# Synthesis and Characterization of VAANI Copolymer for Corrosion Inhibition of Mild Steel and Stainless Steel in Acid Medium

BY

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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 and Characterization of VAANI Copolymer 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 **R. Femina Mary** 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.

**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 and Characterization of VAANI Copolymer 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. R. Rajalakshmi,** 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.

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Place : coimbatore

Date : 30.11.2005

**Signature of the Guide**

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**R. FEMINA MARY**

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# LIST OF ABBREVIATIONS

$\theta$ - Surface Coverage

$b_a$ - Anodic Tafel slope

$b_c$ - Cathodic Tafel Slope

CR - Corrosion Rate

$C_{dl}$ - Double layer capacitance

Conc. - Concentration

$E_{corr}$ - Corrosion Potential

HCl - Hydrochloric acid

IE - Inhibitor Efficiency

$I_{corr}$ - Corrosion Current

mpy - Mills per year

MS - Mild Steel

PANI - Polyaniline

PVA - Poly Vinyl Alcohol

ppm - Parts per million

$R_{ct}$ - Charge transfer resistance

SS - Stainless Steel

VAANI Copolymer - Vinyl Alcohol Aniline Copolymer

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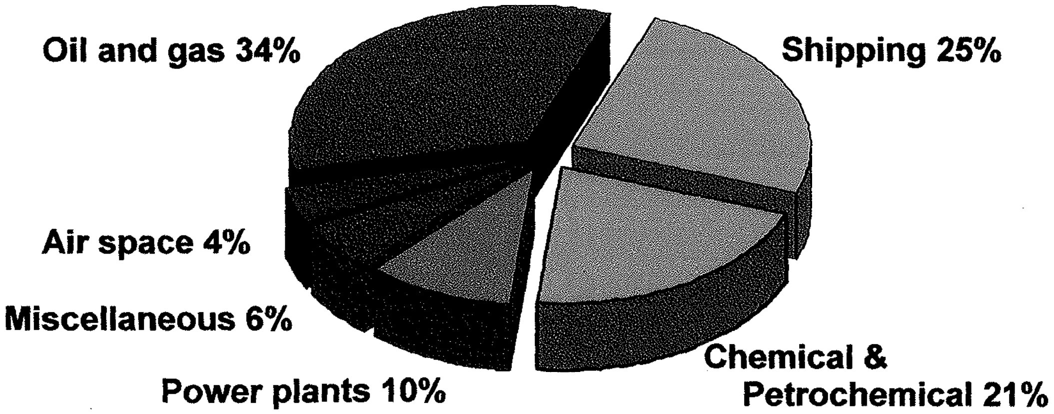
# 1. INTRODUCTION

Corrosion studies have become important due to awareness of the world's metal resources. All civilized activity aims at improvising the quality of life. This inevitably leads to demands for more energy production and for other artifacts upon which our modern civilization depends. This demand for durability can be achieved by carrying out research into corrosion science to gain a better understanding of the process involved, research into collection and the proper application of corrosion control measures.

A great majority of people equate corrosion with 'rust', mostly an object of aversion. Corrosion is defined as the gradual eating away or deterioration of a metal by chemical or electrochemical reactions with its environment. The environment can be water, air, carbon dioxide, organic liquids, molten salts, gaseous sulfur etc.

Corrosion poses perennial problems to big industries like petrochemicals, fertilizer, nuclear establishments as well as small industries like dye stuffs, pharmaceuticals food processing etc. Necessary steps to prevent corrosion are imperative from the point of view of economy and conservation of metals for a better and longer utilization.



**Sawant, K.D. (2002)**

**FIGURE – 1**

**Corrosion in different types of industries**

The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood but generally refers to metals. The most widely used metals are iron and steel. The corrosion of iron and steel are of fundamental, academic and industrial concern that has received a considerable amount of attention. Hence the present work is aimed to investigate corrosion studies on mild steel and stainless steel.

Any process of deterioration or destruction and consequent loss of a solid metallic material through an unwanted or unintentional chemical or electrochemical attack by its environment, starting at its surface is called "corrosion". Corrosion is a process which is the exact reverse of extraction of metals **(Jain and Jain, 1988)**

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## FORMS OF CORROSION

There are several **forms** of corrosion, also referred to as **modes or mechanisms** of corrosion. **Sub-forms** can also be identified for several forms of corrosion. The different forms and sub-forms of corrosion are analogous to different failure mechanisms in the mechanical world (fast fracture, fatigue, ductile tearing, brittle cleavage, wear etc...). A popular classification of forms of corrosion has been made by **Fontana,** on the basis of the visual appearance of corrosion damage. More information on monitoring different forms of corrosion is available from the list below:

- Uniform (or general) corrosion
- Pitting
- Crevice Corrosion
- Intergranular Corrosion
- Stress Corrosion Cracking (SCC)
- Erosion Corrosion
- Selective Leaching
- Hydrogen Embrittlement
- Galvanic Corrosion

## ELECTROCHEMICAL PRINCIPLE OF CORROSION

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly buildup in the metal and prevent further anodic reaction, or corrosion. ~~Thus~~ This dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of anodic and cathodic reactions must be equivalent according to Faraday's laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", $I_{corr}$. Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on the metal surface.

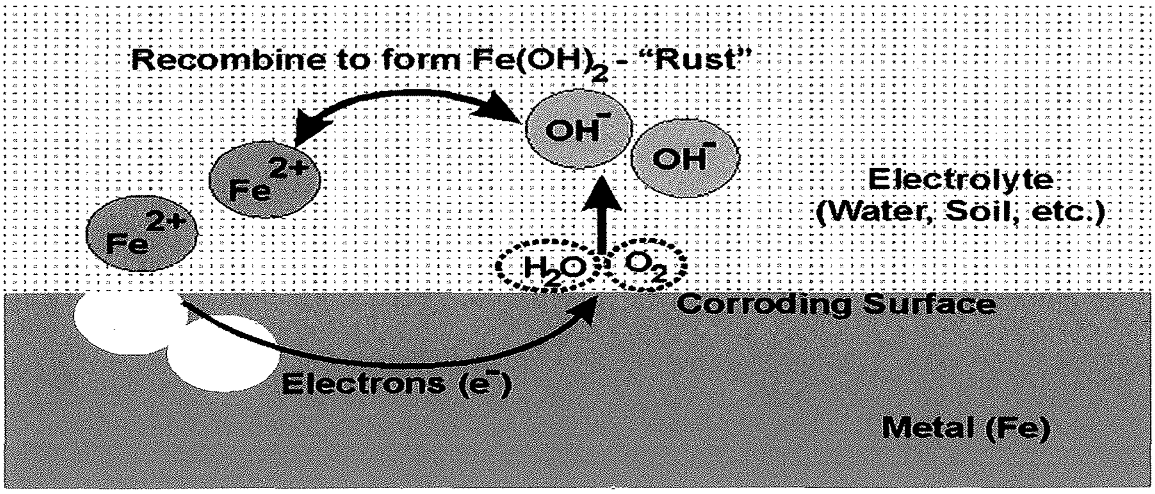


**FIGURE - 2**

**Schematic representation of electrochemical corrosion process**

**(Aqueous corrosion of iron)**

The most common and important electrochemical reactions in the corrosion of iron are thus

Anodic reaction (corrosion)

$Fe \rightarrow Fe^{2+} + 2e^-$ (1)

Cathodic reactions (simplified)

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

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

Reaction 2a is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction (2b). In this latter case corrosion is usually accompanied by the formation of solid corrosion describes from the reaction between the anodic and cathodic products.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$, iron (II) hydroxide

Pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish colour due to partial oxidation in air,

$2Fe(OH)_2 + H_2O + \frac{1}{2} O_2 \rightarrow 2Fe(OH)_3$, hydrated iron (III) oxide.

Further hydration and oxidation reactions can occur and the reddish rust that eventually is a complex mixture whose exact constitution will depend on other trace elements which are present. Because the rust is precipitated as a result of secondary reactions it is porous and absorbent and tends to act as a sort of harmful poultice which encourages further corrosion. For other metals or different environments different types of anodic and cathodic reactions may occur. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation. These may provide a highly protective surface film which regards further corrosion, the surface is then said to be "passive". An example of such a process would be the production of an oxide film on iron in water, a reaction which is encouraged by oxidizing conditions or elevated temperatures.

$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^-$

## THERMODYNAMIC CORROSION CYCLE

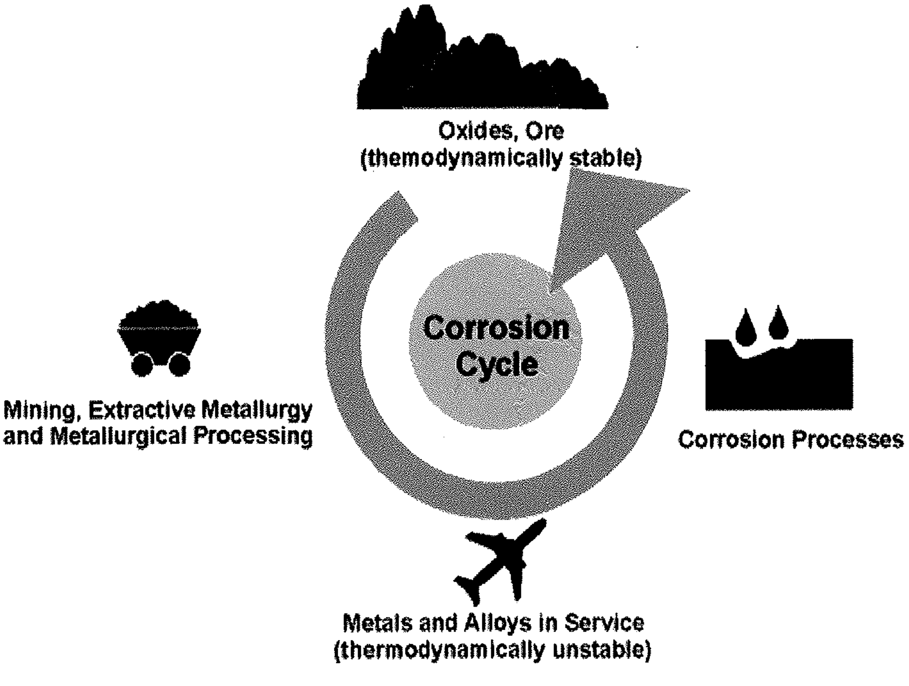


FIGURE – 3

A further corrosion cycle, often used as introduction to corrosion theory, is a thermodynamic one. Almost all metals and alloys used in service are actually in an unstable thermodynamic state. There is thus a fundamental thermodynamic tendency for them to return to a stable state through corrosion processes. In essence, corrosion revert the metals/alloys back to the stable state of the ores from which they were derived. Corrosion products tend to be thermodynamically stable species, similar to the original ores.

Thermodynamics is concerned with energy states. The original metallic ores are said to be in a state of low energy. External energy is applied in the conversion of the ores to usable metals and alloys, transforming them to a higher energy state. They tend to revert to a lower (more stable) energy state by reacting with a corrosive environment. While thermodynamics can predict whether a corrosion reaction will take place, it does not provide an indication of the rate of corrosion reactions. The rate of reactions is described by kinetic theory **(Fontana, 1987)**.

## THE CONSEQUENCES OF CORROSION

Corrosion is the destructive attack of a material by reaction with its environment. The serious consequences of the corrosion process have become a problem of worldwide significance. The colossal losses due to corrosion are huge.

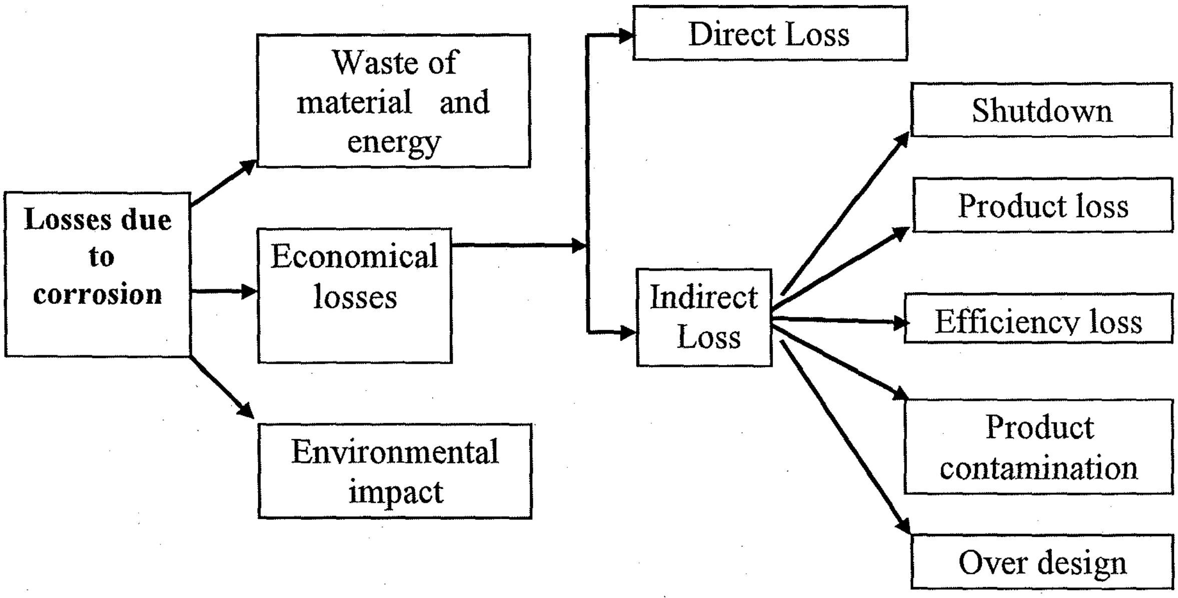


**FIGURE – 4**

**Unfortunately, damage caused by corrosion is not just a financial burden to society—it has an impact on safety**

For some examples are,

- **Swimming Pool Roof Collapse**

The unexpected collapse May 9, 1985, of a ceiling above a swimming pool in Uster, Switzerland, showed how a simple structural concept could be sensitive to the loss, through corrosion, of support from one of many hangers. Twelve people died.

The collapse was the result of chloride-induced stress corrosion cracking. The steel rods had been pitted, causing the roof to cave in. The roof collapsed in a zipper like fashion, starting with the corroded rods. Chloride can overcome the passivity of the natural oxide film on steel's surface and is a major factor in the corrosion of reinforced concrete.

- **Sinking of the Erika**

A large oil spill off France's Brittany coast occurred Dec. 12, 1999, when the tanker Erika broke up in gale force winds and rough seas. When the Erika broke up, it was carrying an estimated 30,000 tons of heavy fuel oil, 10,000 tons of which were spilled. This was equal to the total amount of oil spilled worldwide in 1998.

Corrosion problems had been apparent on the Erika since at least 1994. Severe corrosion had been discovered just weeks before the incident; however, no immediate remedial action had been taken.

- **Sewer Explosion due to Corrosion**

A sewer explosion killed 215 people in Guadalajara, Mexico, in April 1992. Besides the fatalities, the series of blasts damaged 1,600 buildings and injured 1,500 people. Damage costs were estimated at $75 million.

The sewer explosion was traced to the installation of a water pipe that leaked water on a gasoline line lying underneath. The subsequent corrosion of the gasoline pipeline, in turn, caused leakage of gasoline into the sewers (Excerpts reprinted from **www.corrosion-doctors.com**).

## COST OF CORROSION IN INDIA AT R~~S~~s. 36,000 CRORE

"The cost of corrosion is estimated to be around $364 billion as of 2004. This 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.

"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."

**Mr. Bahri** (India section trustee in NACE) stressed the need to create awareness on the cost of corrosion in India. ***"It may be necessary for the universities to include corrosion science as a subject compulsory in the curriculum not only for the engineering colleges but also for general education,"*** he added.

Corrosion is a natural impact of atmospheric environments like marine, industrial, urban and rural and affects the structural stability of buildings. The annual loss due to corrosion can be compared with that of other natural calamities like earthquakes and cyclones; only its impact is indirect. Loss due to corrosion has been reported to account for more failures in terms of cost and tonnage than any other environment," said **Dr. Palaniswamy** (Deputy director, State corrosion protection committee, CECRI). The overall loss due to corrosion alone amounts to at least 2 to 4 percent of GNP and at least 25 percent of this could be avoided by using appropriate corrosion-control technology.

Dr. Palaniswamy, adding that it contains a warning for other industrialized zones too. So how does one offset losses due to corrosion? **More corrosion-resistant alloys need to be developed and vehicles need more anti-corrosion coatings.**

## 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 spectroscopy (EIS)
- Potentiodynamic polarization

### Corrosion Coupons for Corrosion Monitoring

The simplest, and longest-established, method of estimating corrosion losses in plant and equipment is **weight loss analysis**. A weighed sample (coupon) of the metal or alloy under consideration is introduced into the process, and later removed after a reasonable time interval. The coupon is then cleaned of all corrosion products and is reweighed. The weight loss is converted to a total thickness loss, or average corrosion rate using equations. Weight loss determination has a number of attractive features that account for its sustained popularity. It is:

- Simple : No sophisticated instrumentation is required to obtain a result.
- Direct : A direct measurement is obtained, with no theoretical assumptions or approximations.
- Versatile : It is applicable to all corrosive environments, and gives information on all forms of corrosion.

The method is not suited for **instantaneous** corrosion monitoring.

### Electrochemical Impedance Spectroscopy (EIS)

EIS has been successfully applied to the study of corrosion systems for thirty years and been proven to be a powerful and accurate method for measuring corrosion rates. An important advantage of EIS over other laboratory techniques is the possibility of using very small amplitude signals without significantly disturbing the properties being measured. To make an EIS measurement, a small amplitude signal, usually a voltage between 5 to 50 mV, is applied to a specimen over a range of frequencies of 0.001 Hz to 100,000 Hz.

### Linear Polarization Resistance (LPR)

Polarization resistance is particularly useful as a method to rapidly identify corrosion upsets and initiate remedial action, thereby prolonging plant life and minimizing unscheduled downtime. The technique is utilized to maximum effect, when installed as a continuous monitoring system. This technique has been used successfully for over thirty years, in almost all types of water-based, corrosive environments.

### Potentiodynamic Polarization Methods

Polarization methods such as potentiodynamic polarization, potentiostaircase, and cyclic voltammeters are often used for laboratory corrosion testing. These techniques can provide significant useful information regarding the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential.

- Anodic polarization: the potential is changed in the anodic (or more positive direction) causing the working electrode to become the anode and causing electrons to be withdrawn from it.
- Cathodic polarization: the working electrode becomes more negative and electrons are added to the surface, in some cases causing electro deposition.
- Cyclic polarization: both anodic and cathodic polarization is performed in a cyclic manner.

**(www.prginc.com)**

## CORROSION CONTROL METHODS

Corrosion of metals in different environments is one of the serious problems facing industry and its control has been approached in from various angles. Since the types of corrosion are so numerous and the conditions under which corrosion occurs are so different that diverse methods are used to control corrosion.

- ☞ Design improvement
- ☞ Change of metal
    - Change of composition
    - Change of microstructure
    - Elimination of tensile stress
    - Introduction of surface compressive stresses
- ☞ Change of metal electrode potential
    - Cathodic production
    - Anodic production
- ☞ Use of coatings
    - Metallic coatings
    - Non-metallic coatings
- ☞ Change of environment
    - Removal of corrosive constituent
    - Change of operating variables
    - Use of inhibitors

**One of the very important methods of minimizing corrosion today is the use of corrosion inhibitors**. Corrosion inhibitors are extensively used in various applications and many plant operations are dependent on their successful application.

## INHIBITORS

A corrosion inhibitor is a chemical additive. Which, when added to corrosive aqueous environment, reduces the rate of metal wastage.

Inhibitors show corrosion processes by either:

- Increasing the anodic or cathodic polarization behavior;
- Reducing the movement or diffusion of ions to the metallic surface;
- Increasing the electrical resistance of the metallic surface.

The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these, only very few are actually used in practice. This is partly due to the fact that the desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability and environmental friendliness are of considerable importance.

