaction between the metal surface and the inhibitor was found to be strong enough to prevent corrosion.

Thermodynamic Parameters

Temperature study results help in the calculation of thermodynamic parameters – change in free energy, entropy and enthalpy. The results of thermodynamic parameters studied using VAANI Copolymer on mild steel and SS in HCl medium are reported in the tables (10, 11).

Analysis of the tables (10, 11) infer that the ΔG values ranges from –13 KJ/mol to –20KJ/mol. from 308K to 348K. For all the systems studied in HCl medium the value of ΔG decreases with increase in concentration and increases with increase in temperature.

Moretti et al., (2002), Abdulaziz et al., (1989, 1990), Gomel et al., (1995), Rudresh et al., (1982) reported that the negative values of ΔG adsorption are characteristic of strong interaction between the inhibitor and the electrode forming a chemisorbed layer on the metallic surface.

The values of ΔG reflected the spontaneity of the adsorption process in the experimental conditions used. Strong interaction on the metal surface had been accompanied by negative free energy of adsorption. The sign of free energy of adsorption for all the inhibitors shows that there was a strong interaction of the inhibitor molecules on the corroding metal surface.

Heat of Adsorption (ΔH) and Change in Entropy (ΔS)

Thermodynamic parameters ΔH and ΔS could be arrived at, from the temperature studies and using a plot of -ΔG Vs T. The values of thermodynamic parameters are listed in the tables (10, 11).

Thermodynamic parameters are useful tool to find out the strength of adsorption of the inhibitor on the electrode surface. In the current study the values of heats of adsorption suggested the favourable condition for adsorption of inhibitors on the metal surface exists in the system investigated.

Positive values of ΔS were observed for the system studied and it reflected a strong interaction between the inhibitor and the electrode surface. Similar observations were furnished by **Bag et al., (1996)**.

From the tables (10, 11) and figures (25, 26, 27 and 28) it is understood that the thermodynamic parameters are relative and emphasize a strong interaction between the metal surface and VAANI Copolymer.

Electrochemical Measurements

Polarization Techniques

The frequency response analyzer (solartron 1284Z) and an personal computer which automatically measures Tafel polarization was used for the polarization study. The data were analysed using computer software.

The cell for the polarization studies was a glass vessel containing the aerated unstirred test solution with a platinum electrode as the counter electrode, a saturated calomel electrode as the reference electrode and the mild steel / stainless steel electrode as the working electrode.

For potentiostatic polarization studies, mild steel stripes of same composition (as in the weight loss method) coated with lacquer with an exposed area of $1cm^2$ was used.

To understand the mode of action of the inhibitor on MS and SS surface in acid medium electrochemical measurements were carried out using solartron 1284Z.

In the current study, the values of polarization parameters and impedance parameters are tabulated in tables (12, 13 and 14, 15) for the systems MS in 1M HCl and SS in 6M HCl in the presence of VAANI Copolymer. Values of Tafel constants (b_a and b_c) were obtained from the slopes of regions of log polarization curves. The values of corrosion current density (I_{corr}) were obtained by extrapolation of Tafel lines. The values of E_{corr} were also tabulated for all the systems studied.

The decrease in I_{corr} values in the presence of VAANI Copolymer and an increase in IE with concentration indicate the adsorption of the inhibitor on metal surface. Maximum inhibition efficiency was found to be 76% and 71% at 108ppm on MS surface and SS surface respectively.

The polarization curves obtained for the copolymer-adsorbed metal systems include both from the metal and copolymer. Thus, the total corrosion current density is result of the redox reactions that occur in the metal / polymer and polymer / electrolyte interfaces. Taking into account that the redox reactions related to the conducting polymer layer do not contribute to the dissolution of the metal, HCl corrosion current densities are presented in tables (12, 13). The values of E_{corr} is the presence of VAANI Copolymer indicate the mixed mode of inhibition.

Tafel constants b_a and b_c obtained in the presence and absence of VAANI Copolymer was found to be altered in both the direction compared to the blank value is the indication that the mode of inhibition is of mixed type. Polarization curves were depicted in the figures (29, 30).

TABLE – 12

TABULATION OF E_{corr}, I_{corr} AND TAFEL CONSTANTS FOR MS IN 1M HCl IN THE PRESENCE OF VAANI COPOLYMER

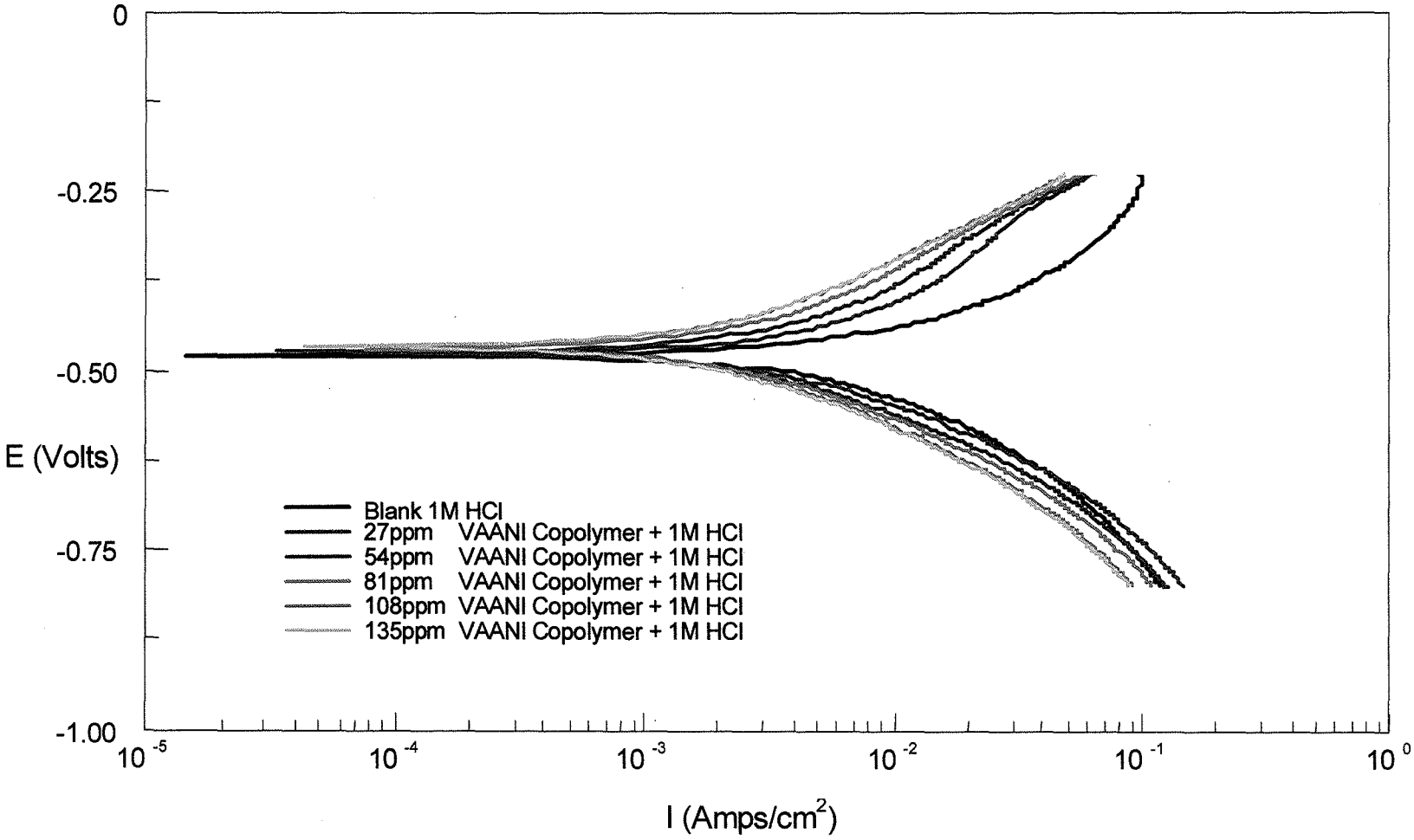
S.No.	Inhibitor conc. (ppm)	b_a mV/dec	b_c mV/dec	I_{corr} x 10^{-4} (Amp/cm^2)	E_{corr} x 10^{-3} mV/sec	CR (mpy)	IE (%)
1	Blank	224	153	76.686	-480		
2	27	184	223	54.504	-478	2524	29
3	54	179	212	39.581	-473	1832	48
4	81	168	191	28.484	-469	1319	63
5	108	146	158	18.456	-466	854	76
6	135	164	175	21.296	-467	986	73