Inhibitors have been classified differently by various authors. Some authors, for example, prefer to group inhibitors by their chemical functionality. However, by far the most popular organization scheme consists in regrouping corrosion inhibitors in a functionality scheme as follows:

- Passivating inhibitors
- Cathodic inhibitors
- Precipitation inhibitors
- Volatile corrosion Inhibitors
- Organic inhibitors

**Passivating Inhibitors**

Passivating inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. There are two types of passivating inhibitors:

- Oxidizing anions, such as chromate, nitrite and nitrate, that can passivate steel in the absence of oxygen
- Non oxidizing ions such as phosphate, tungstate and molybdate that require the presence of oxygen to passivate steel.

These inhibitors are the most effective and consequently the most widely used.

**Cathodic Inhibitors**

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by three different mechanisms as:

- Cathodic poisons
- Cathodic precipitates
- Oxygen scavenger

### Precipitation Inhibitors

Precipitation inducing inhibitors are film forming compounds that have a general action over the metal surface, blocking both anodic and cathodic sites indirectly. Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. The most common inhibitors of this category are the silicates and the phosphates.

### Volatile Corrosion Inhibitors

Volatile Corrosion Inhibitors (VCI), also called Vapor Phase Inhibitors (VPI), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine are used.

On contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions.

### Organic Inhibitors

Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors but, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors usually designated as 'film-forming', protect the metal by forming a hydrophobic film on the metal surface. The effectiveness of these inhibitors depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors.

Recently, organic polymers with considerable inhibition potency in stringent conditions have been used as acid pickling inhibitors.

**The most important prerequisites for compounds / chemical substances to be efficient inhibitors are:**

- Substances should be polymeric or should polymerize in situ on the substrate metal.
- The inhibitors should be film-forming in nature and should form a defect-free, compact barrier film.
- They should chemisorb on the metal surface.
- Promote monolayer / multilayer formation.

Check Grammar

- Have a high adsorption energy on the surface and
- The barrier layer thus formed should increase the inner layer thickness. In order for the formation of strong and efficient covalent bonds between the surface metal atoms and the adsorbate, the energy levels of the donor orbital and the acceptor empty orbital, as well as their symmetry, should match.

## 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.

**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.

The inhibitive action of these organic compounds has been explained in terms of number of mobile electron pairs, $\pi$ - 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

$$\mathrm{Org}_{(sol)} + nH_2O_{(sol)} \leftrightarrows \mathrm{Org}_{(ads)} + nH_2$$

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

The inhibitive action of 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. With this objective in view the present investigation was undertaken to examine the effect of polymer as corrosion inhibitor on the corrosion of MS and SS in HCl.

## POLYMERS

Polymers (or plastics as they are also called) 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 as Corrosion Inhibitor

Most common corrosion control methods use ~~of~~ coatings and conversion layers which contain toxic and environmentally hazardous materials-specifically hexavalent chromium compounds. There is a need to find non toxic and environmental friendly alternative, compatible with current industrial techniques. Conducting polymers introduce such an alternative.

Thin films of conducting polymers acting as coatings may block the metal surface reactions by the transfer of metal reactions on the coating surface. It is therefore, anticipated that conducting polymers will provide active protection rather than serve merely as barrier films.

### Electro Deposition of Conducting Polymers – An Active Area of Research

The electro deposition 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 electro polymerization of inert anodes such as Pt, Au or various forms of carbon.

Electro polymerization on oxidisable metals with high corrosion rates is not an easy task. This is due primarily to the fact that the metal substrate is dissolved in most of the solutions from which polymerization can be carried out.

If deposition of conducting polymers on the metal surface could be possible, then the electrochemical reactions leading to the metal 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** etal**, 1985)**.

**Potential Applications of Conducting Polymers**

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

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

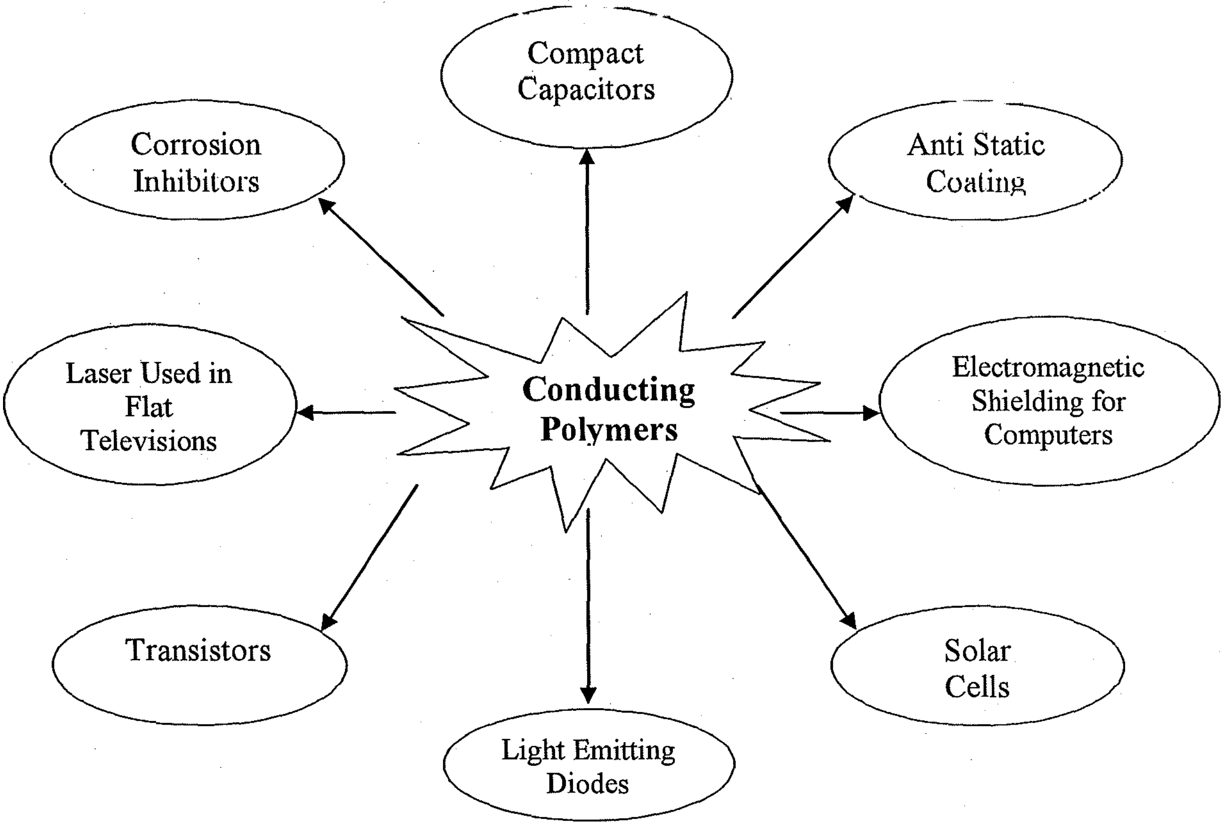


**FIGURE – 5**

## WATER SOLUBLE POLY ANILINE

PANI is probably the most important conducting polymer today. Due to its

- Ease of synthesis and processing
- Environmental stability
- Low synthetic cost

The most advantageous property of poly aniline 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 PANI. Considerable progress was made in preparation of poly aniline in the form aqueous colloidal dispersions.

PANI is not charge conjugation symmetric, i.e. the valence and conduction bands are asymmetric to a great extent (**Ghos *et al* 2001**). A partial oxidation of PANI usually leads to the reorganization of bonds, resulting in an increase in electronic conductivity. The physicochemical properties of PANI are strongly related to the proportion of aryl amine, quinone and imine units present (**Genies *et al* 1988**). PANI possesses two Volta metric redox pairs including three stable oxidation states, with the half-oxidized state (emaraldine) being highly conductive in its protonated state. Existence of different oxidation states of PANI makes it useful as an electrode material in electrochemical capacitors (**Roberg *et al* 1998; Fusalba *et al* 2001; Hu and Chu 2000, 2001**).

### PANI as Anticorrosive Coatings

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

It is believed that in acidic solutions PANI is acting as a redox mediator, passivating metal subtracts at the metal polymer interface and re-oxidizing it self by dissolved oxygen at the polymer solution interface.

Concerns over the environmental hazards caused by applications of Cr (VI) in protective coatings was a stimulating idea to verify the possibility of an application pf PANI as a Cr (VI) replacement I so-called post rinse in phosphating process.

Electrochemical synthesis of conducting PANI is an efficient technique to obtain protective PANI coatings on metals and alloys. However, to form a film of conducting PANI on reactive metals such as iron and steel is difficult because of its preferred dissolution at a potential lower than the oxidation potential of monomer. Key to the deposition is to design electrochemical conditions which lead to partial passivity of the metal and decrease its dissolution rate with out precluding electro polymerization.

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

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. With this objective in view the present investigation was undertaken to synthesis copolymer as corrosion inhibitor.

### Scientific Applications of Conducting PANI

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

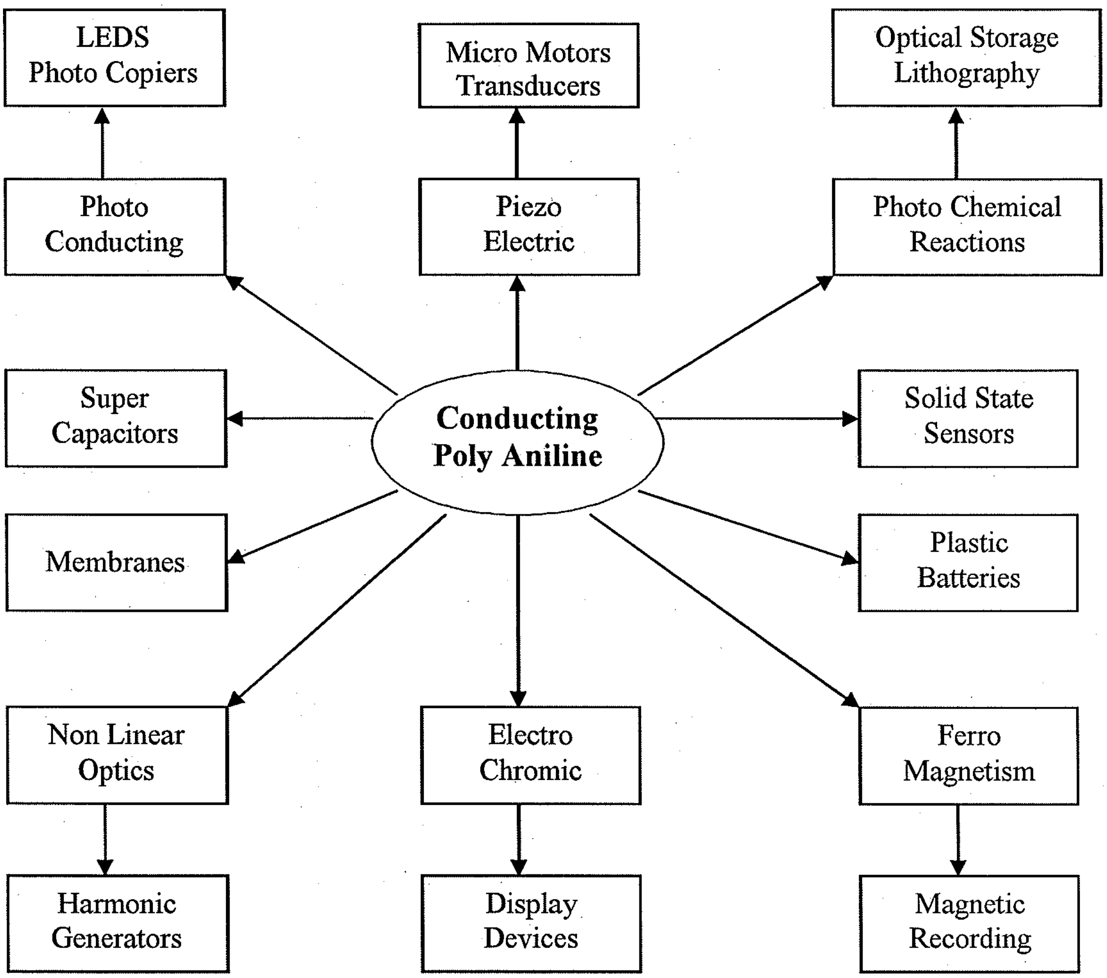


**FIGURE – 6**

## OBJECTIVES

**The main objective of this work ~~was~~ is 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 and Characterization of VAANI Copolymer 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),

$$\mathrm{Org}_{sol} + nH_2O_{ads} \rightarrow \mathrm{Org}_{ads} + nH_2O_{sol}$$

## 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 $10^5 A^0$ as compared to simple molecules having dimensions of 10$A^0$. 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 $- C \equiv C$ 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 metals '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 that 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 tetraoxo – 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 $C \equiv CH$ 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,** et al **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.
- **Sudeshan Chaudari et al., (1999)**, studied electrochemically polymerized ortho anisidine on copper from aqueous sodium salicylate solution to generate a uniform and strongly adherent poly (O-anisidine) (POA) coating. This coatings were used to mitigate copper corrosion. Cyclic voltammetry, UV-visible absorption spectroscopy, Fourier transform infrared spectroscopy and Scanning electron

microscopy (SEM) were used to characterize these coatings. 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.

## 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=1x$10^4$, 2.45x$10^4$ and 4x$10^4$), poly-2-vinylpyridine (M=2.85 x $10^5$) 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°C 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

- 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 electro polymerized in acidic aqueous solutions (HCl, $H_2SO_4$) on noble metal electrodes (Pt, Au).The growth of the 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 electro deposition of protective PANI 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 a 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 PANI 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 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 electro polymerization 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 PANI 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 PANI / 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 electro synthesized 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 electro synthesize a PANI 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.
- 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 PANI.
- 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 PANI in various paints at low concentrations cause tremendous effects in corrosion protection. It was studied by scanning voltapotential and EIS measurements.
- **Marcin A. Malik (1999),** investigated the ability of a PANI 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 PANI film can be coupled to the self-passivation of steel.

- **Camalet et al., (2000),** stated that aniline has been electro polymerized on platinum from neutral aqueous electrolytes. The properties of the resulting PANI 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 PANI coated iron samples in various environments. Protective properties of the conductive polymer were compared with a conventional polymer such as polyvinyl chloride (PVC). Comparative experiments revealed that emeraldine base form of PANI 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 PANI which is crystalline in nature compound to parent polymer PANI which was amorphous as revealed by XRD analysis. The water soluble PANI can be used as a corrosion inhibitor for iron in HCl medium **(Sarswat Koul et al., 2001).**
- PANI was able to protect mild steel against corrosion owing to the stabilization of the iron oxide passive layer **(Bernard et al., 2001).** The electro polymerization 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 PANI and polypyrrole. Polypyrrole composite coatings on aluminium alloy (AI– 2024). The coatings were electrodeposited using galvanostatic and cyclic voltametry 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 PANI – 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 PANI coated steel in a high pH solution **(Nicholar M. Martyak et al., 2002)**. 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 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 PANI emeraldine salt affected the corrosion rate of coated steel. The 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 up to 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 electro synthesized 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 electro synthesized on stainless steel from aniline containing phosphate buffer solutions. The electro polymerizations 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)**.
- 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 PANI, 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 PANI composite by potentiodynanmic curves.
- Stable and adherent polymer films of PANI and of poly (2-anisidine) were gown on 304-stainless steel by cyclic voltammetry in tetra butylammonium perchlorate / acetonitrile solution containing perchloric acid. The anti-corrosion behaviour of PANI 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 PANI **(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 PANI in polyvinyl alcohol and this copolymer (VAANI) is water soluble in acid medium and hence this current studies and conducted using PANI and PVA as corrosion inhibitor.

# Materials and Methods

# 3. MATERIALS AND METHODS

In the present work, efforts have been taken to study the inhibition efficiency of VAANI Co-polymer on the corrosion of MS and SS in HCl medium.

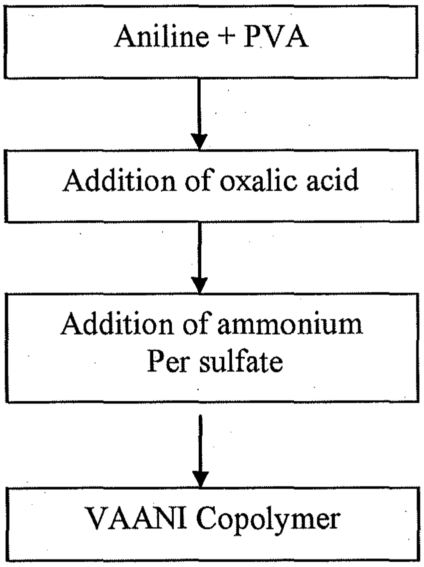
Design of the present investigation of the following steps

- Synthesis of VAANI Copolymer
- Selection of the sample
- Preparation of the specimen
- Test media
- Techniques used

The above headings are discussed in the following pages.

## SYNTHESIS OF VAANI COPOLYMER

Distilled Aniline (1ml) mixed with 20ml of 5% Poly Vinyl Alcohol (PVA dissolved in water) and 20ml of oxalic acid. The solution mixer was stirred well. The initiator Ammonium per sulfate (2ml) was added drop by drop. The temperature of the reaction bath was maintained at $10 \pm 0.2^0C$ by circulating chilled water. At the end of the reaction, the reaction mixture was filtered. The polymer thus obtained was green solution. The polymer was characterized by recording FTIR and cyclic voltammeter.



## SELECTION OF THE SAMPLE

The investigations were carried out using Mild Steel and Stainless Steel. Due to low cost and easy availability, MS / SS is a material of choice to fabricate various reaction vessels, pipes, tanks, etc., in sugar, petrochemical, brewery, food, paper, textile and marine industries.

In recent years, the convenience of substitution of carbon steel by SS as rein forcing material for concrete has been proposed in various international instances. SS and MS suffer from severe corrosion in aggressive environment, which needs to be protected. Hence the study of corrosion inhibition of MS and SS in aqueous aggressive media is the subject of pronounced technological significance.

## PREPARATION OF THE SPECIMENS

Cold rolled MS and SS coupons were cut into pieces of 1cm * 5cm area. The specimens 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 | 69.77 |

## 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 and 6M HCl.

## SELECTION OF INHIBITOR

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 also 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 MS and SS.

PANI, poly pyrrole, poly thiophene and polyfuran are organic polymers that exhibit conductivity in the semi conductor regime. Conductive polymers are often used as corrosion resistant coatings. The most widely studied polymer is PANI because of its air and thermal stability and ease of processing and increased corrosion protection to coated steel. Although the mechanism of enhanced corrosion protection of steel by PANI is still unresolved, studies have pointed to a shift in the passivation potential of steel due to PANI.

In this connection, the present study is undertaken to find out the efficacy of PANI homogenously dispersed in 5% PVA solution on the corrosion inhibition of mild steel and stainless steel in 1M HCl and 6M HCl medium respectively.

## POLYMERIZATION MEDIUM

The important aspect of PANI synthesis is the acid dissociation constant ($pK_a$) of the acid, because in PANI 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

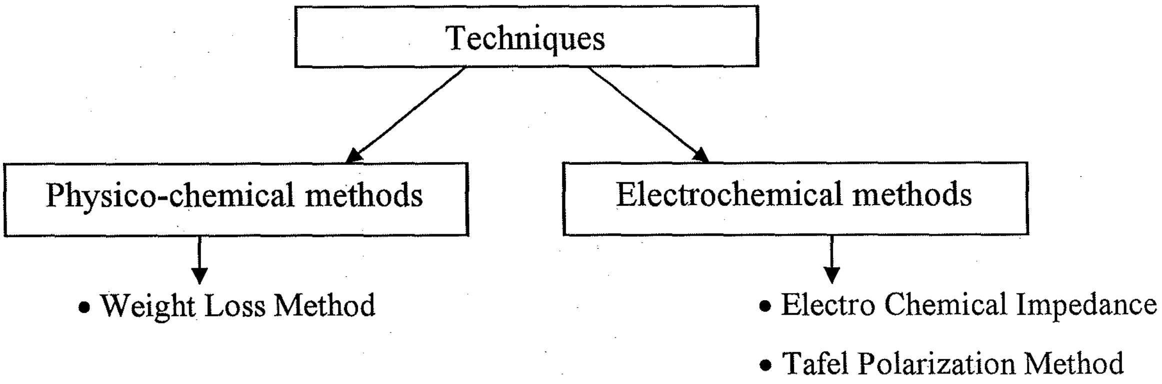
| ACID | $pK_a$ | | | |
|---|---|---|---|---|
| | $K_1$ | $K_2$ | $K_3$ | $K_4$ |
| α-Amino acetic acid (glycine) | 2.35 | 9.78 | | |
| Arsenic acid | 2.22 | 6.98 | 11.4 | |
| Trichloroacetic acid | 0.89 | | | |
| Dichloroacetic acid | 1.26 | | | |
| Oxalic acid | 1.27 | 4.27 | | |
| Phorphoric acid | 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 Chemical polymerization and Electro polymerization of aniline was carried out in acidic media with the aim of obtaining well adherent PANI layer. 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. 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 for the dibasic acids especially for oxalic acid. The increase of the oxalic acid concentration ($C_{ox}$) favours polymerization of all the monomeric anilines considered in the present study in the sense that it results in higher values of the polymer growth rate. Organic acid ranks among the most important chemicals in industry today. The reactive carboxylic group (COOH) makes a basic building block for many compounds such as drugs, pharmaceuticals, plastics and fibers.

## TECHNIQUES EMPLOYED

Corrosion techniques have been classified into two main categories



## PHYSICO-CHEMICAL METHOD (WEIGHT LOSS METHOD)

The MS and SS coupons were weighed in Denwar balance. Weighed samples in triplicate were immersed in 100 ml of acid solution (with and without inhibitor) for a specific time viz, ½ an hour, 3 hrs, 6 hrs and 24 hrs. The specimens were removed and washed with saturated sodium bicarbonate solution and water, dried and reweighed.

The experiments were also performed for other parameters such as,

- Concentrations of inhibitor – 27ppm, 54ppm, 81ppm, 108ppm and135ppm
- Various temperature – 308K, 318K, 328K,338K and 343K

## DETERMINATION OF CORROSION RATE

Many expressions are available to express the corrosion rate (CR). The widely used one is miles per year. The rate of corrosion was calculated using the formula

$$\mathbf{CR\ (mpy)} = \frac{\mathbf{534W}}{\mathbf{DAT}}$$

Where,

W is the weight loss in mg

D is the density of the specimen in gm / $cm^2$

A is the area of the specimen in $cm^2$

T is the exposure time in hours

## DETERMINATION OF PERCENTAGE OF INHIBITOR EFFICIENCY

The inhibitor efficiency was obtained from the following formula

$$\mathbf{IE} = \frac{\mathbf{W_0 - W}}{\mathbf{W_0}} \mathbf{x\ 100}$$

Where,

IE = Inhibitor efficiency in percentage

$W_0$ = Corrosion rate without inhibitor

W = Corrosion rate with inhibitor

## SURFACE COVERAGE

The degree of surface coverage (θ) for different concentrations of the inhibitor have been evaluated by using the following equation

$$\theta = \frac{\mathbf{W_0 - W}}{\mathbf{W_0}} \mathbf{x\ 100}$$

Where,

$\theta$ = Surface coverage
$W_0$ = Corrosion rate without inhibitor
$W$ = Corrosion rate with inhibitor

## DETERMINATION OF THERMODYNAMIC PARAMETERS

The change in free energy ($\Delta G$) of adsorption for various concentration of the inhibitors can be calculated using the following equation **(Abdel and EI Saied)**.

$$\textbf{Log of inhibitor concentration (Log C)} = \left(\log \frac{\theta}{1-\theta}\right) - \log B$$

Log B = $-1.74 - (\Delta G/2.303RT)$
R = Gas constant 8.134J/mol
T = Temperature
C = Concentration of the inhibitor
$\theta$ = Surface coverage

The change in heat of adsorption $\Delta H$ and change in enthalpy $\Delta S$ can be calculated using **Gibbs Helmholtz** equation.

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

A plot of $\Delta G$ versus T will be a straight line with intercept $\Delta H$ and slope $\Delta S$.

## ADSORPTION ISOTHERMS

Corrosion inhibition is a surface process with specific adsorption of inhibitor on the metal surface. In recent years, attempts have been made to understand the nature of interaction between the inhibitor and the metal surface in terms of adsorption isotherm. Interpretation of the performance of the adsorbent type of inhibitor can be enhanced by fitting the data in one of the known adsorption isotherms.

- Langmuir ($\log(\theta/1-\theta)$ Vs $\log C$)
- Temkin ($\theta$ Vs $\log C$)
- Freundlich ($\log \theta$ Vs $\log C$)
- Flory-Huggins ($\log \theta/C$ Vs $\log(1-\theta)$) and
- El-Awady isotherm.

## DETERMINATION OF ACTIVATION ENERGY ($E_a$)

This activation energy at different concentrations of the inhibitor at various temperature was determined by plotting log CR Vs 1/T from the slope. The activation energy (Ea) was calculated using the following formula

**Ea = -2.303 x R x Slope of the isotherm**

Where, R = Gas constant (8.314 Joule / mole)

## POTENTIODYNAMIC POLARIZATION AND IMPEDANCE MEASUREMENTS

The corrosion monitoring techniques like

- Potentiodynamic polarization (Tafel polarization)
- Electrochemical impedance spectroscopy (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 2** and **Corr ware 2**. The system includes a potentiostat, personal computer and 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-sec-1. Super script

**Impedance Measurements** were carried out at corrosion potential. The A.C. amplitude f 10m V 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 (Rt + Rs) 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.

Subscript

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

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 $\eta$ 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

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

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

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

## SURFACE ANALYSIS TECHNIQUES

### Optical Electron Microscope

The surface examination of MS and SS in the absence and presence of VAANI Copolymer under study in both 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 made of electronic conduction.

Cyclic voltammetry experiments was performed in a typical single compartment three electrode cell using frequency analyzer solartran 1284Z.

- The composition of SS 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 69.77% Fe.
- The composition of MS used was found to be 0.048% C, 0.238% Mn, 1.081% Si, 0.031% P, 0.030% S, 0.016% Cr, 0.018% Mo, 0.023% Ni and 98.55% Fe.

This SS and 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. Oxalic 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 has been recently used in the development of effective inhibitors for corrosion. FTIR spectra were recorded using **Shimadzu** FTIR spectro photometer.

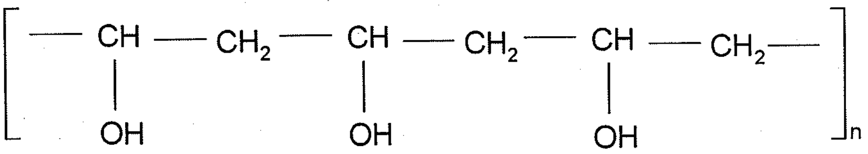
FTIR spectral data are presented in the table 3. In the current study, VAANI Copolymer is chemically and electro chemically synthesized and utilized as corrosion inhibitor for MS and SS surface.

**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. | - | 3545 | -NH group |
| 5. | - | 1018 | -CH stretching |
| 6. | - | 1648 | Aromatic nucleus |
| 7. | 625 | 608 | End group C-H bending |
| 8. | 849 | 850 | C-H bending |
| 9. | - | 928 | Poly conjugated system |

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

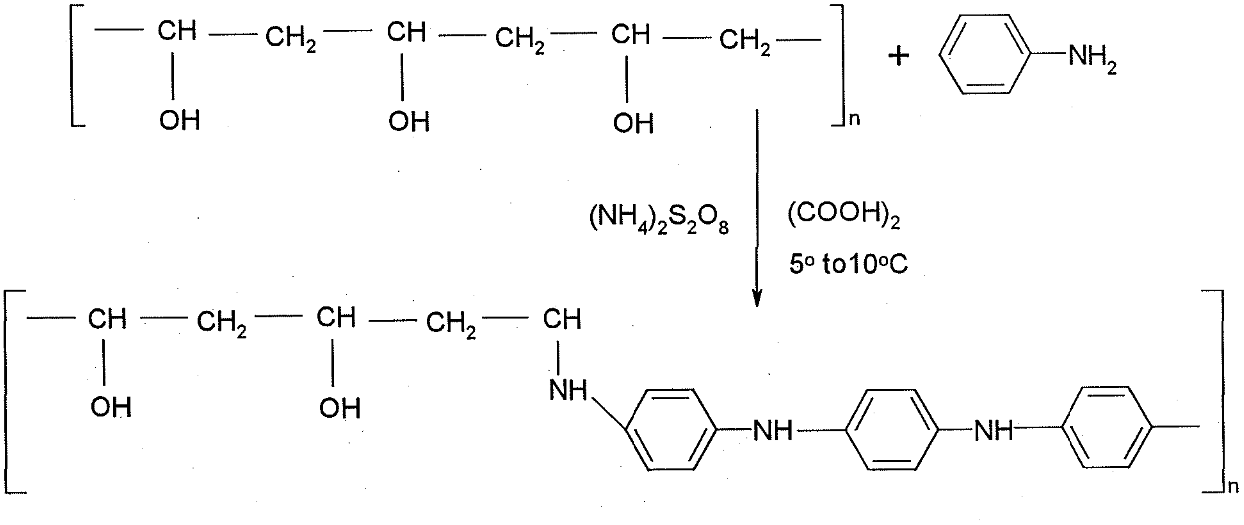


$$\left[-CH(OH)-CH_2-CH(OH)-CH_2-CH(OH)-CH_2-\right]_n$$

From the structure, we understand that PVA contains free –OH groups and a long alkyl chain. Analysis of IR spectrum of PVA (Figure 7) 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 stretches 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 of 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 is as follows.



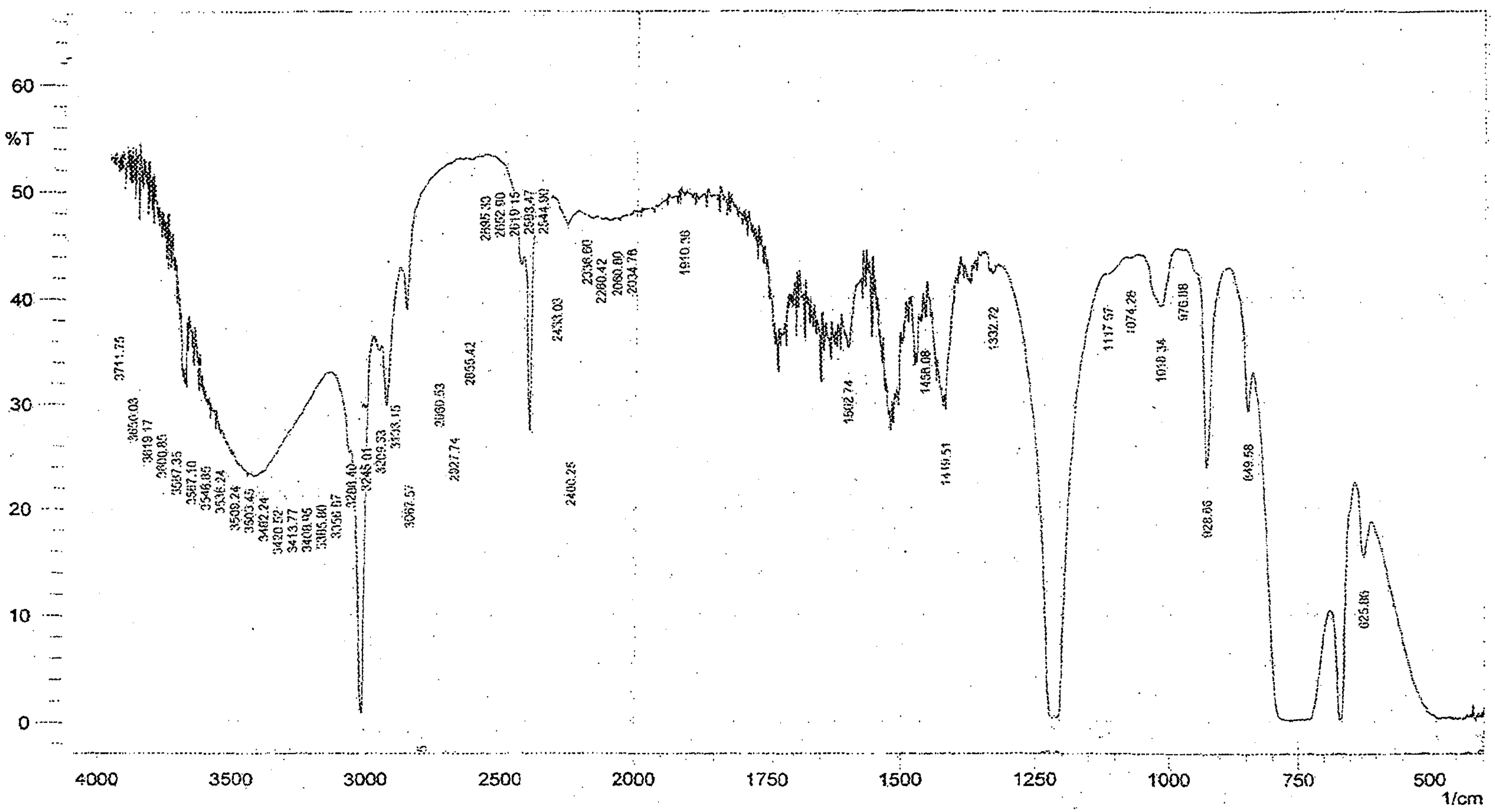


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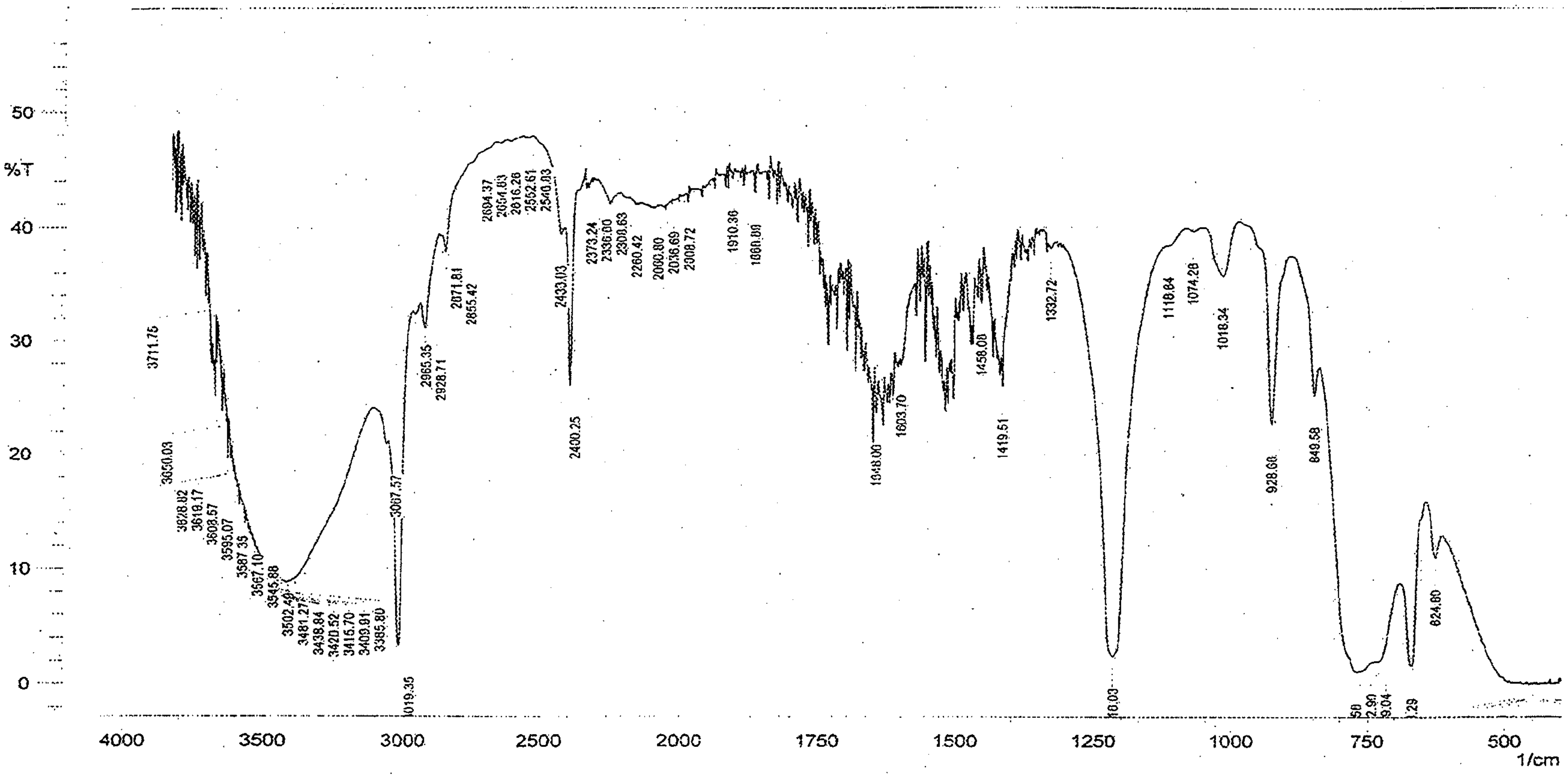
FIGURE – 7
FIIR – spectra recorded for Poly Vinyl Alcohol



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Resolution; 2 [1/cm]
Apodization; Happ-Genzel

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FIGURE – 8
FTIR Spectra Recorded for VAANI Copolymer

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. Characterization is also carried out using FTIR spectra, to confirm VAANI and its structure and its solubility in water.

# Results and Discussion

# 4. RESULTS AND DISCUSSION

The results pertaining to the present investigation on **"Synthesis of VAANI Copolymer for Corrosion Inhibition of MS and SS in Acid Medium"** are tabulated and discussed in the light of the objectives set forth.

Results of the present investigation are discussed under following headings.

- **Weight loss method**

  In Weight loss method the following parameters were investigated.

  - Effect of concentration (27ppm to 135 ppm)
  - Impact of immersion time (½ hr to 24 hrs)
  - Temperature variation (308K to 348K)
- **Electro chemical method**

  In electro chemical method the following techniques were carried out.

  - Tafel polarization method
  - Electrochemical impedance spectroscopy
- **Surface analytical technique**
  - Optical electron micrograph
- **Cyclic voltammetry**
- **Mechanism of inhibition**

## WEIGHT LOSS METHOD

### Role of inhibitor concentration on the corrosion behaviour of MS in 1M HCl

Table 4 shows the corrosion rate and inhibitor efficiency of VAANI copolymer on exposing the MS sample for ½ hr, 3 hrs, 6 hrs and 24 hrs. The inhibition efficiencies are estimated by

$$\mathrm{IE}\ (\%) = \frac{\mathrm{CR}_{(b)} - \mathrm{CR}_{(I)}}{\mathrm{CR}_{(b)}} \times 100$$

The corrosion rate was found to decrease with the increase in concentration of the inhibitor for all the periods of immersion. The inhibitor efficiency increases with concentration, at various interval of time. The efficiency of the inhibitor increased up to 6 hrs. After 24 hrs there is a slight decrease in the efficiency. This indicates the consistent behaviour of the inhibitor.

The maximum of 89% was noted with 108 ppm concentration at 6 hrs. Further increase in concentration does not show an increase in efficiency. This may be due to the total coverage of the metal surface by the inhibitor molecules.

### Effect of inhibitor concentration on the corrosion rate of SS in 6M HCl

When SS was immersed in 6M HCl it suffered weight loss. The corrosion rate was found to be 244mpy for ½ hr exposure. The corrosion rate was maximum at 24 hrs (345 mpy). When the inhibitor was added to the acid the corrosion rate was decreased and it was more pronounced as the concentration of the inhibitor increased. Maximum efficiency of the inhibitor was noticed with 135 ppm of the inhibitor from 6 hrs to 24 hrs. The efficiency was found to be 73%.

The inhibitor efficiency was found to increase with the exposure time up to 6 hrs. After 6 hrs there was a slight decrease in the inhibitor efficiency. The inhibitor behaved consistently at 135 ppm concentration.

The performance evaluation of VAANI copolymer as inhibitor on SS in 6M HCl acid with various immersion time and concentration of a copolymer is presented in table 5. From the tables 4 and 5 following information can be arrived at:

- Inhibitor efficiency increased with 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 a metal surface, thus preventing the dissolution of the metal. This observation was supported by **Taha et al (1995)** who indicated an increase in concentration of the polymer causes more blockages of the active sites of the metal. As a result, the surface coverage by the polymer increases and the inhibition efficiency also increases. **Muralidharan & Iyar (1997)** also explained maximum inhibition at high concentration can be attributed to the maximum blockage of the active sites on the metal surface.