TABLE – 13

CORROSION KINETIC PARAMETERS FOR SS IN 6M HCl IN THE PRESENCE OF VAANI COPOLYMER

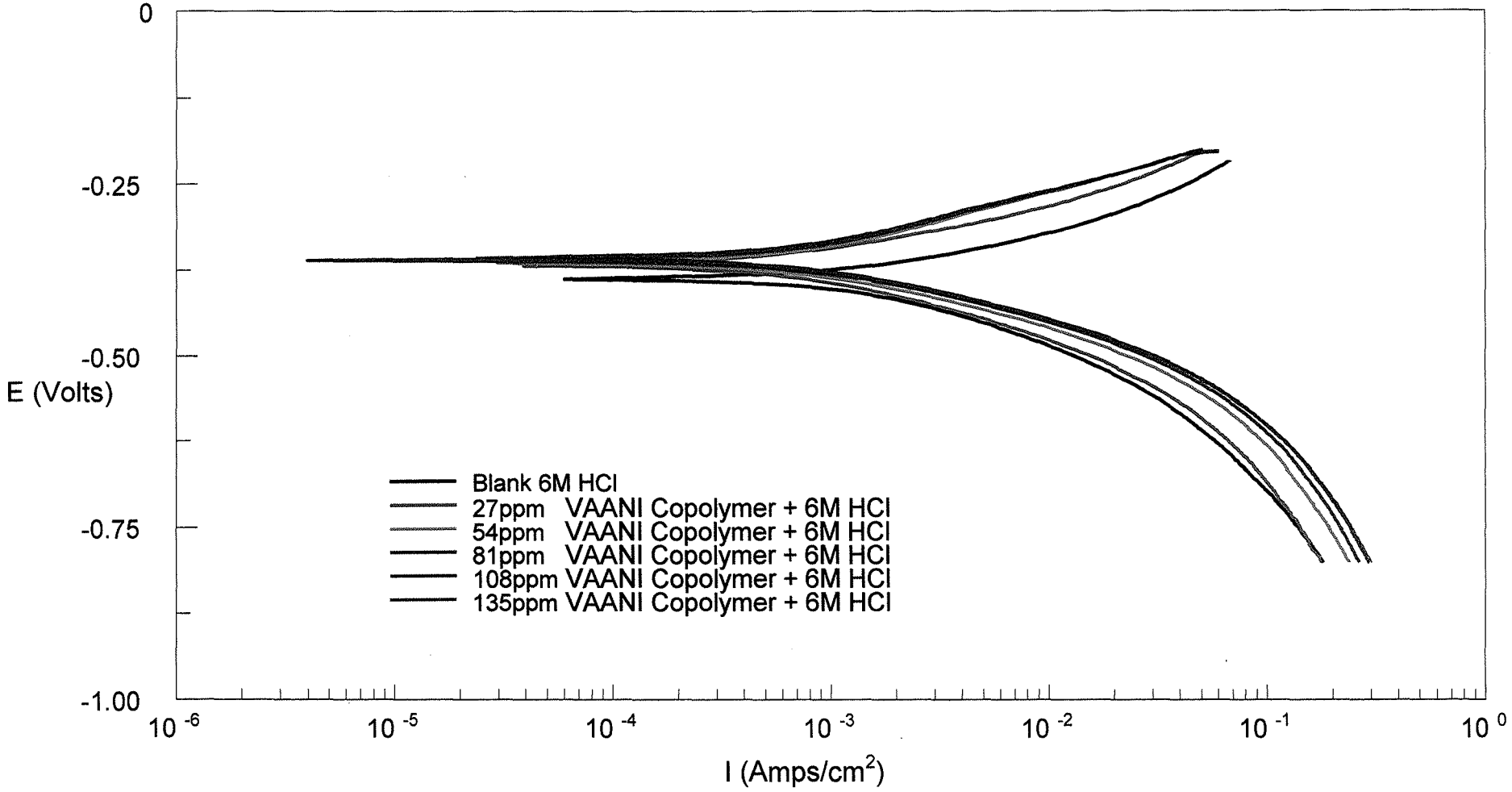
S.No.	Inhibitor conc. (ppm)	b_a mV/dec	b_c mV/dec	I_{corr} x 10^{-4} (Amp/cm^2)	E_{corr} x 10^{-3} mV/sec	CR (mpy)	IE (%)
1	Blank	134	96	18.423	-388	839	
2	27	101	82	7.784	-367	365	58
3	54	90	94	8.292	-365	377	55
4	81	91	91	8.174	-360	372	56
5	108	79	75	5.379	-354	245	71
6	135	86	86	8.017	-355	365	56

FIGURE – 29



Potentiodynamic polarization of MS in 1M HCl in the presence of VAANI Copolymer

FIGURE - 30



Potentiodynamic polarization of SS in 6M HCl in the presence of VAANI Copolymer

Electrochemical Impedance Spectroscopy (EIS) results

EIS is one of the most successful technique used to evaluate the effectiveness of an inhibitor. The corrosion behaviour of mild steel in acidic solutions in the presence of VAANI Copolymer was investigated by the EIS method at room temperature after immersion for 10 to 15 min. The Nyquist plots and Bode plots on MS for inhibited and uninhibited acidic solutions containing various concentrations of the VAANI Copolymer are shown in the figure (31). The semicircles obtained in the present system are not perfect semicircles and this depressed semicircles may be due to frequency dispersion. The locus of the plots was regarded as one part of a semicircle (in acidic solution with VAANI Copolymer). The results pertaining to EIS measurements are furnished in the table (14).

The charge transfer resistance R_{ct} and C_{dl} values of the present systems studied indicate the adsorption characteristics of VAANI Copolymer on MS and SS surface.

The charge transfer resistance (R_{ct}) values were found to be higher for maximum concentration of VAANI Copolymer. R_{ct} values increase with increase in concentration of VAANI Copolymer on MS in 1M HCl.

Figure (31) illustrate the radius of the semicircle and is found to increase with increase in concentration of the inhibitor and this indicate the dissolution of the metal and the corrosion of mild steel is controlled by charge transfer process.

The charge transfer reactions are known to take place at the metal/polymer interfaces. Consequently, the high R_{ct} values of inhibited electrodes can be explained by the build up of protective passive layers and the effective barrier behaviour of polymer layers.

C_{dl} is the double layer capacitance which is due to the charge separation at metal/electrolyte interface. The value of C_{dl} decreases as the concentration of VAANI Copolymer increases. This decrease in C_{dl} values is due to the adsorption of VAANI Copolymer on the metal surface.

TABLE – 14

VALUES OF R_{ct} AND C_{dl} FOR THE ADSORPTION OF VAANI COPOLYMER ON MS IN 1M HCl

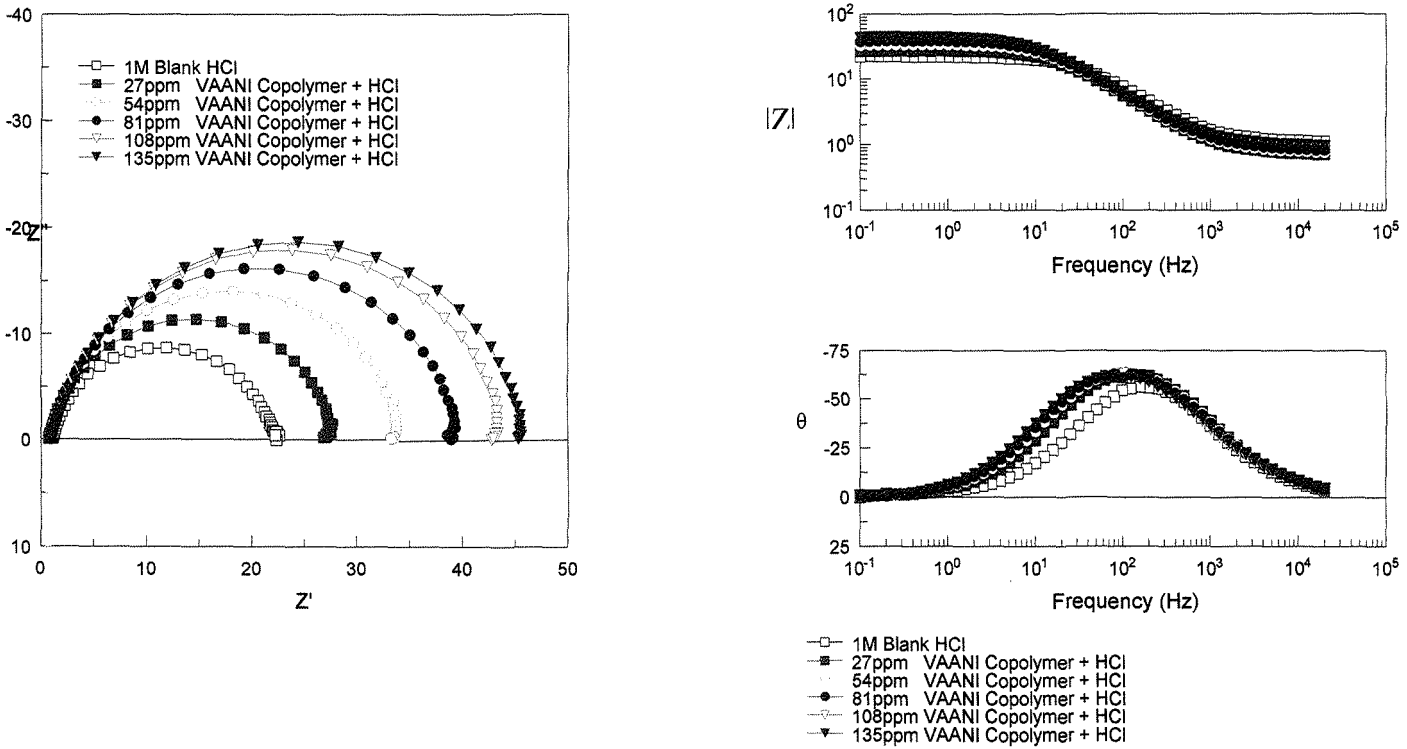
S.No	Conc (ppm)	R_{ct} (ohms)	C_{dl} μ(farads)
1	Blank	21.246	2.25
2	27	26.707	3.49
3	54	33.008	3.53
4	81	38.498	3.45
5	108	42.492	3.36
6	135	44.741	3.30

TABLE - 15

VALUES OF IMPEDANCE PARAMETERS R_{ct} AND C_{dl} FOR VAANI COPOLYMER ON SS IN 6M HCl

S.No	Conc (ppm)	R_{ct} (ohms)	C_{dl} μ (farads)
1	Blank	15.746	0.653
2	27	33.062	0.688
3	54	23.099	1.00
4	81	22.41	1.18
5	108	22.256	1.33
6	135	22.257	1.45