Figures 9 and 10 represent the variation of inhibition efficiency with concentrations of VAANI Copolymer.

## TABLE – 4

## TRENDS IN IE RANGE OVER IMMERSION PERIOD CONTAINING VARIOUS CONCENTRATION OF VAANI COPOLYMER IN 1M HCl ON MS

| 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 | 895 | 51 | 771 | 59 | 800 | 62 | 774 | 53 |
| 3. | 54 | 630 | 65 | 489 | 74 | 556 | 73 | 593 | 64 |
| 4. | 81 | 561 | 69 | 468 | 76 | 372 | 82 | 445 | 73 |
| 5. | 108 | 470 | 70 | 268 | 86 | 277 | 89 | 346 | 79 |
| 6. | 135 | 444 | 72 | 250 | 87 | 234 | 89 | 329 | 80 |

## TABLE – 5

## RELATIONSHIP BETWEEN TIME OF IMMERSION AND CONCENTRATION OF VAANI COPOLYMER ON SS IN 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 | 166 | 32 | 137 | 35 | 58 | 56 | 162 | 53 |
| 3. | 54 | 144 | 41 | 122 | 58 | 48 | 63 | 145 | 58 |
| 4. | 81 | 124 | 49 | 75 | 64 | 42 | 68 | 127 | 63 |
| 5. | 108 | 102 | 58 | 71 | 66 | 38 | 71 | 110 | 68 |
| 6. | 135 | 188 | 23 | 84 | 60 | 35 | 73 | 93 | 73 |

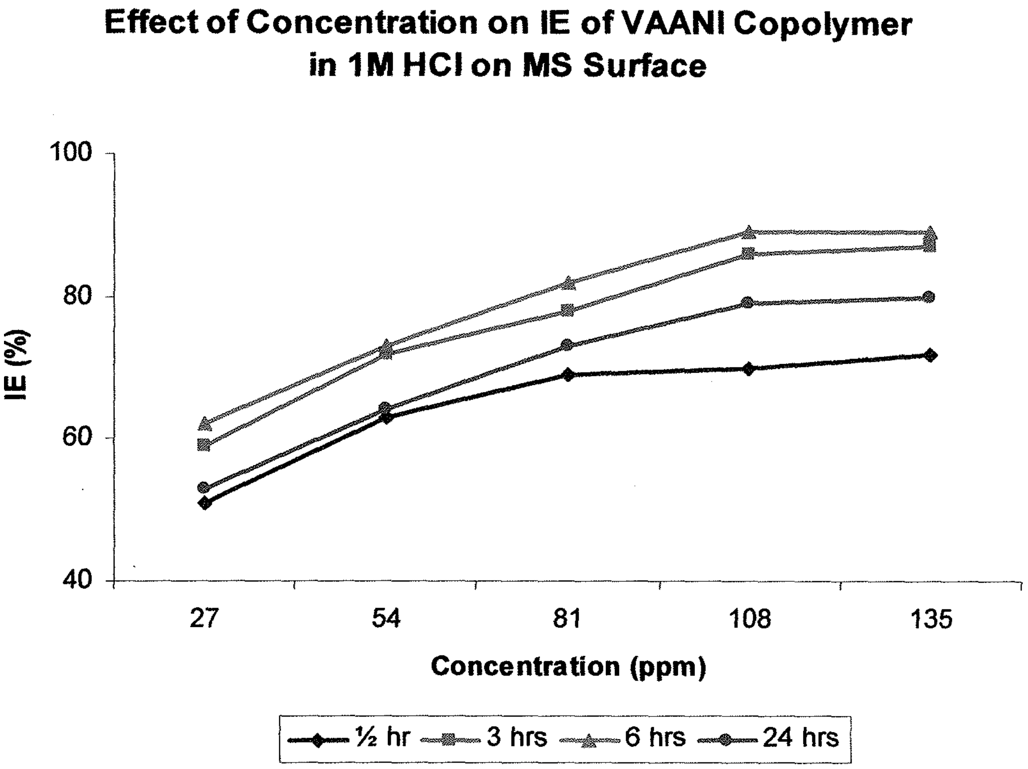


FIGURE - 9

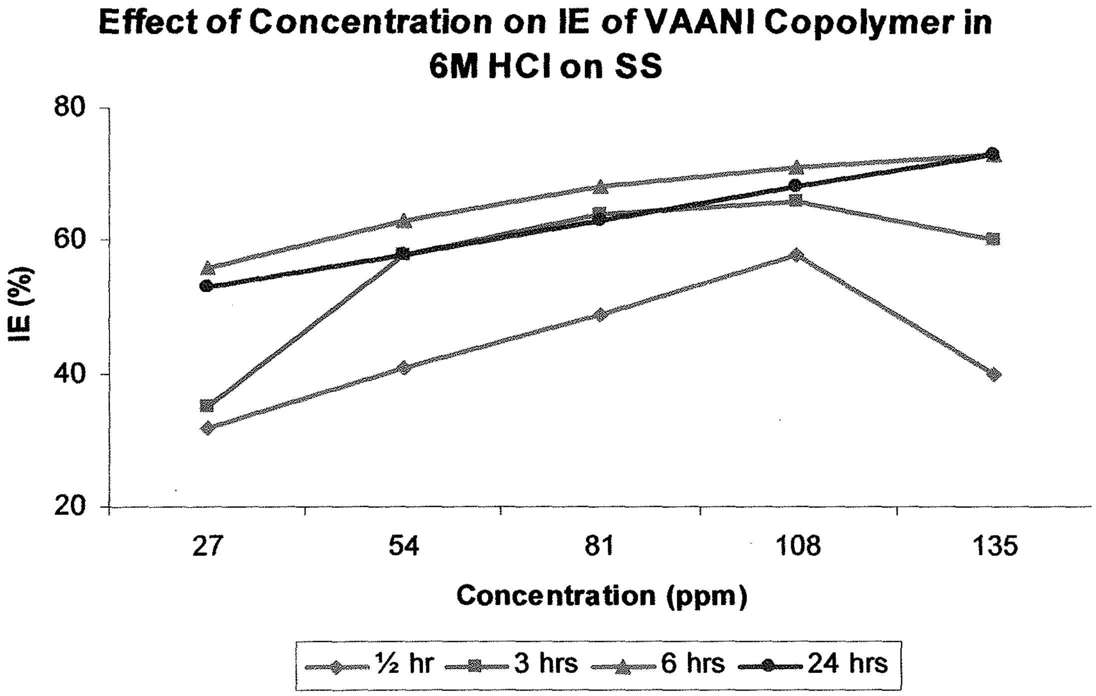


FIGURE – 10

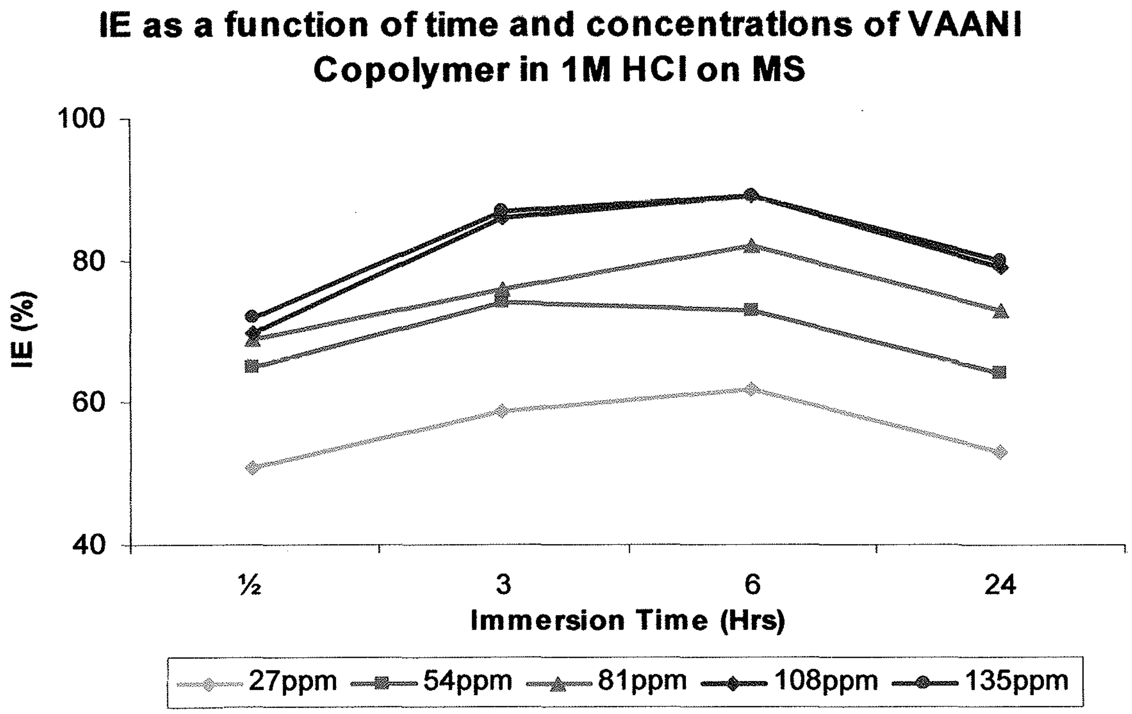


FIGURE – 11

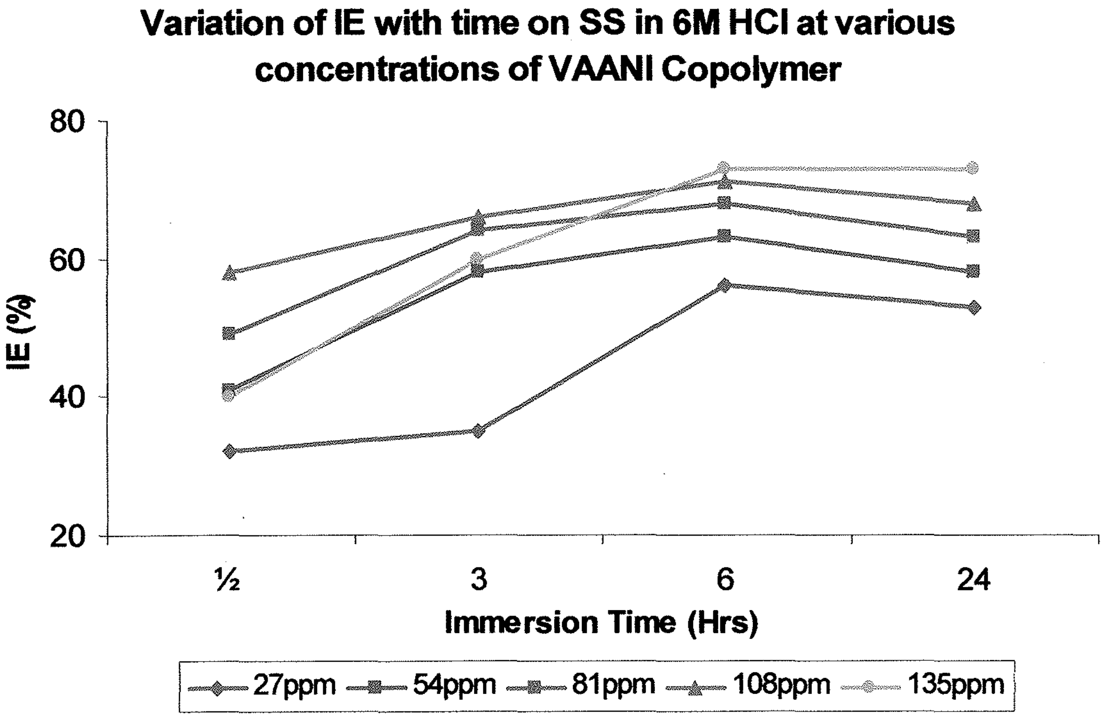


FIGURE – 12

**Role of VAANI Copolymer on Exposure Time**

From the tables 4 and 5 it was observed the inhibitor efficiency increased with increasing time of immersion. But after 6 hrs slight decrease in inhibitor efficiency for both the metals. This increase in inhibition efficiency with period of immersion may be explained as follows:

Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exist between these two processes (**~~Arora &~~ Choudary** et al., **2002**).

At early period of immersion the concentration of the copolymer is more and 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.

The inhibitor efficiency of VAANI copolymer generally decreased for prolonged time of immersion. This behavior can be discussed on the basis that prolonged immersion of MS and SS in acid solution increases the concentration of the ferrous ions. These ions are known to stimulate the corrosive attack of the acid on the metal **(Schmitt, 1984)**. The present studies indicated that performance of VAANI Copolymer was appreciable at room temperature for MS. Figures 11 and 12 represent the variation of inhibition efficiency with time of immersion.

**Outcome of the temperature studies on MS**

To investigate the inhibition mechanism and to determine the activation energy and free energy of adsorption of the corrosion process gravimetric measurements were taken in the temperature range from 308K to 348K in the absence and presence of various concentrations of VANNI copolymer. Corresponding data obtained are given in table 6 and figures 13, 15. For each temperature the corrosion rate of MS decreased and values of inhibitor efficiency of the copolymer increased with increase in concentration of the VAANI copolymer.

Generally, for each concentration of the VAANI copolymer the corrosion rate of MS decreased with raise in temperature and the inhibitor efficiency increased with increase in temperature. Maximum inhibition efficiency of 72% was noticed with 135 ppm of VAANI copolymer at 348K.

## TABLE – 6

## PERFORMANCE EVALUATION OF VAANI COPOLYMER AT VARIOUS TEMPERATURE IN 1M HCl ON MS SURFACE

| 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 | - | 3536 | - |
| 2. | 27 | 1641 | 10 | 2285 | 17 | 3321 | 48 | 4419 | 53 | 5956 | 56 |
| 3. | 54 | 1195 | 34 | 1703 | 38 | 2805 | 56 | 3760 | 60 | 5008 | 63 |
| 4. | 81 | 1052 | 42 | 1648 | 40 | 2486 | 61 | 3478 | 63 | 4467 | 67 |
| 5. | 108 | 943 | 48 | 1538 | 44 | 2422 | 62 | 3290 | 65 | 4196 | 69 |
| 6. | 135 | 725 | 60 | 1456 | 47 | 2422 | 62 | 2914 | 69 | 3790 | 72 |

# TABLE – 7

## VARIATION OF CORROSION RATE AND INHIBITOR EFFICIENCY FOR VAANI COPOLYMER IN 6M HCl ON SS

| 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 | 166 | 32 | 459 | 44 | 1089 | 49 | 3199 | 57 | 6183 | 45 |
| 3. | 54 | 144 | 41 | 426 | 48 | 940 | 56 | 3124 | 58 | 5508 | 51 |
| 4. | 81 | 124 | 49 | 377 | 54 | 812 | 62 | 2529 | 66 | 5059 | 55 |
| 5. | 108 | 109 | 55 | 360 | 56 | 769 | 64 | 2380 | 68 | 4834 | 57 |
| 6. | 135 | 1146 | 40 | 295 | 64 | 641 | 70 | 1785 | 76 | 4159 | 63 |

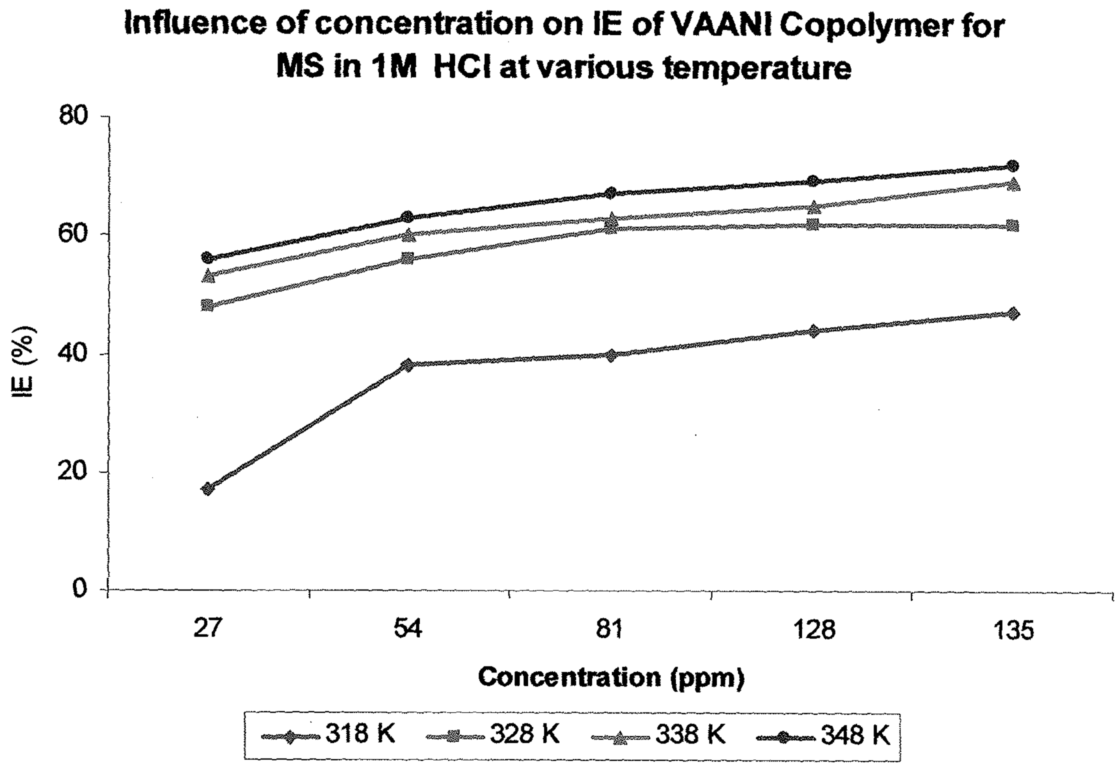


FIGURE – 13

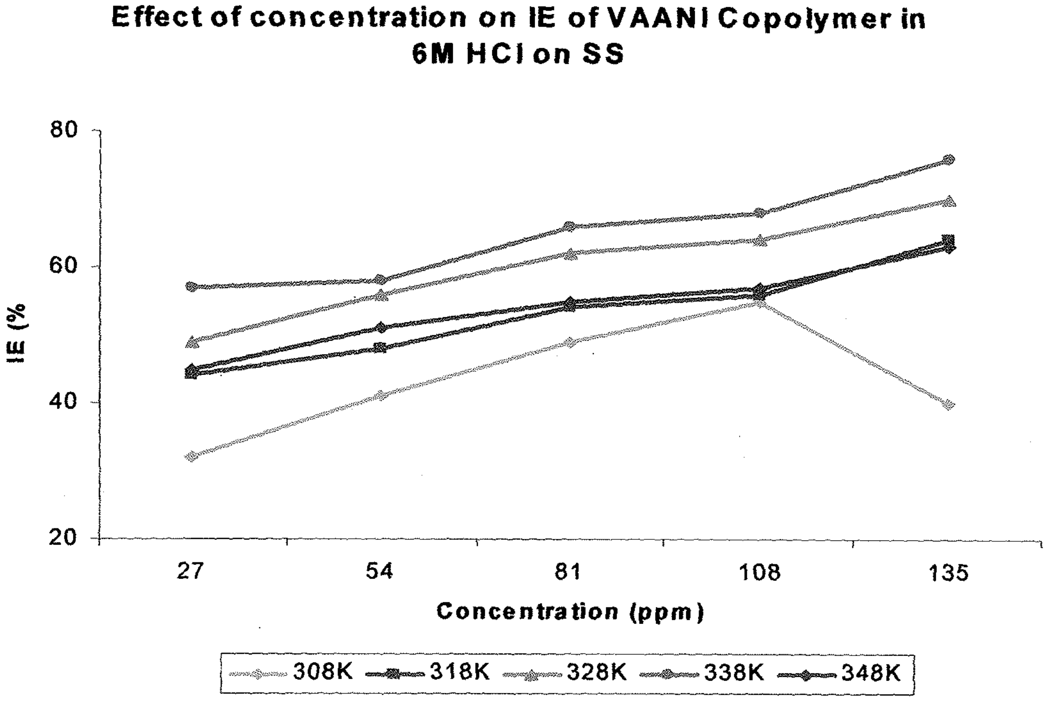


FIGURE – 14

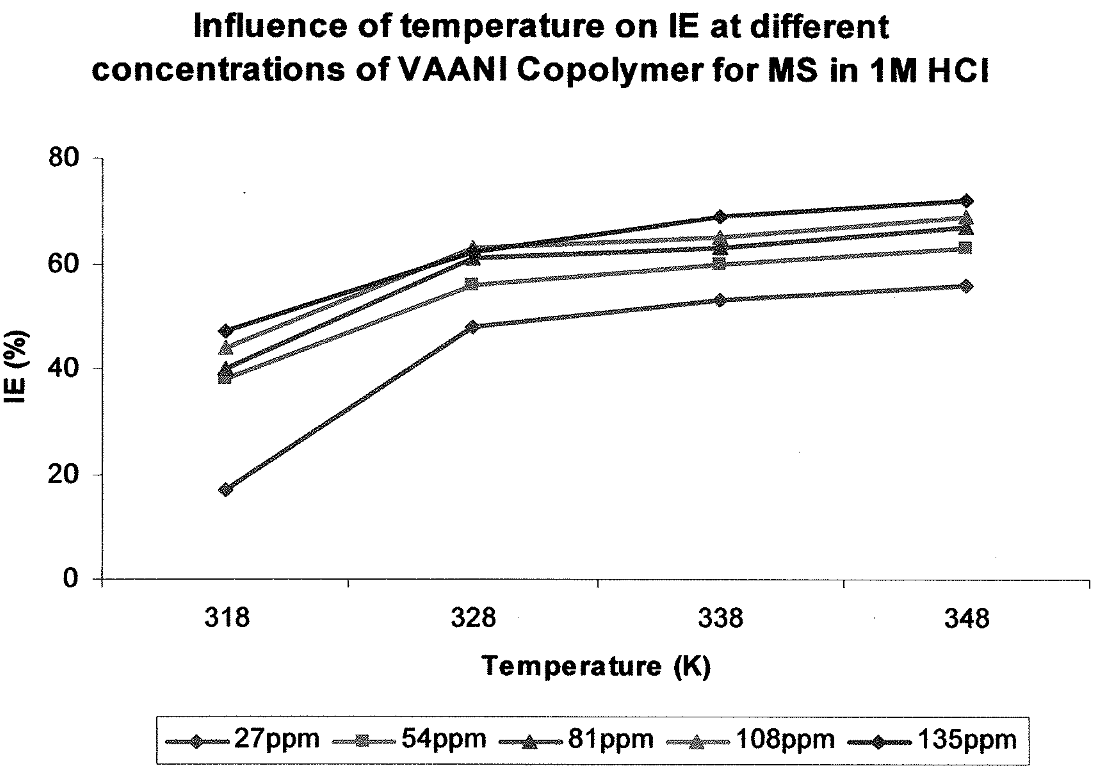

Influence of temperature on IE at different concentrations of VAANI Copolymer for MS in 1M HCl