FIGURE - 31

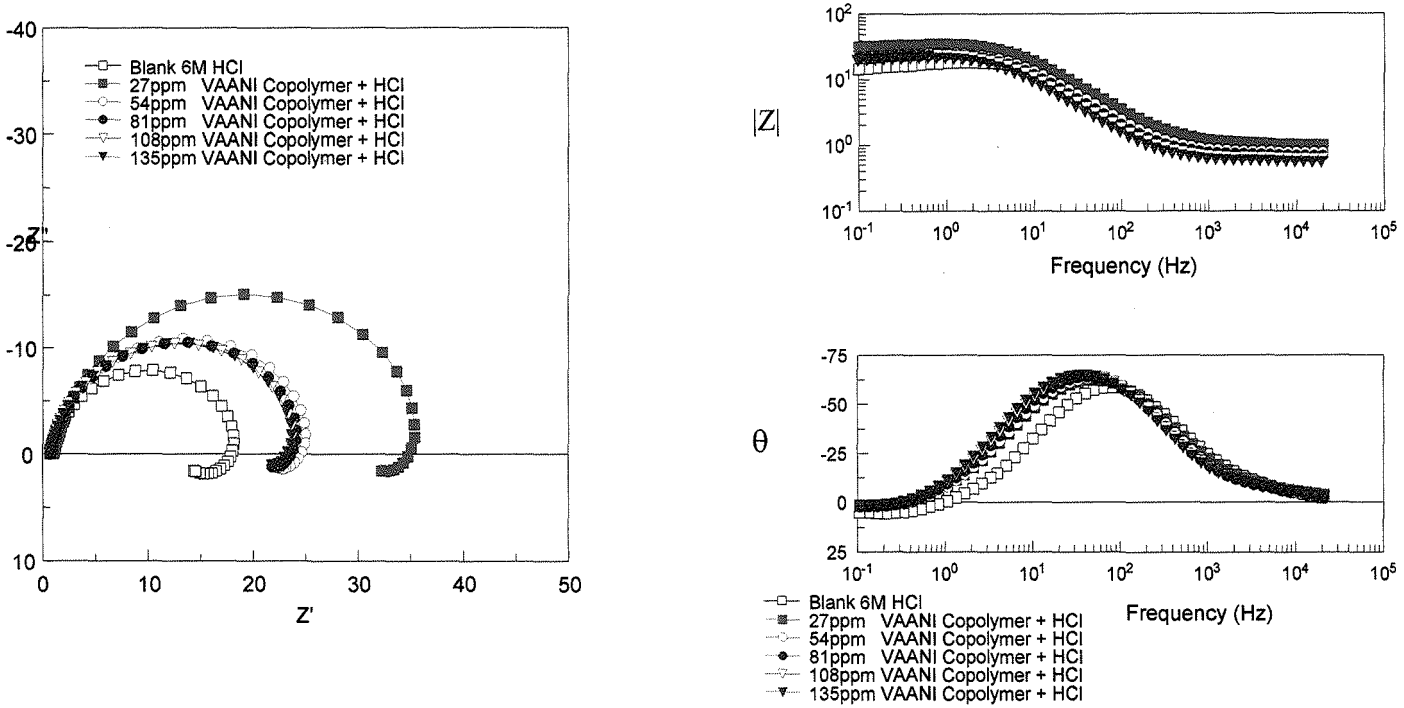


NYQUIST PLOTS

BODE PLOTS

Impedance measurements for MS in 1M HCl in the presence of VAANI Copolymer

FIGURE - 32



NYQUIST PLOTS

BODE PLOTS

Impedance measurements for SS in 6M HCl in the presence of VAANI Copolymer

The adsorption of VAANI Copolymer on the metal surface can occur either directly on the basis of donor – acceptor interactions between the π-electrons of the polymer chain and then vacant d-orbital of iron surface atoms or an interaction of VAANI Copolymer with already adsorbed chloride ions as proposed by **Hackerman et al., (1965)**. Either way, with more time, more inhibitor molecules are adsorbed and the protective layer grows proportionally until saturation occurs. This fact supports the observed decrease in C_{dl} values in the EIS measurement at the corrosion potential.

Electrochemical Impedance Spectroscopy for SS in 6M HCl

EIS studies were carried out for the systems-VAANI Copolymer in 6M hydrochloric acid on SS Surface. The resistance and capacitance of SS surface have been obtained with Z view software. The values of R_{ct} and C_{dl} are furnished in the table (13). The Nyquist plots pertaining to this system is given in the figure (24).

In stainless steel/electrolyte interface solution the R_{ct} values increases with increase in concentration. This may be due to the formation of passive film which is responsible for the increase in R_{ct} values.

The resistance values in the presence of VAANI Copolymer are in the range between 15.746 ohms to 22.257 ohms and the capacitance values are in the range of 0.653×10^{-4} ohms to 1.4×10^{-4} ohms.

The high resistance values and low capacitance values indicate the highly protective nature of VAANI Copolymer. It has been reported that VAANI Copolymer containing alkyl and vinyl based polymers are able to protect more than 50h of exposure **Miller et al (1999).**

Cylic Voltammetry

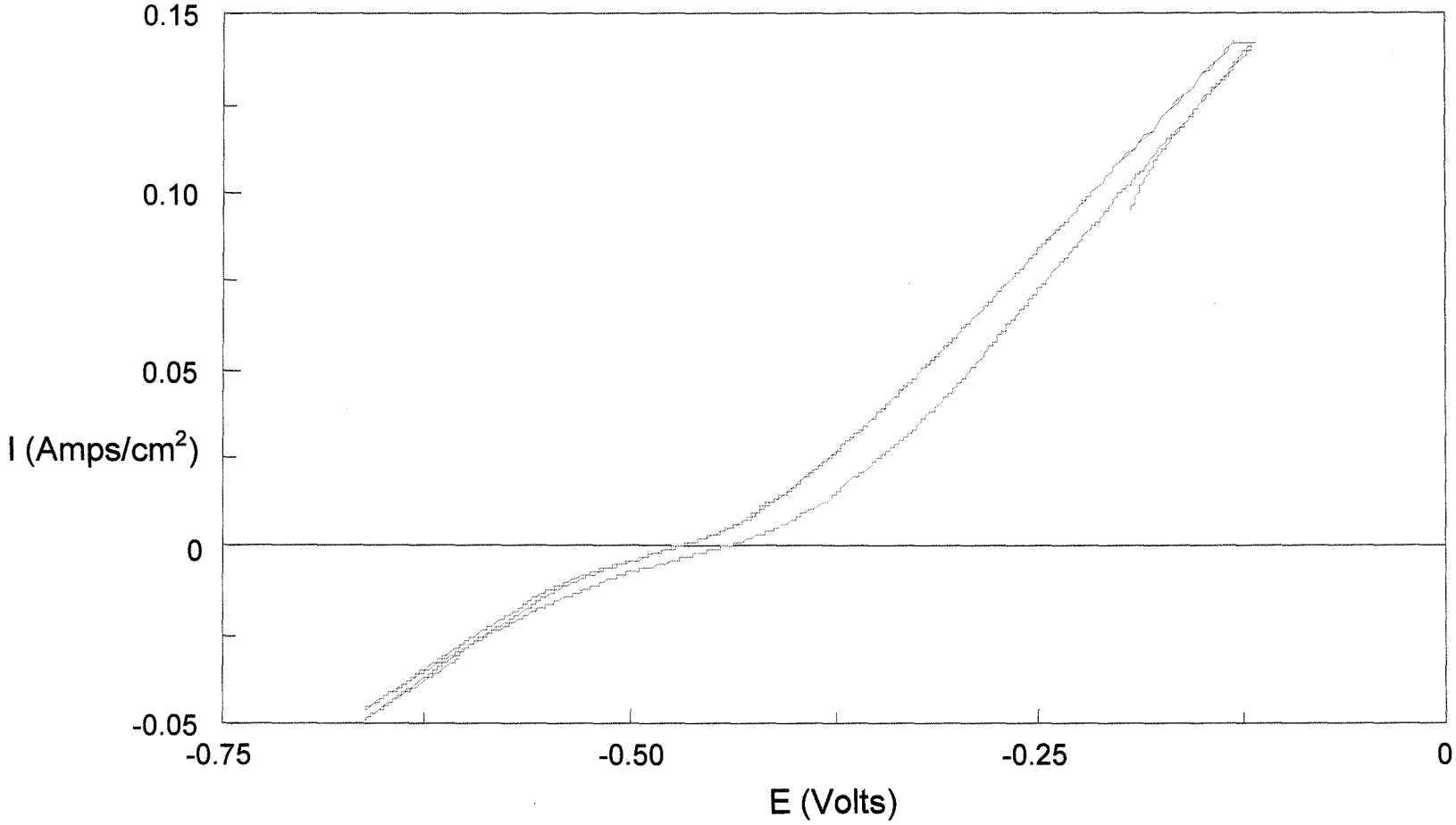
Cyclic voltammetry experiments are frequently used to obtain information on the mechanism of polymer growth as well as the redox behaviour and mode of conduction.