FIGURE – 15

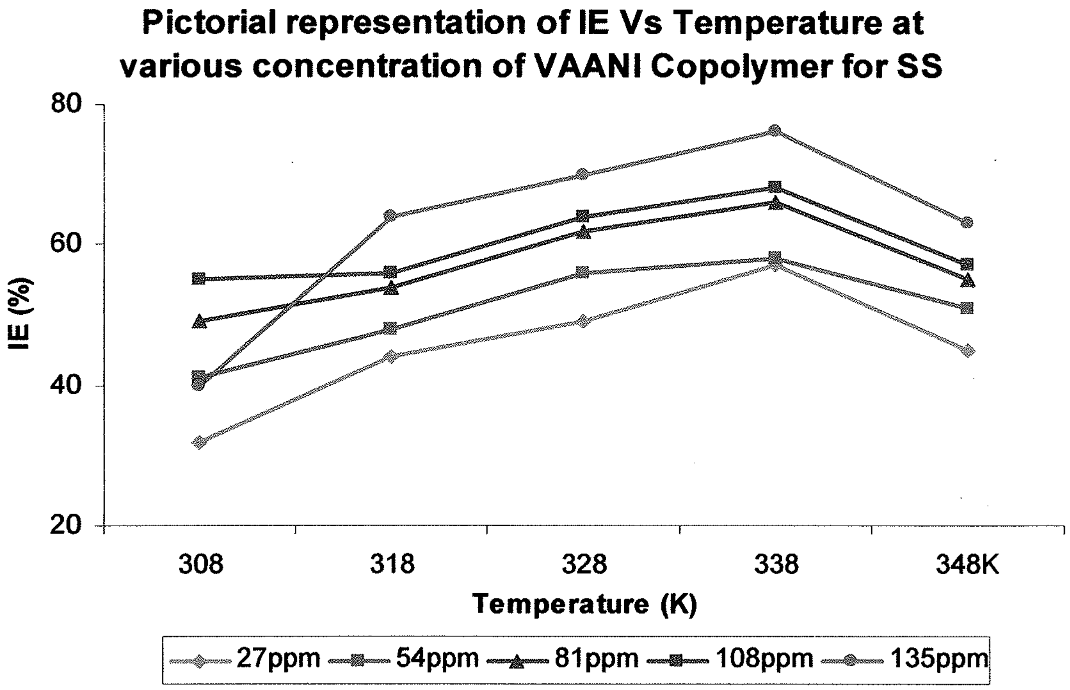

Pictorial representation of IE Vs Temperature at various concentration of VAANI Copolymer for SS

FIGURE – 16

The stability of the additive effectiveness at high concentrations and at high temperatures indicate the stability of the inhibitor and the strong adsorption of its active molecules on the metal surface. The current study was confirmed with the past studies carried out by **Zacchini et al (1971)**.

**Effect of Temperature on SS in the presence of VAANI in 6M HCl**

The results obtained on temperature studies are depicted in table 7 and figures 14, 16. Generally corrosion rate decreased with increase in temperature of corroding medium with different concentrations of the inhibitor. At all temperatures studied, as the concentration of inhibitor increased the corrosion rate of SS was decreased and inhibitor efficiency was increased. The effectiveness of the polymer increased with increase in temperature for all the concentration of the inhibitor examined. A maximum inhibition efficiency of 76% was obtained with 135ppm at 338K. The inhibitor was found to be effective at 338K.

VAANI copolymer exhibit good inhibition efficiency even at very high temperatures. This can be explained as VAANI molecules are strongly adsorbed on the metal surface. It was suggested by **Hoar and Holliday (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 inhibitor present at the metal surface is greater than that at lower temperature.

According to **Hariharputhran et al., (1999)**, the high inhibitor efficiency at high temperature was due to the strong adsorption of the inhibitor on metal surface with less desorption process.

The lower inhibitor efficiency at higher temperature was explained by **Arora & Choudary (2002)**. According to them with the increase of temperature the equilibrium between adsorption and desorption process is shifted, leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of a equilibrium constant. It explains the lower inhibitor efficiency of the polymer with SS at higher temperature.

**Adsorption isotherms**

Various isotherms are:

- ☞ Langmuir (log ($\theta$/1-$\theta$) Vs log C)
- ☞ Temkin ($\theta$ Vs log C)
- ☞ Freundlich (log $\theta$ Vs log C)
- ☞ Flory-Huggins (log $\theta$/C Vs log (1-$\theta$))
- ☞ El-Awady isotherm

Corrosion inhibition is a surface process in which specific adsorption of the inhibitor on the metal surface takes place. To understand the nature of the interaction between the inhibitor and the metal surface, various adsorption isotherms were tried.

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

In the current study, the regression co-efficient were calculated for all the adsorption isotherm studied and the results were tabulated in table 8, 9 and figures 17 to 24 represent Langmuir, Temkin, Freundlich, & Flory-Huggins isotherms respectively.

**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,

$\theta$ 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 $\theta$ 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-efficient were calculated for all the adsorption isotherms studied and the results were tabulated in table 8, 9. Figures 17 to 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 model are furnished in the tables 8 and 9. From this finding 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 $\theta$ / 1-$\theta$ Vs Log C.

The data obtained give a straight line with the regression coefficient 0.881 to 0.996 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.

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 11, 12 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. $\theta$ 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.

## TABLE – 8

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

| **Isotherms** | **Regression Values** | | | | |
|---|---|---|---|---|---|
| | **308K** | **318K** | **328K** | **338K** | **348K** |
| Langmuir | 0.9803 | 0.9551 | 0.5179 | 0.9623 | 0.9965 |
| Temkin | 0.9907 | 0.9726 | 0.9828 | 0.9925 | 0.9984 |
| Flory-Huggins | 0.8452 | 0.9503 | 0.9494 | 0.9550 | 0.9894 |
| Freundlich | 0.8401 | 0.7793 | 0.8749 | 0.9435 | 0.9375 |
| El-awady | 0.9803 | 0.5230 | 0.5179 | 0.9623 | 0.9965 |

## TABLE – 9

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

| **Isotherms** | **Regression Values** | | | | |
|---|---|---|---|---|---|
| | **308K** | **318K** | **328K** | **338K** | **348K** |
| Langmuir | 0.8816 | 0.9718 | 0.9828 | 0.9001 | 0.9752 |
| Temkin | 0.6712 | 0.9478 | 0.9872 | 0.9121 | 0.9775 |
| Flory-Huggins | 0.1917 | 0.9061 | 0.9521 | 0.9300 | 0.9221 |
| Freundlich | 0.8421 | 0.9639 | 0.9930 | 0.9222 | 0.9865 |
| El-awady | 0.6816 | 0.9718 | 0.9828 | 0.9001 | 0.9752 |

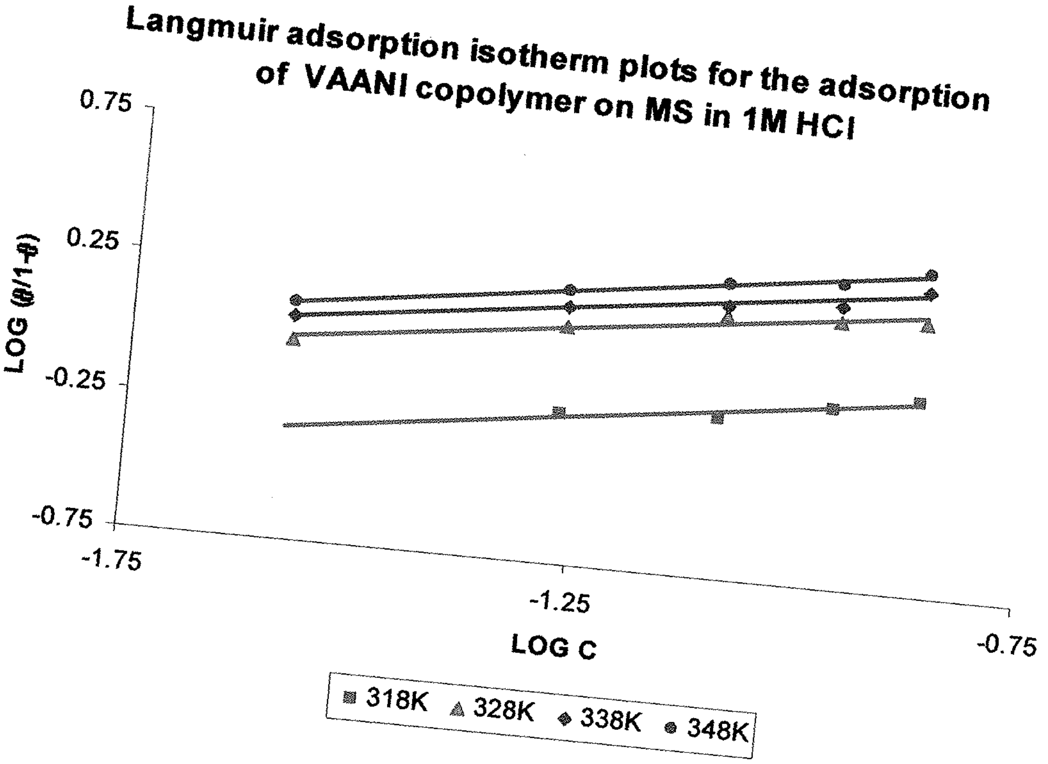


FIGURE - 17

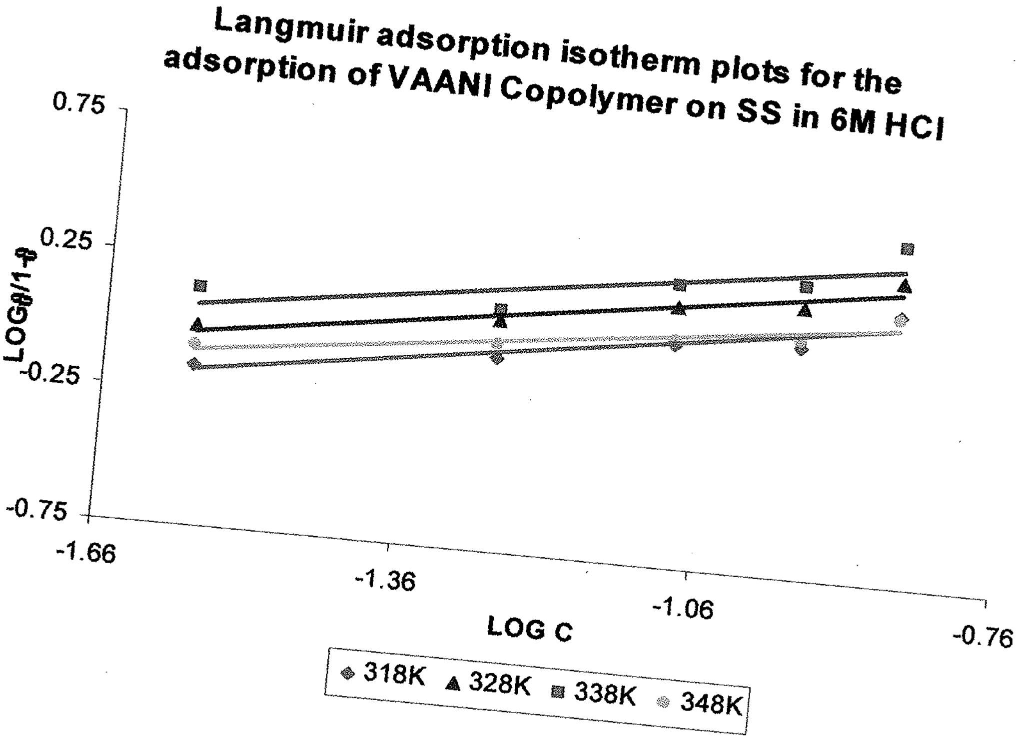
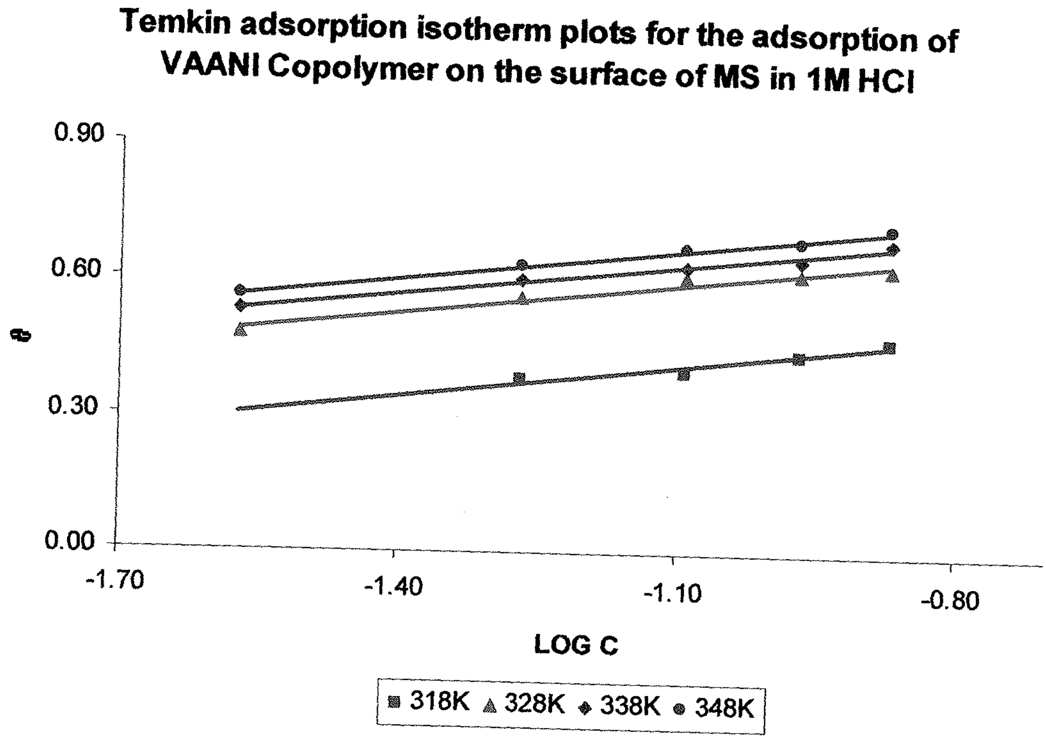
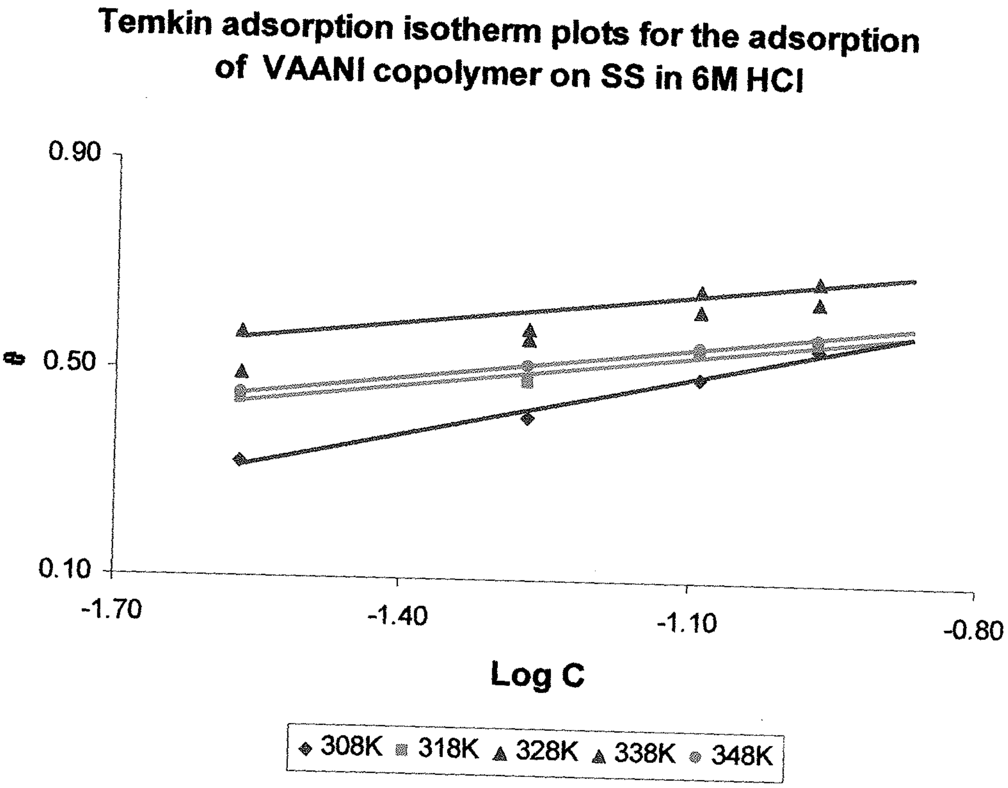


FIGURE - 18



Temkin adsorption isotherm plots for the adsorption of VAANI Copolymer on the surface of MS in 1M HCl

FIGURE – 19



Temkin adsorption isotherm plots for the adsorption of VAANI copolymer on SS in 6M HCl

FIGURE – 20

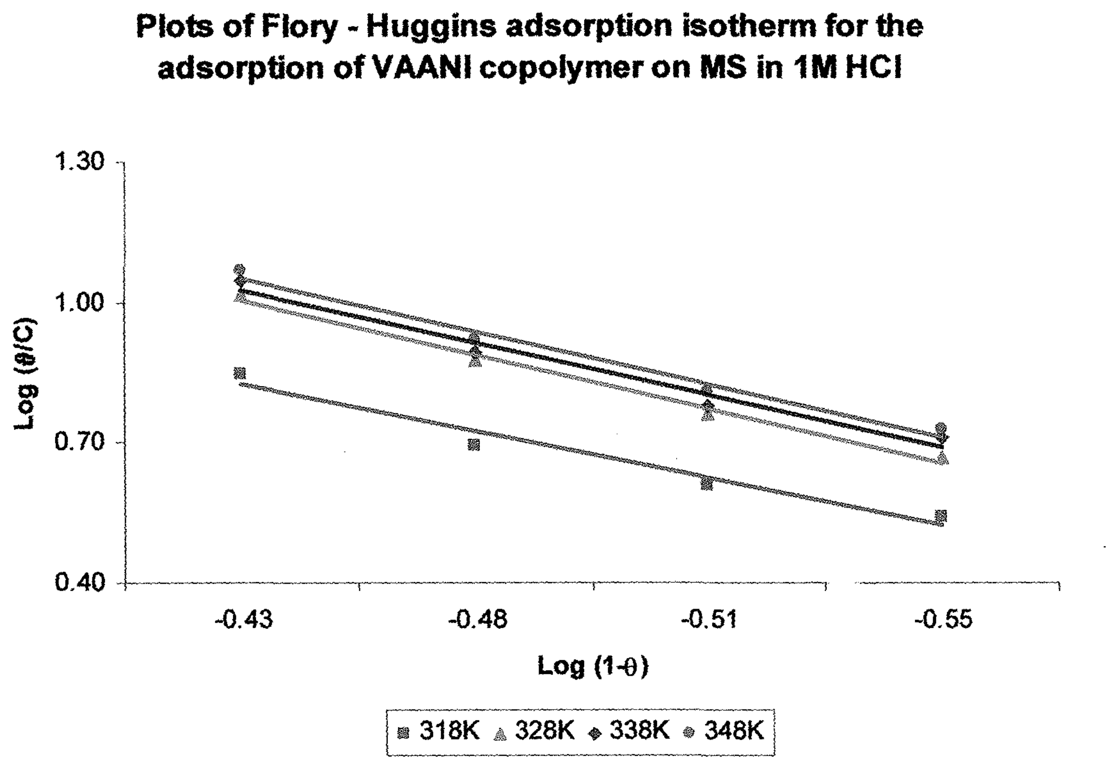


FIGURE – 21

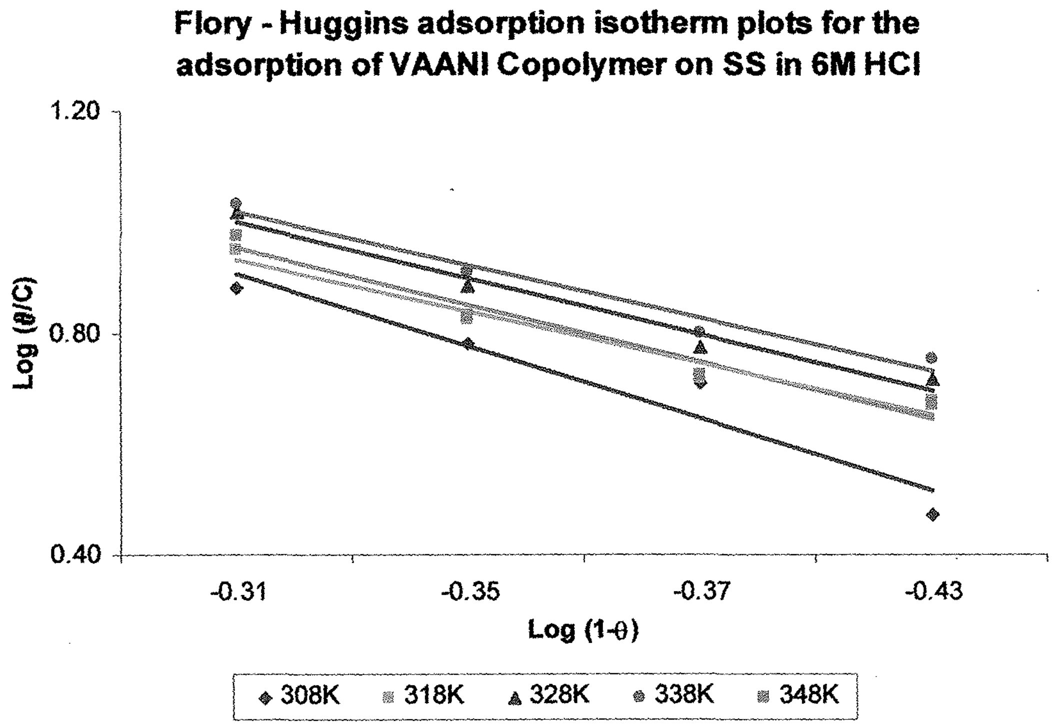
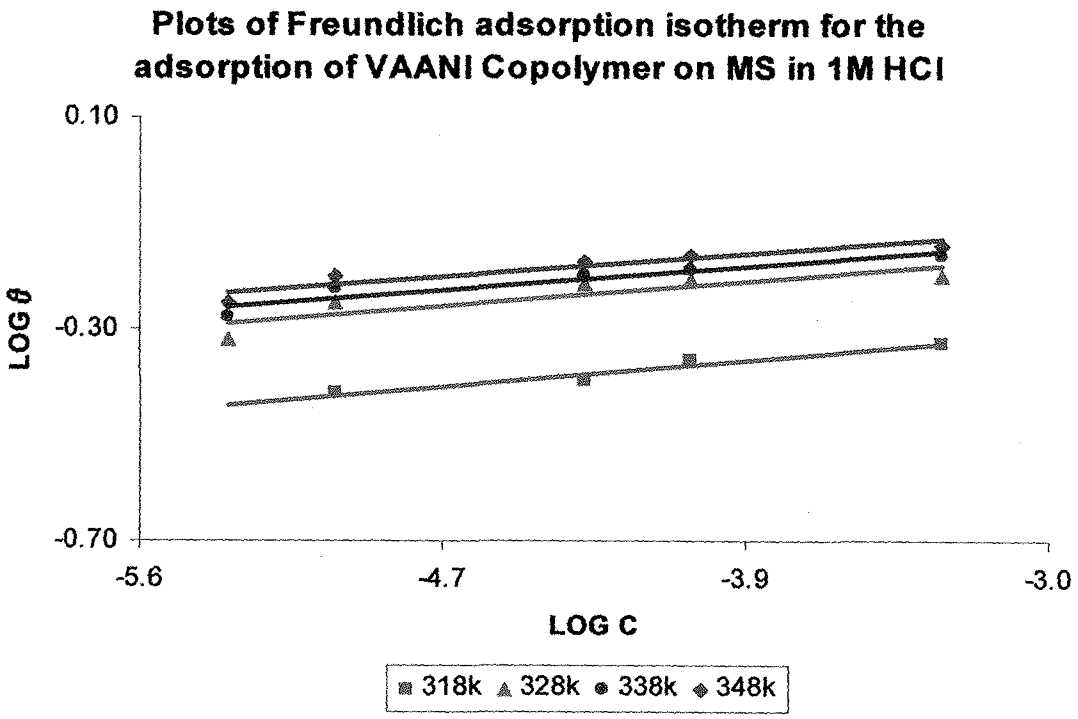
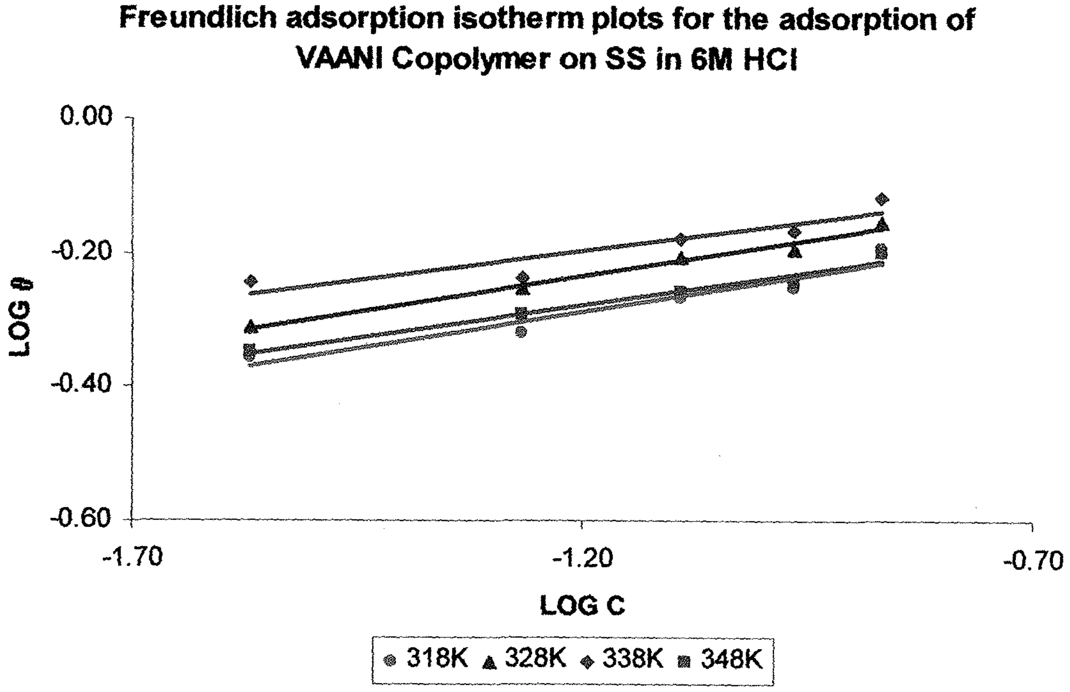


FIGURE – 22



Plots of Freundlich adsorption isotherm for the adsorption of VAANI Copolymer on MS in 1M HCl

FIGURE – 23



Freundlich adsorption isotherm plots for the adsorption of VAANI Copolymer on SS in 6M HCl

FIGURE – 24

### 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

$$\mathbf{Log\ CR = \frac{-E_a}{2.303\ RT} + Constant}$$

Where, CR. - 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 and 26. Activation energies were calculated from the slopes.

The estimated values of $E_a$ for MS VAANI Copolymer in 1M HCl and SS VAANI Copolymer in 6M HCl are listed and from the tables 10 and 11, 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 which means that an inhibitor becomes more effective as the temperature increases was explained by **Putilova, (1960)** 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.

## TABLE – 10

## INFLUENCE OF TEMPERATURE AND CONCENTRATION OF VAANI COPOLYMER ON THERMODYNAMIC AND KINETIC PARAMETERS (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 | 45.48 | - | - | - | - | - | - | - |
| 0.027 | 27.99 | 13.66 | 15.20 | 18.99 | 19.50 | 19.80 | 0.17 | -36.97 |
| 0.054 | 31.67 | 15.78 | 16.22 | 18.06 | 18.47 | 18.79 | 0.08 | -9.69 |
| 0.081 | 31.55 | 15.61 | 15.41 | 17.55 | 17.77 | 18.21 | 0.08 | -7.88 |
| 0.108 | 32.51 | 15.50 | 15.09 | 16.94 | 17.26 | 17.72 | 0.07 | -5.15 |
| 0.135 | 34.86 | 16.16 | 14.84 | 16.48 | 17.16 | 17.52 | 0.05 | -0.08 |

## TABLE – 11

## VALUES OF ΔG, ΔH AND ΔS FOR VARIOUS CONCENTRATION OF VAANI COPOLYMER FOR SS 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 | 76.30 | 17.30 | 18.59 | 19.09 | 19.91 | 18.69 | 0.04 | 5.25 |
| 0.054 | 77.16 | 16.53 | 17.25 | 18.06 | 18.26 | 17.55 | 0.03 | 7.52 |
| 0.081 | 77.43 | 16.33 | 16.83 | 17.66 | 18.10 | 16.93 | 0.02 | 9.04 |
| 0.108 | 78.62 | 16.21 | 16.31 | 17.15 | 17.60 | 16.41 | 0.02 | 11.16 |
| 0.135 | 70.61 | 14.12 | 16.59 | 17.28 | 18.04 | 16.48 | 0.06 | -3.77 |

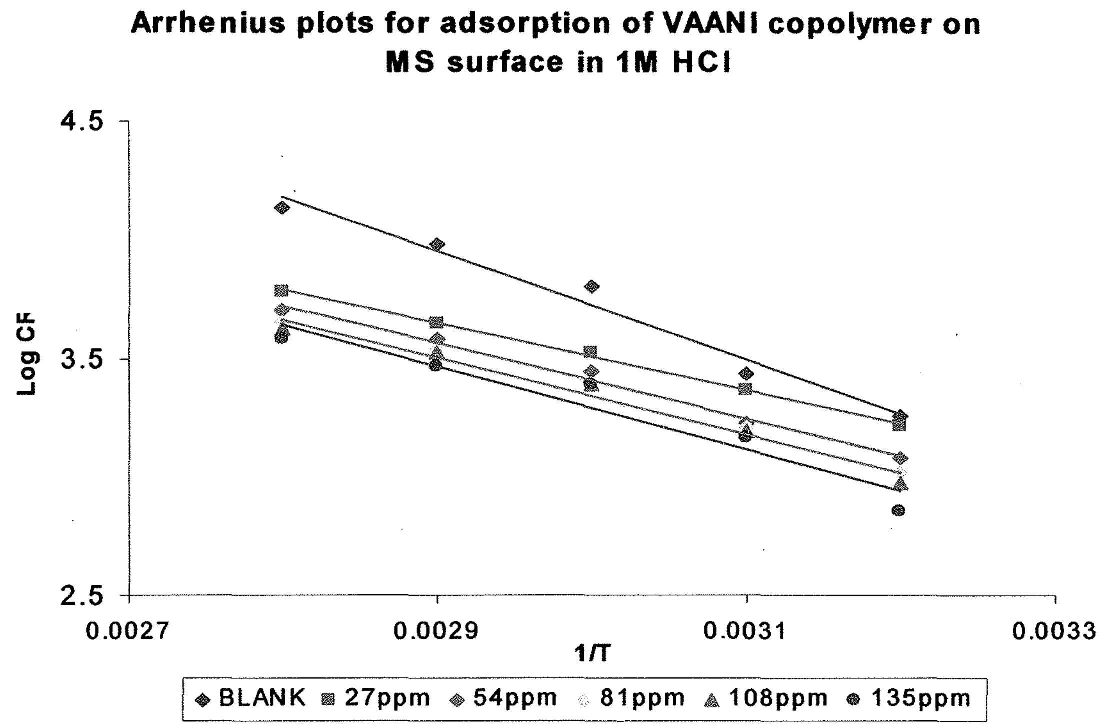


FIGURE - 25

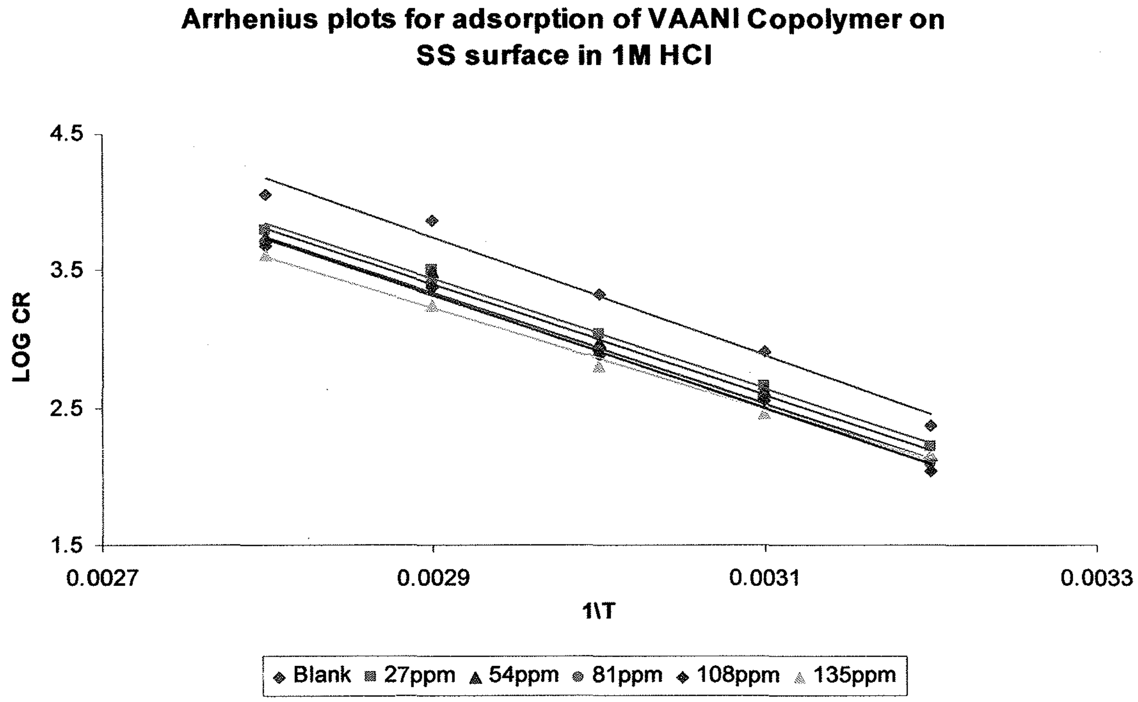


FIGURE – 26

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 estimation $E_a$ 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.

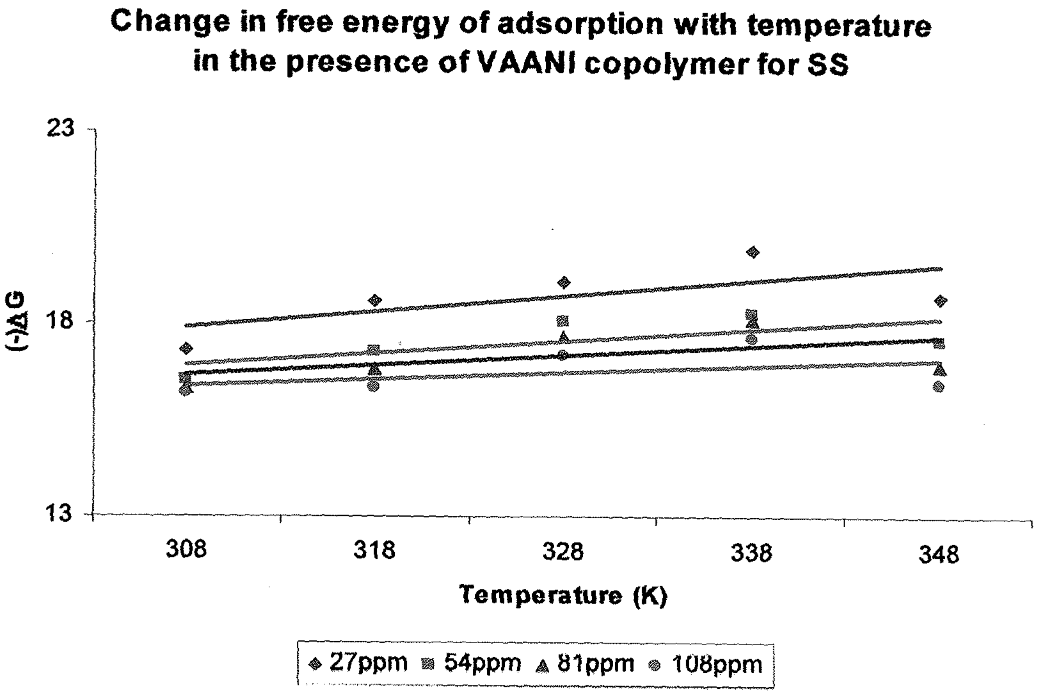
## Thermodynamic Parameters

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

Analysis of the tables 10 and 11 infer that the ΔG values ranges from about –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.