Cyclic voltammetry experiment was performed in a typical single compartment three electrode cell using frequency analyzer solartran 1284Z. This SS / MS was used as a working electrode. Prior to deposition they were mechanically polished with abrasive paper, rinsed with water and acetone and air dried. A platinum electrode placed parallel to the working electrode, was used as counter electrode and all the measurements were

made against saturated calomel electrode (KCl sat) as reference electrode. The monomer aniline was distilled prior to use. Sulphamic acid and PVA were used as received. Purified water (obtained by passing house –distilled water through a purifying system) was used to prepare all the solutions.

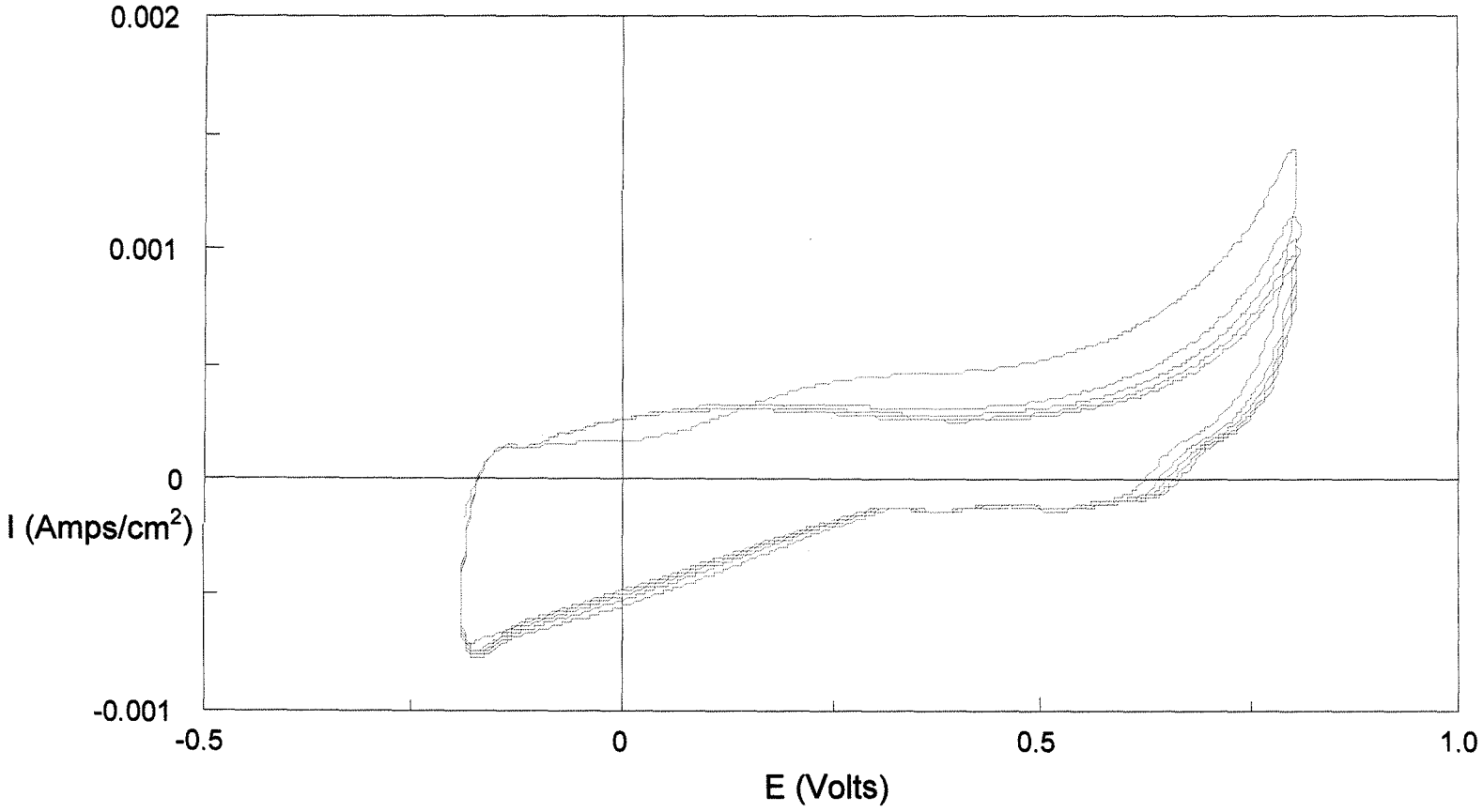
The polymernzation of Aniline/PVA was carried out by sweeping the potential region between -0.1V to -0.7V at dE / dt = $50mvs^{-1}$ for MS and potential range between +0.8V to -0.3V at dE / dt = $50mVs^{-1}$ for SS.The growth of VAANI Copolymer took place on the MS and SS was evident from the increase in peak current values with number of cycles. It was seen that the surface of the electrode was covered with a pale green colour polymer layer.

During successive potential cycles the electrochemical response is changed resulting in a decrease of the reduction peak and an increase of the oxidation peak. This behaviour was observed during the electrochemical synthesis of VAANI Copolymer on Fe. It is well known that VAANI Copolymer layers in acidic media are susceptible to dissolution processes at potentials higher than 1.2V. Application of more positive potentials above 0.9V the transpassive dissolution of stainless steel begins and the adhesion of the VAANI Copolymer layer to the steel surface decreases. Figures (33, 34) deficts the cyclicvoltammogram of MS / SS in sulphamic acid medium.



Cyclic Votammogram of VAANI Copolymer on MS in Sulphamic acid

FIGURE - 33



Cyclic Voltammogram of VAANI Copolymer on SS in Sulphamic acid

FIGURE - 34

It is well known that an autocatalytic process occurs during the electropolymerization of aniline **Mu and Kan (1996)**. This can be concluded from the following main features.

i) The aniline oxidation peak potential shifts towards negative potentials with increasing number of sweeps.

ii) The current associated with the polymeric film creation rises with increasing number of cycles.

iii) The polymeric film oxidation takes part in the polymer growth mechanism because the polymeric film created is oxidized again and another neutral aniline molecule is incorporated in to the polymeric chain.

From the results of **Mu and Kan (1996),** the conclusion can be drawn that the aniline oxidation peak potential shifts towards negative potentials with increasing number of sweeps and the current associated with polymeric layer formation rises with increasing number of cycle.

The copolymerization of aniline and polyvinyl alcohol in sulphamic acid medium was successfully carried out by electro polymerization using cyclic voltammetry.The growth of the copolymer formation was also confirmed from the voltammogram obtained.