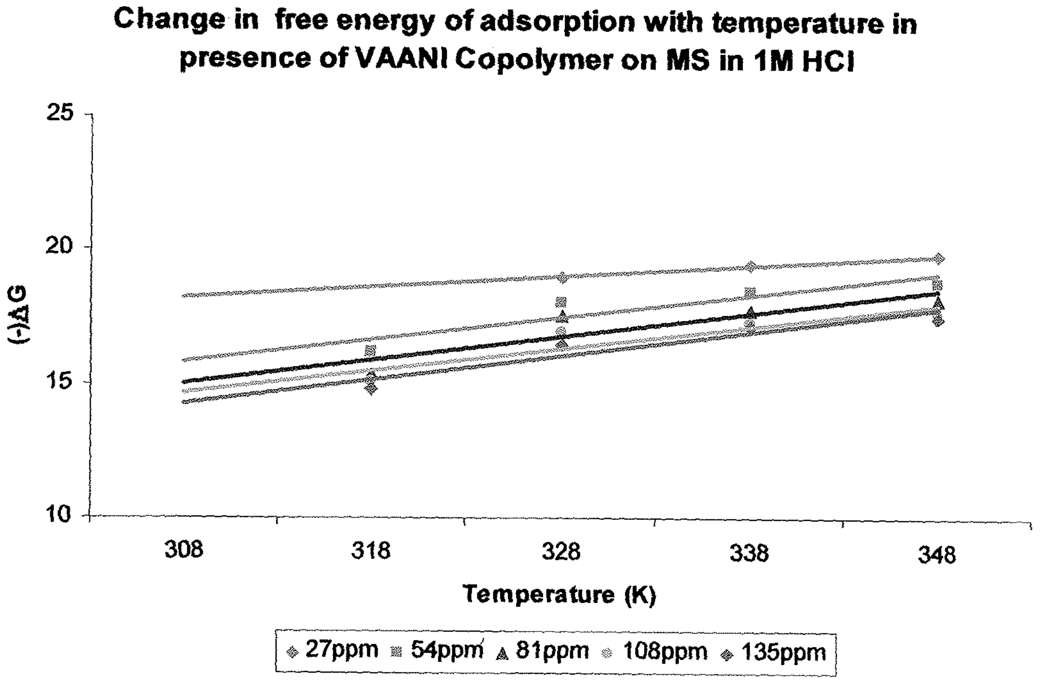
**Moretti et al., (2002), Abdulaziz et al., (1989, 1990), Gomel et al., (1995), Rudresh et al., (1982)** reported that the negative values of ΔG adsorption are characteristic of strong interaction between the inhibitor and the electrode forming a chemisorbed layer on the metallic surface.

The value 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 show that there was a strong interaction of the inhibitor molecules on corroding metal surface.



Change in free energy of adsorption with temperature in the presence of VAANI copolymer for SS

FIGURE – 27



Change in free energy of adsorption with temperature in presence of VAANI Copolymer on MS in 1M HCl

FIGURE – 28

### Heat of Adsorption ($\Delta H$) and Change in Entropy ($\Delta S$)

Thermodynamic parameters $\Delta H$ and $\Delta S$ could be arrived at, from the temperature studies and using a plot of $-\Delta G$ Vs T (figure 27 and 28). The values of thermodynamic parameters are listed in the tables 10 and 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 $\Delta S$ were observed for the systems 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 to 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 IBM 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 MS / SS electrode as the working electrode.

For potentiostatic polarization studies, MS 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 to 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 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 75% at 135 ppm on MS and 78% at 81 ppm on SS.

The polarization curves obtained for the copolymer adsorbed metal systems include both from the metal and from the 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 and 13. The values of $E_{corr}$ are the presence of VAANI Copolymer indicates 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 and 30.

## TABLE – 12

## TABULATION OF $E_{corr}$, $I_{corr}$ and TAFEL CONSTANTS IN THE PRESENCE OF VAANI COPOLYMER (MS IN 1M HCl)

| S.No. | Conc. of inhibitor (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 | 183 | 131 | 40.70 | 488 | 1885 | - |
| 2 | 27 | 176 | 195 | 35.18 | 480 | 1629 | 14 |
| 3 | 54 | 142 | 167 | 19.67 | 478 | 911 | 52 |
| 4 | 81 | 160 | 214 | 18.99 | 478 | 879 | 53 |
| 5 | 108 | 150 | 194 | 14.30 | 474 | 662 | 65 |
| 6 | 135 | 131 | 190 | 10.19 | 474 | 472 | 75 |

## TABLE – 13

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

| S.No. | Conc. of inhibitor (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 | 135 | 97 | 18.42 | -388 | 839 | - |
| 2 | 27 | 113 | 82 | 11.07 | -392 | 504 | 40 |
| 3 | 54 | 97 | 78 | 5.29 | -371 | 241 | 71 |
| 4 | 81 | 90 | 75 | 4.10 | -366 | 187 | 78 |
| 5 | 108 | 86 | 83 | 5.71 | -368 | 260 | 69 |
| 6 | 135 | 78 | 75 | 4.30 | -365 | 196 | 77 |

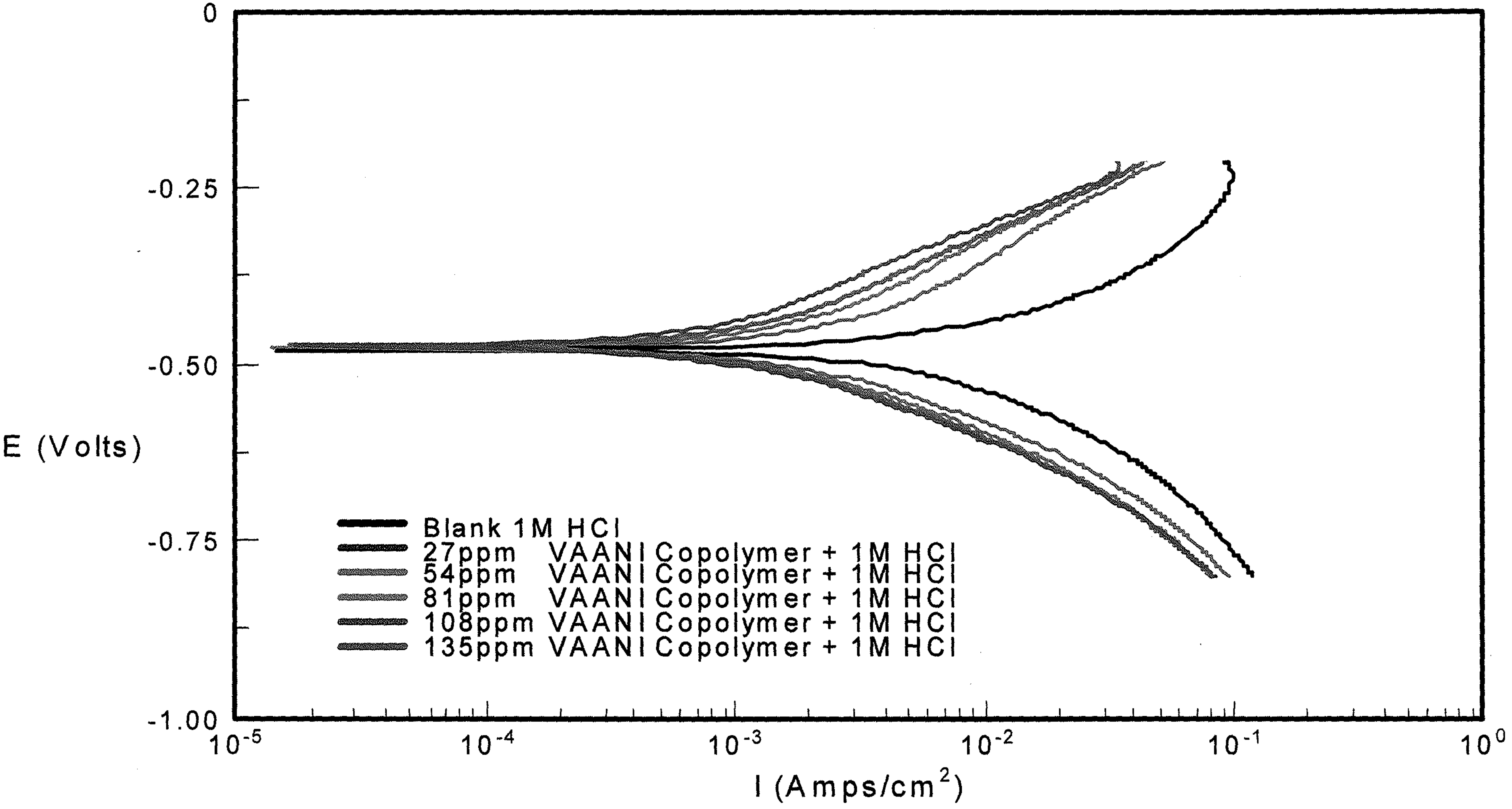


**FIGURE - 29**
**Electrochemical polarization plots for MS in 1M HCl in the presence of VAANI Copolymer**

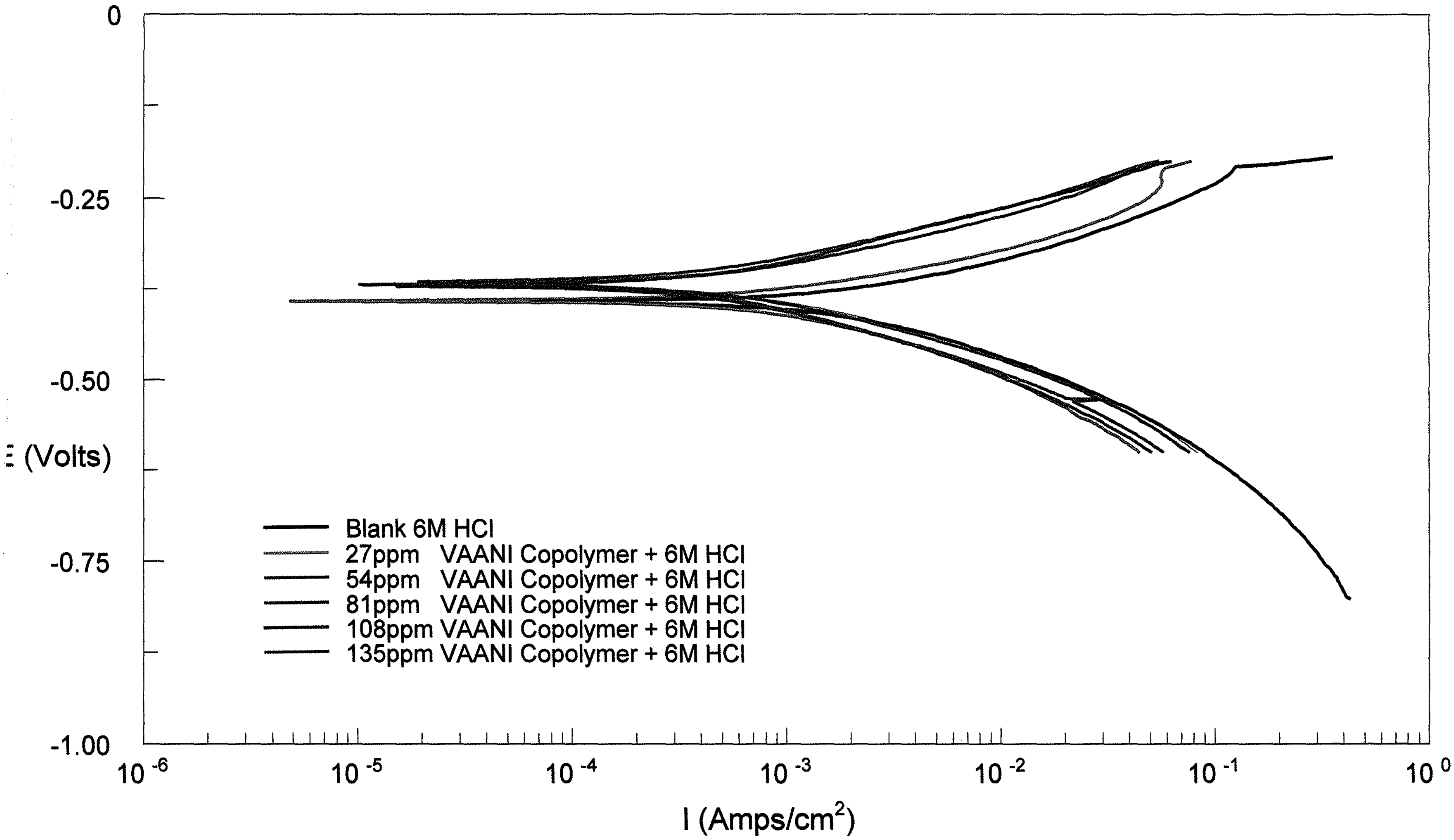


**FIGURE – 30**

**Electrochemical polarization plots for 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 concentration of the VAANI copolymer are shown in the figure 31. The semicircles obtained in the present system are not perfect semicircles and these 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 change 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 i.e., the radius of the semicircle is found to increase with increase in concentration of the inhibitor and this indicate the dissolution of the metal and the corrosion of MS is controlled by charge transfer process.

Maximum inhibition efficiency of VAANI Copolymer on mild steel surface was found to be 71% at 135 ppm concentration.

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

$C_{dl}$ 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

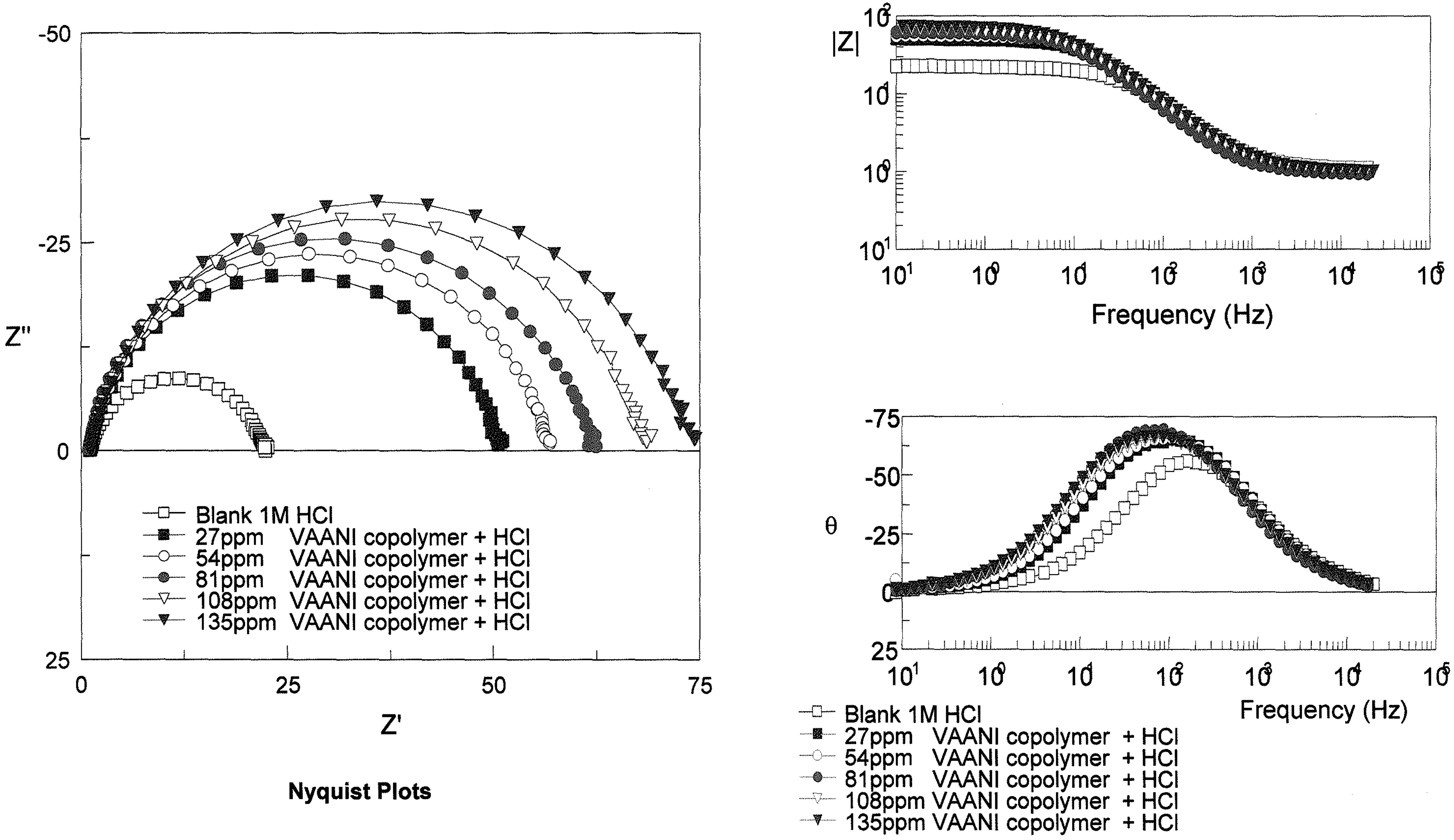
| S.NO | Conc. (ppm) | $R_{ct}$ (ohms) | $C_{dl} \times 10^{-4}$ (μ farads) |
|---|---|---|---|
| 1 | Blank | 21 | 2.25 |
| 2 | 27 | 50 | 2.29 |
| 3 | 54 | 56 | 2.37 |
| 4 | 81 | 61 | 3.12 |
| 5 | 108 | 67 | 2.62 |
| 6 | 135 | 73 | 2.85 |

## 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) | $C_{dl} \times 10^{-4}$ (μ farads) |
|---|---|---|---|
| 1 | Blank | 16 | 6.53 |
| 2 | 27 | 47 | 4.43 |
| 3 | 54 | 44 | 5.67 |
| 4 | 81 | 39 | 7.01 |
| 5 | 108 | 34 | 8.37 |
| 6 | 135 | 33 | 9.80 |

FIGURE – 31

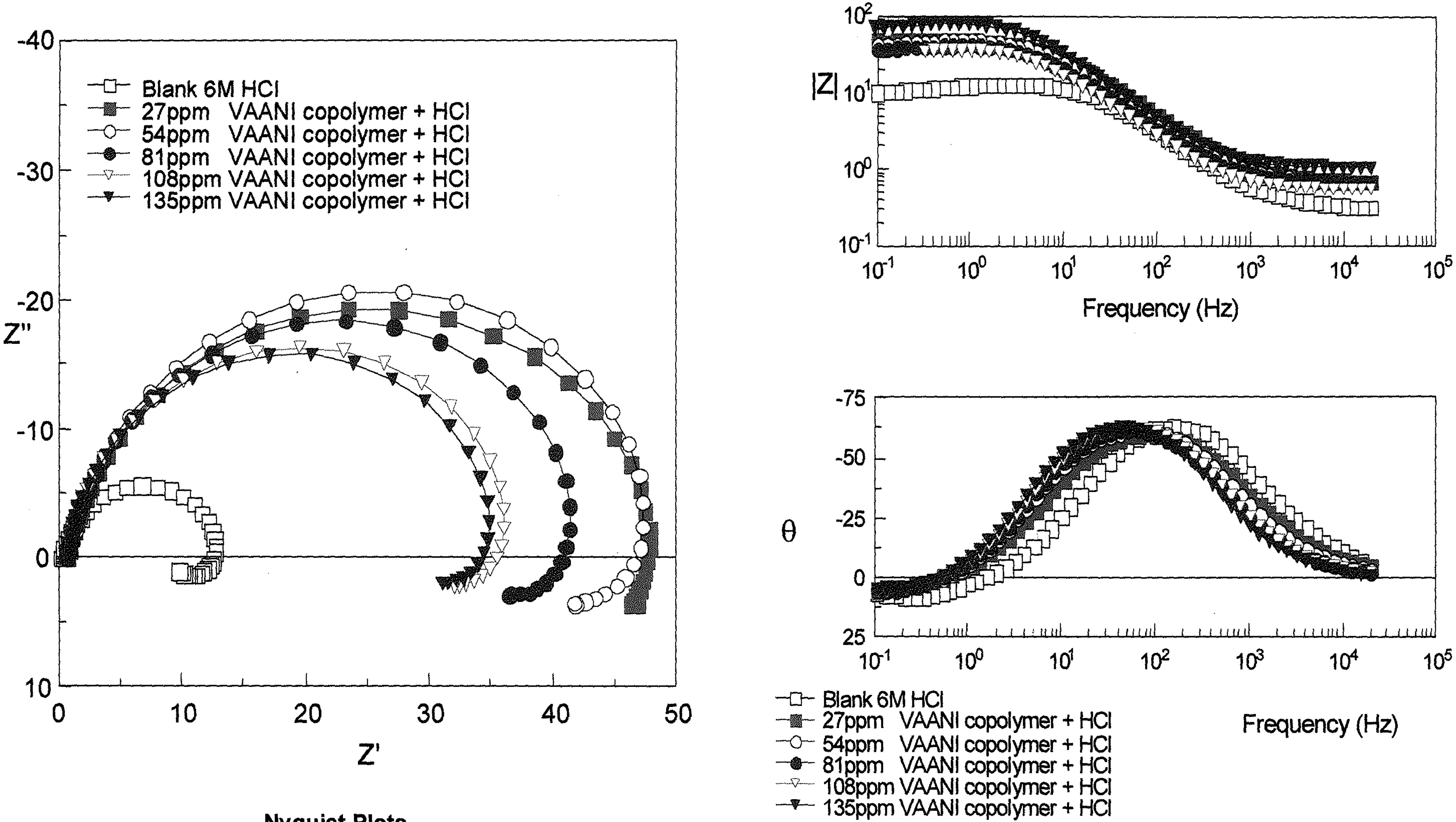


**Nyquist Plots**

**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 $\pi$-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 **Hacherman et al**. 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 Results on SS in 6M HCl

EIS studies were carried out for the system VAANI Copolymer in 6M HCl 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 15. The Nyquist plots pertaining to this system is given in the figure 32.