Similar voltammogram was presented by **Sazou (2001)**, during the anodic polymerization of toludine monomers in 0.3m oxalic acid.

Performance evaluation of VAANI Copolymer

Performance evaluation of VAANI Copolymer on SS and MS by weightloss method, temperature studies and electrochemical measurements are represented in the figures (35, 36 and 37).

Performance evaluation of VAANI Copolymer by weight loss method for MS and SS at room temperature

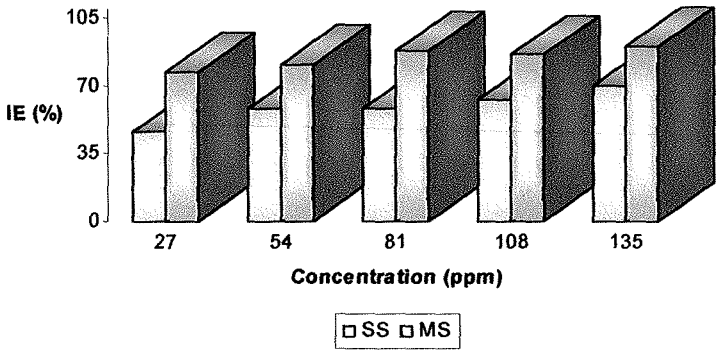


FIGURE - 35

Performance evaluation of VAANI copolymer by weight loss method for MS and SS at various temperatures

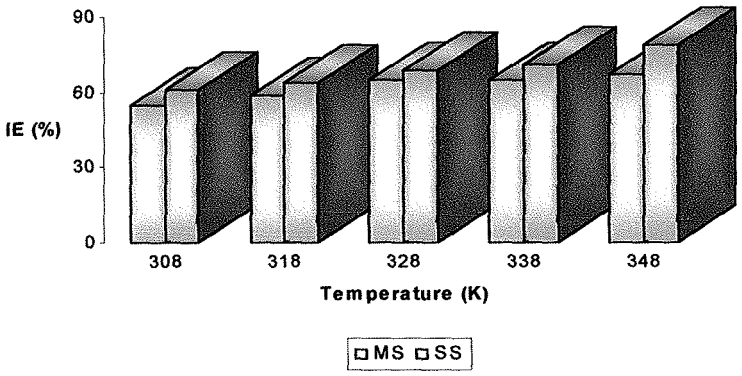


FIGURE – 36

Performance evaluation of VAANI copolymer by linear polarization technique for MS and SS

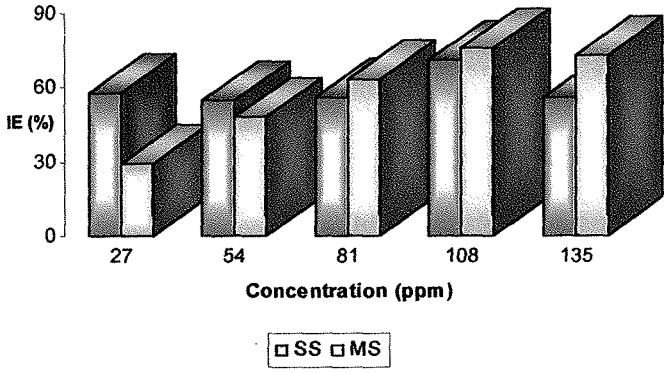
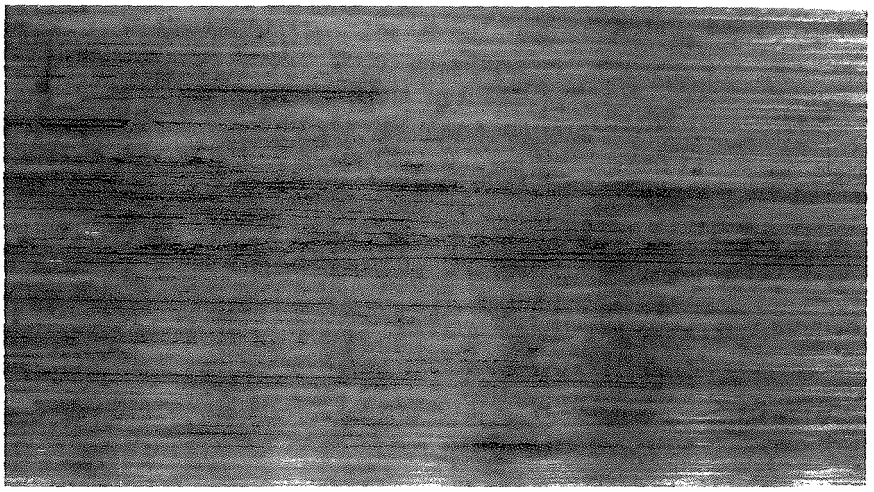


FIGURE – 37

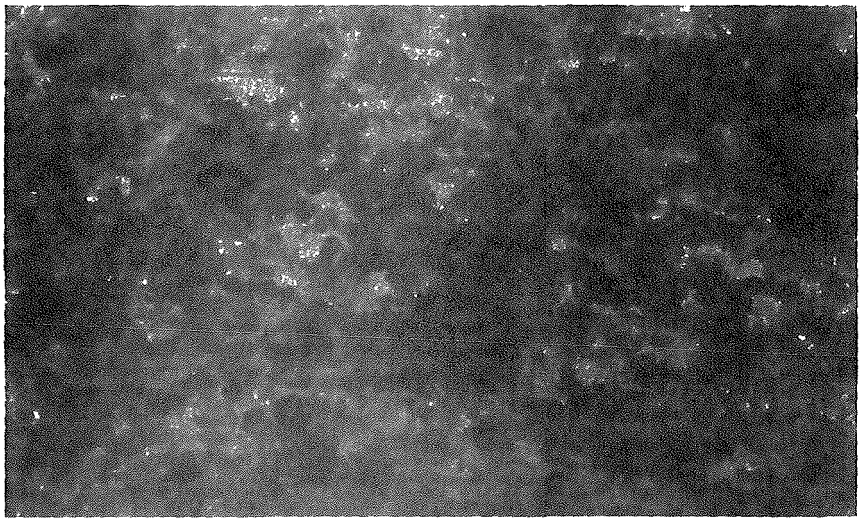
Surface Analysis

Optical Electron Micrograph

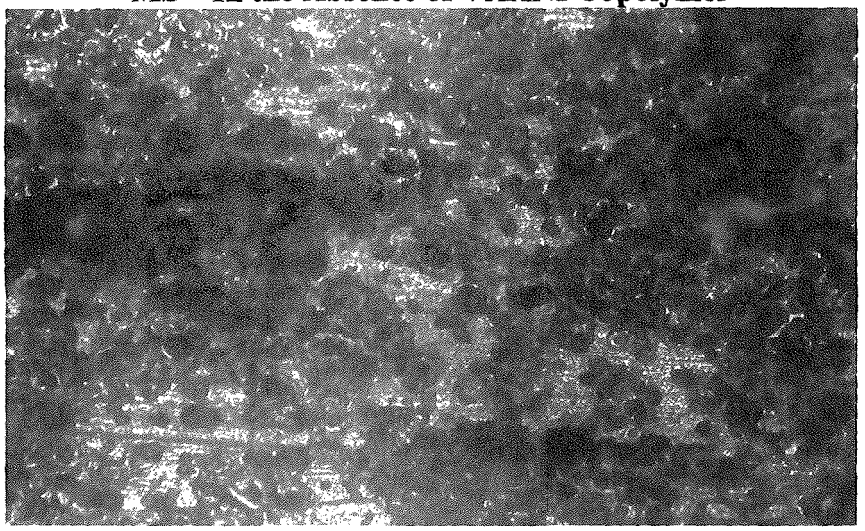
The morphological characteristics of the VAANI Copolymer was examined by using optical electron micrograph. Figures (38, 39) shows optical electron micrograph of the VAANI Copolymer adsorbed on the iron surface / SS surface in hydrochloric acid for 6 hrs. From the figures we understand that a larger amount of polymer molecules adsorbed on the metal surface.



MS – Polished Surface

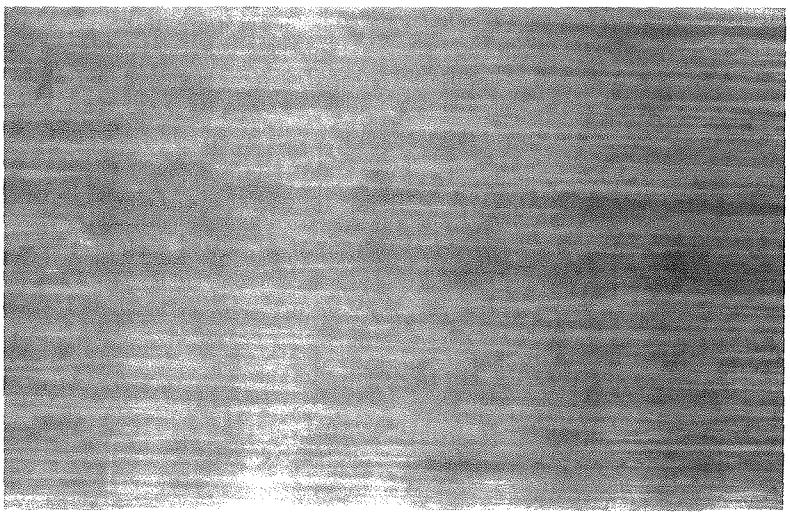


MS – In the Absence of VAANI Copolymer

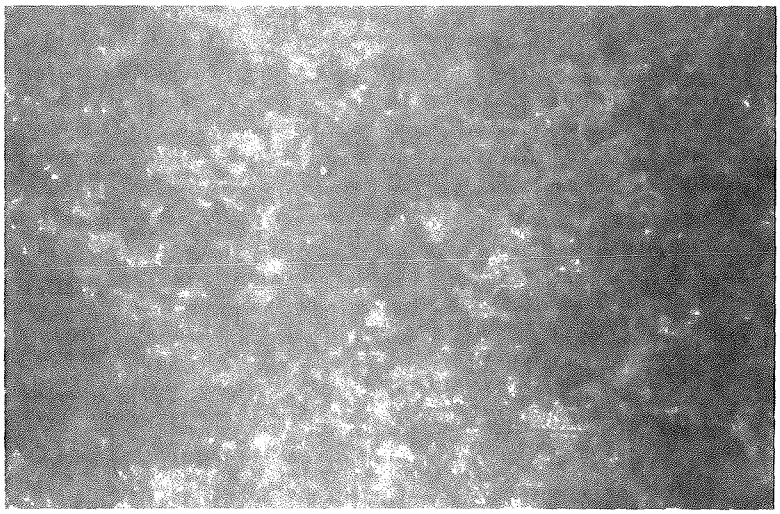


MS – In the Presence of VAANI Copolymer

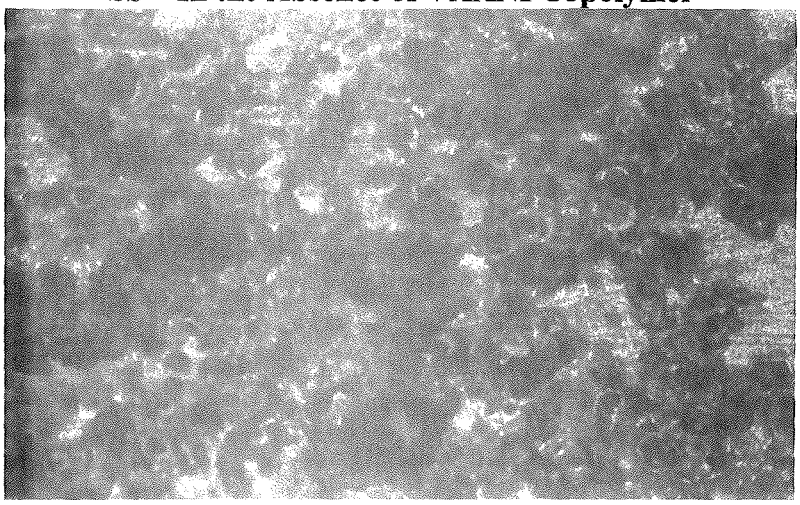
FIGURE – 38
OPTICAL MICROGRAPH OF MS EXPOSED FOR 6 hrs IN 1M HCl



SS – Polished Surface



SS – In the Absence of VAANI Copolymer



SS – In the Presence of VAANI Copolymer

FIGURE – 39
OPTICAL MICROGRAPH OF SS EXPOSED FOR 6 hrs IN 6M HCl

MECHANISM

Literature shows that the extensively used acid inhibitors are organic compounds having unsaturated bonds and other functional groups such as –NH, – N ≡ N–, -CHO, –OH etc. Organic compounds imparts extraordinary property of adsorption on active metal surface by replacing the H_2O molecule at the interface to protect the metal from corrosion. This reaction can be represented as

$$Org_{(sol)} + nH_2O \rightarrow Org_{(sol)} + nH_2O_{(sol)}$$

Hence the IE of an inhibitor depends on the extent of the adsorption of inhibitor and its coverage over the metal surface. In addition, to the functional groups present in the inhibitor, its molecular dimension, orientation and their solvation property also influence the adsorption characteristics thereby influence its IE.

Many researchers have reported polymers as effective corrosion inhibitors having very high IE at low ppm levels. They also indicated how the molecular size and delocalization are responsible for better adsorption over the surface and hence the corrosion inhibitor.

Sathiyanarayanan et al., (1999) studied water soluble, commercially available polymer – Acid black II as corrosion inhibitor on mild steel in acid medium and explained that these polymers are capable of forming quaternary ammonium salt and this large cation gets adsorbed on the metal surface offer a high degree of corrosion inhibitor.

Trivedi (1994) has suggested that in copolymers electron transfer is always faster than in pure polymer, which may be due to the difference in charge density on saturated and unsaturated constituents of the polymer chain as a result of the electron effect of substituents which may facilitate faster electron transfer.

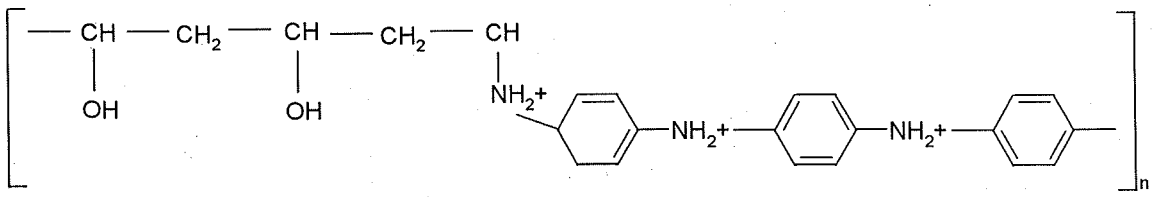
Quaternary ammonium salts finds relevant support in the foot that they have been extensively used as corrosion inhibitors **(Friginani et al., (1991, 1985))**.

In the present invention, VAANI Copolymer is used to study inhibitive action on MS and SS surface in acid medium. We understand that VAANI Copolymer contains free –NH C_6H_5 groups. In acid medium, –NH C_6H_5 nitrogen are capable of forming ammonium salts.

Thus the polymer, under investigation forms a large number of positively charged nitrogen ions. In hydrochloric acid medium, the chloride ions are adsorbed on the metal

surface. This adsorbed chloride ions enhance the adsorption of positively charged ammonium ions **(Iofa et al., 1952)**. This adsorption is influenced by the non polar material, surrounding the positively charged ion which reduces the loss of energy due to mutual repulsion between the ions, allowing a close packed layer to form more easily **(Driver and Meakins, 1980)**.

The scheme of positively charged polymer is given below.



It is envisaged that the quaternary ammonium nitrogen and π e ˉs of the aromatic ring in VAANI Copolymer help in promoting both strong adsorption and uniform surface coverage by the copolymers.

Summary and Conclusion

5. SUMMARY AND CONCLUSION

Protection of oxidizable metals against corrosion is a one method which has been intensively investigated. Many corrosion control methods using coating and conversion films have been proposed, but all involve environmentally hazardous materials. Consequently it is necessary to find non toxic replacement. Conducting polymers can be used as protective primer coatings that can either chemically or electrochemically deposited. Chemical deposition has been performed with PANI and to a lesser extent with Copolymers with the latter method, the main problems of the process are essentially related to the nature of the substrate, since each metal need specific conditions to deposit the conducting polymer.

The synthesis of conducting polymers by electrochemical or chemical oxidation of aniline and exhaustive studies in aqueous acidic solutions and organic media.

The strong affinity of polyaniline for water has motivated many groups to investigate the compatibility of polyanline with water soluble polymers such as polyvinyl alcohol and carboxy methyl cellulose. In this direction the synthesis of VAANI Copolymer is prepared & utilized.

Electro active VAANI Copolymer was deposited on stainless steel and mild steel and their performance as protective coatings against corrosion was evaluated, in the current study.

Conducting polymers can also find applications as corrosion inhibitors. In the current study efforts are made to synthesis a copolymer of Aniline and polyvinyl alcohol in the sulphamic acid medium. The efficiency of copolymer VAANI (vinyl alcohol + Aniline) was studied by weight loss method, polarization technique and electrochemical impedance spectroscopy (EIS) techniques. (To obtain information of mechanism of polymer group as well as redox behavior cyclic voltammetry experiments were carried out. All these methods confirmed the effectivencss of the inhibitor indicating the possibility of monitoring its effectiveness by electrochemical techniques. Double layer capacitance studies indicated strong adsorption of polymer. Experimental data are fitted with various adsorption isotherms, kinetic and thermodynamic parameters were also

evaluated from weightloss measurements. The morphological characteristics of the polymer was examined by using optical electron micrograph.

Salient features of the present study:

- VAANI Copolymer proved as promising inhibitor to protect iron and steel from acid corrosion.
- Maximum efficiency of VAANI Copolymer on MS and SS was found to be 90% and 78% at 6hrs and 24hrs of immersion.
- Generally the effectiveness of VAANI Copolymer on MS and SS increases with increase in temperature indicating the stability of the conducting polymer on metal surface.
- Statistical analysis of experimental data confirmed that the adsorption of VAANI Copolymer on MS and SS obey Langmuir and Temkin isotherms.
- Thermodynamic parameters are relative which indicate a strong adsorption of VAANI Copolymer on the surface of the electrodes.
- The E_a values infer that VAANI Copolymer decrease the activation energy of the reaction. This may be a results of strong adsorption of inhibitor on surface of the electrodes.
- Potentiodynamic electropolymerization of VAANI Copolymer in sulphamic acid solution leads to the formation of protective layer on Fe. The presence of aniline monomers in sulphamic acid solutions slow down the Fe dissolution rate. The oxidation of the monomer is allowed to occur on passive iron surfaces. Iron oxide provides a polymerization substrate that is similar to other substrates such as Au, Pt or glassy carbon.
- Electrochemical measurements indicate decrease in I_{corr} values and increase in R_p values which confirm that the inhibition process, is accelerated in the presence of VAANI Copolymer.
- The values of Tafel slopes b_a and b_c obtained from Tafel intercept method would confirm the inhibition of corrosion of MS and SS in under mixed controls.
- No noticeable shift in E_{corr} infer that VAANI Copolymer acts as mixed mode of inhibition.

- Increase in R_{ct} values on MS surface confirms the corrosion of MS was controlled by charge transfer process.
- The adsorption phenomena of VAANI Copolymer on metal surface is noticed by decrease in C_{dl} values.
- High resistance values and low capacitance values indicate the highly protective nature of VAANI Copolymer.
- The inhibition effect of VAANI Copolymer was quite comparable with conventional weight loss methods and electrochemical techniques.
- Electrochemical polymerization by using cyclic voltammetry occurs readily giving rise to a well defined oxidation – reduction response of the polymer.
- Examination of the surface of the metals in the presence of VAANI Copolymer confirmed the deposition of polymer on the metal surfaces.
- The effectiveness of VAANI Copolymer on SS surface in 6M HCl was more pronounced in comparative to MS in 1M HCl.

SUGGESTIONS

Corrosion of metals involves the transfer of electrical charge in aqueous solutions at the metal electrolyte interface. Corrosion protection is often afforded by isolating metals from the corrosive environment using polymers. These polymer layers need to have good barrier properties and to remain adherent in the presence of corrosive product such as strong acid media.

- Polymer coatings may be worked out by electropolymerization t iques.
- Different water soluble PANI may be synthesized and its effectiveness may also be evaluated.
- Universal micro hardness measurements may be used to determine mechanical characteristics of the polymer coatings.
- Cyclic voltammetry and "in situ" FTIR spectroscopy may be combined to redox behaviour of the oxidation products.

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