In SS / electrolyte interface solution the $R_{ct}$ values increase 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 16 ohms to 33 ohms and the capacitance values are in the range of $6.53 \times 10^{-4}$ $\mu$ farads to $9.80 \times 10^{-4}$ $\mu$ farads.

The high resistance values and low capacitance values indicate the highly protective nature of VAANI Copolymer. It has been reported that VAANI Copolymer containing alkyal and vinyl based polymers are able to protect more than 50 hrs 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. Oxalic acid and PVA were used as received.

The polymerization of Aniline and PVA was carried out by sweeping the potential region between -0.6V to +0.5V at dE / dt = 50mvs$^{-1}$ for MS and potential range between -0.3V to +0.8V at dE / dt = 50mVs$^{-1}$ for SS. The growth of VAANI Copolymer took place on the MS and SS were 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 MS and SS. 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 and 34 predict the cyclic voltammogram of MS / SS in acid medium.

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

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- The aniline oxidation peak potential shifts towards negative potentials with increasing number of sweeps.
- The current associated with the polymeric film creation rises with increasing number of cycles.
- 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.

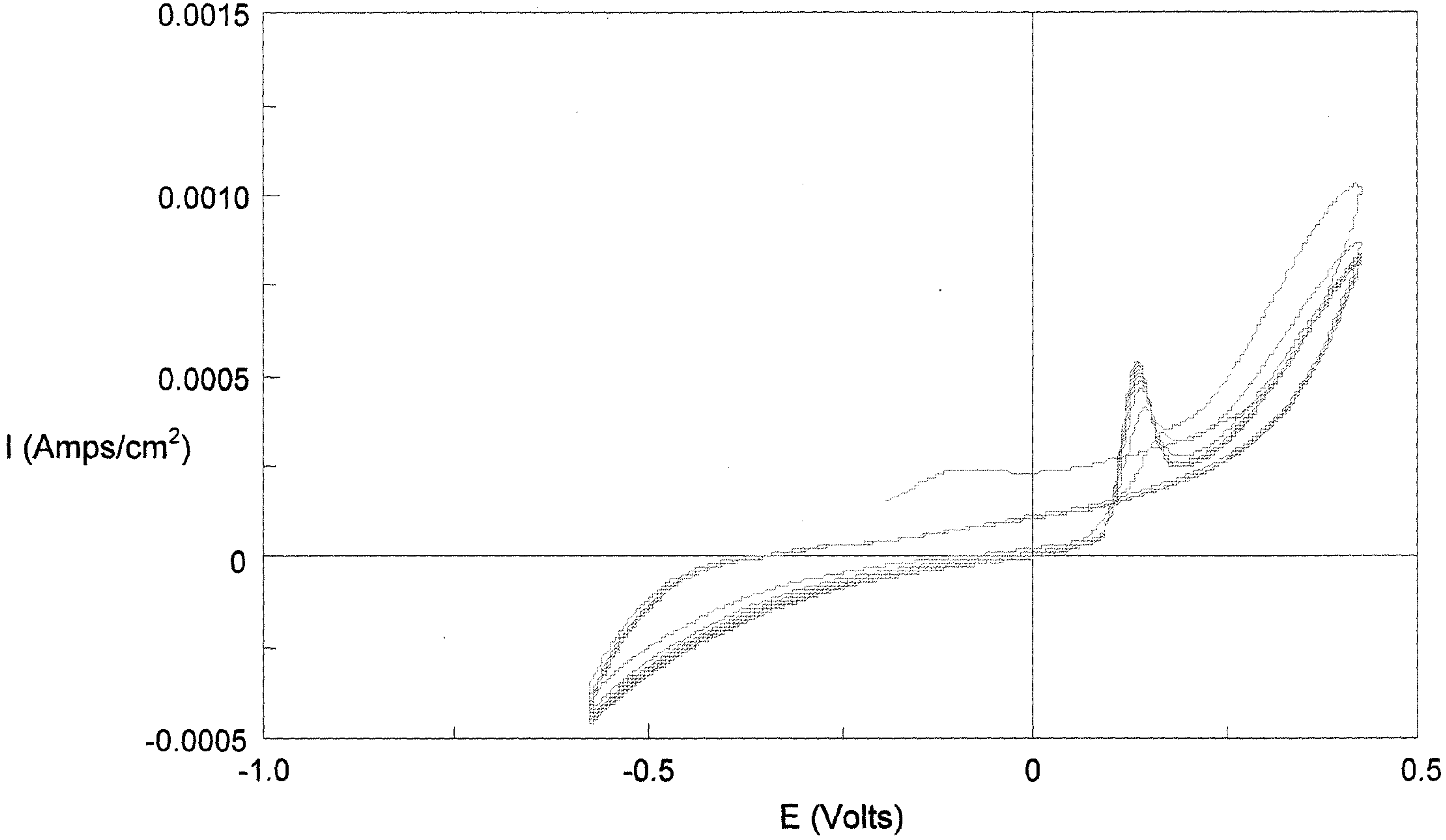


**FIGURE – 33**
**Cyclic Voltommogram of VAANI Copolymer on MS in Oxalic Acid**

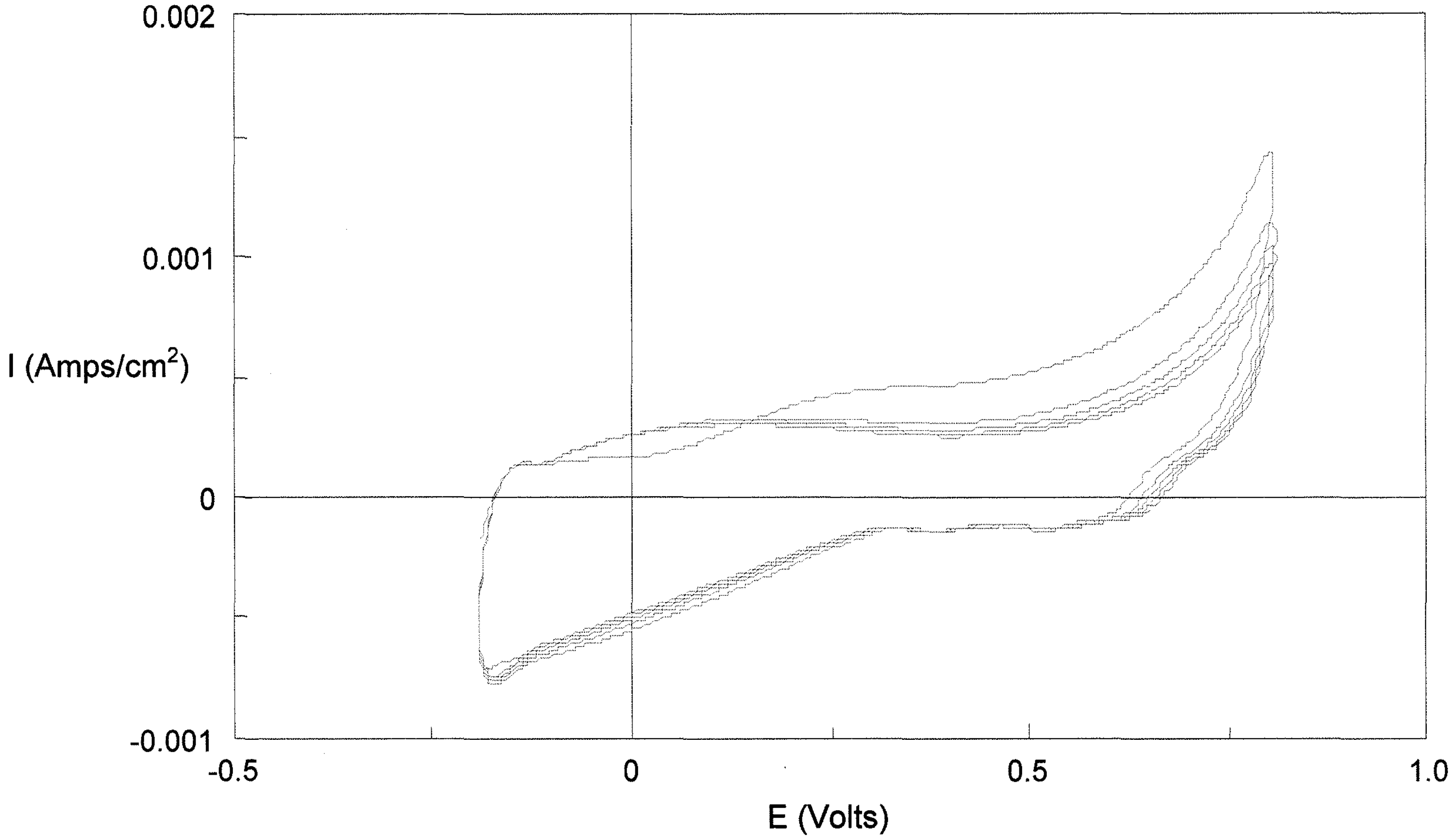


**FIGURE – 34**
**Cyclic Voltommogram of VAANI Copolymer on SS in Oxalic Acid**

From the reports 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 vinyl alcohol in oxalic acid medium was successfully carried out by electro polymerization using voltagrame.

The growth of the copolymer formation was also confirmed from the voltammogram obtained.

Similar voltammogramm 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 MS and SS by weight loss method, temperature studies and electrochemical measurements are represented in the figures 35, 36 and 37.

## Surface Analysis

### Optical Electron Micrograph

The morphological characteristic of the VAANI Copolymer was examined by using optical electron micrograph. Figures 38 and 39 shows optical electron micrograph of the VAANI Copolymer deposited on the iron surface / SS surface in hydrochloric acid for 6 hrs. From the figure we understand that a larger amount of polymer molecules deposited on the metal surface.

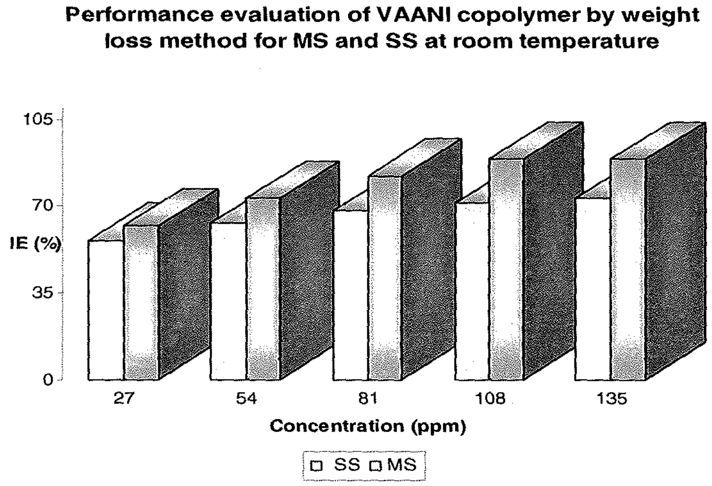


FIGURE – 35

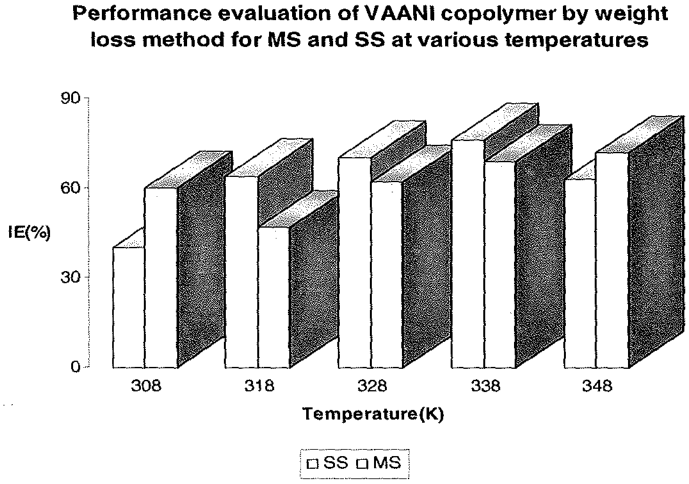


FIGURE – 36

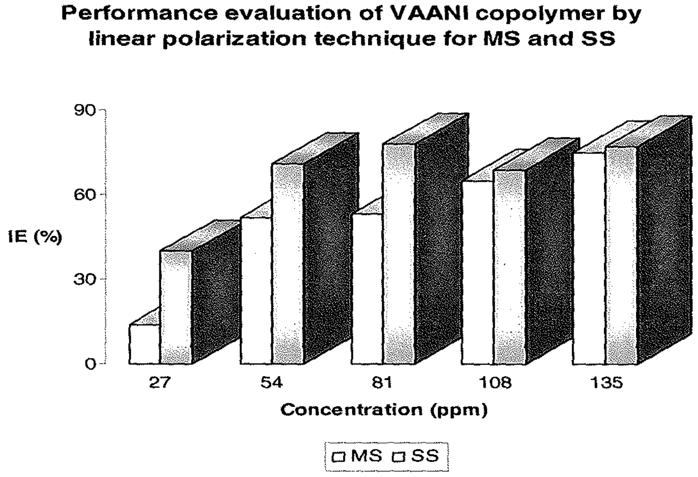


FIGURE – 37

## 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.

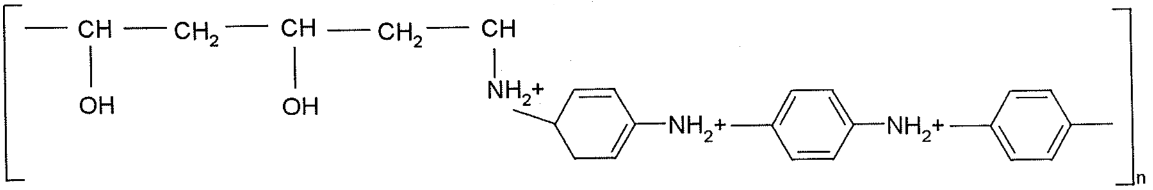
Quaternary ammonium salts finds relevant support in the foot that they have been extensively used as corrosion inhibitors **(Friginani et al., (1991, 1985))**.

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 HCl 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 ⁻s 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 VAANI Copolymer and to a lesser extent with PANI 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 PANI for water has motivated many groups to investigate the compatibility of PANI with water soluble polymers such as polyvinyl alcohol and carboxy methyl cellulose. In this direction the synthesis of VAANI Copolymer is prepared and utilized.

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 oxalic 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 effectiveness 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 weight loss 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 89% and 73% at 6hrs of immersion.
- Generally the effectiveness of VAANI Copolymer on MS and SS increases with increase in temperature indicating the stability of the copolymer 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 results of strong adsorption of inhibitor on surface of the electrodes.
- Potentiodynamic electro polymerization of VAANI Copolymer in oxalic acid solution leads to the formation of protective layer on Fe. The presence of aniline monomers in oxalic 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 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 shifts 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 electro polymerization techniques.
- 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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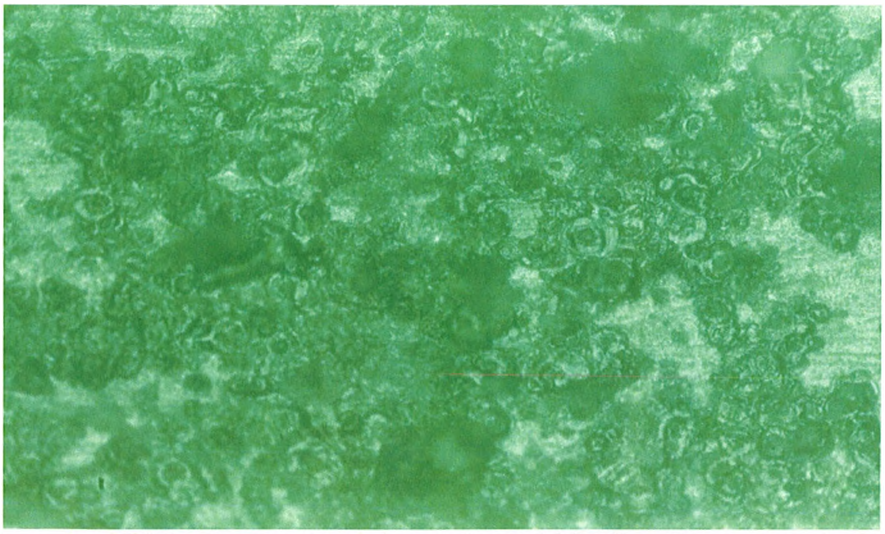
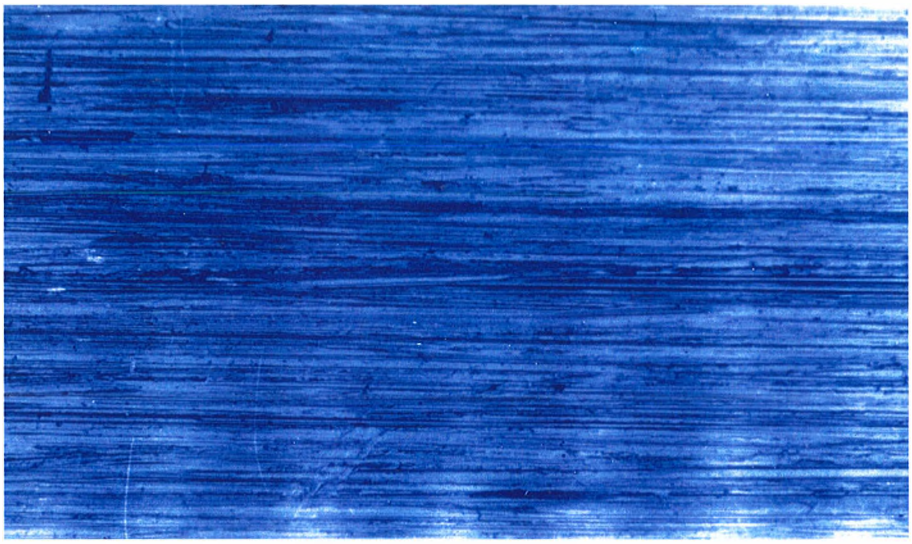
MS – Polished Surface

MS – In the Absence of VAANI Copolymer

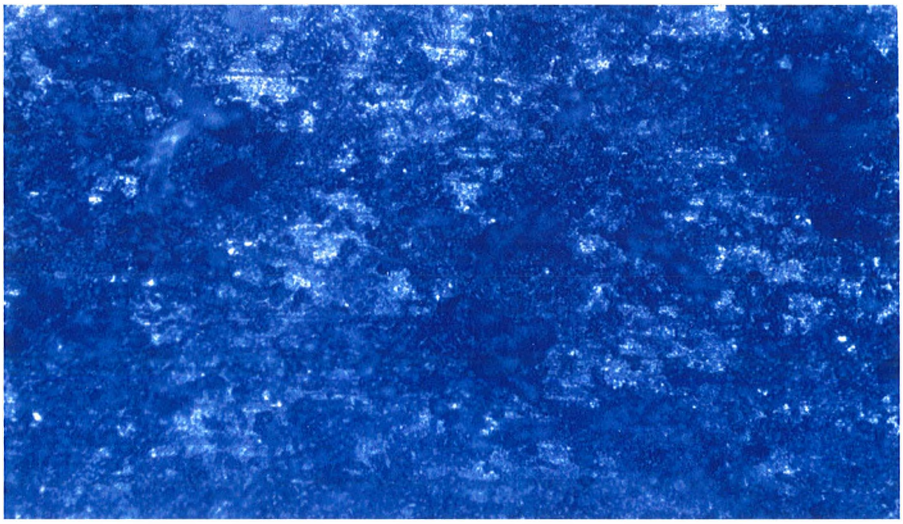


MS – In the Presence of VAANI Copolymer

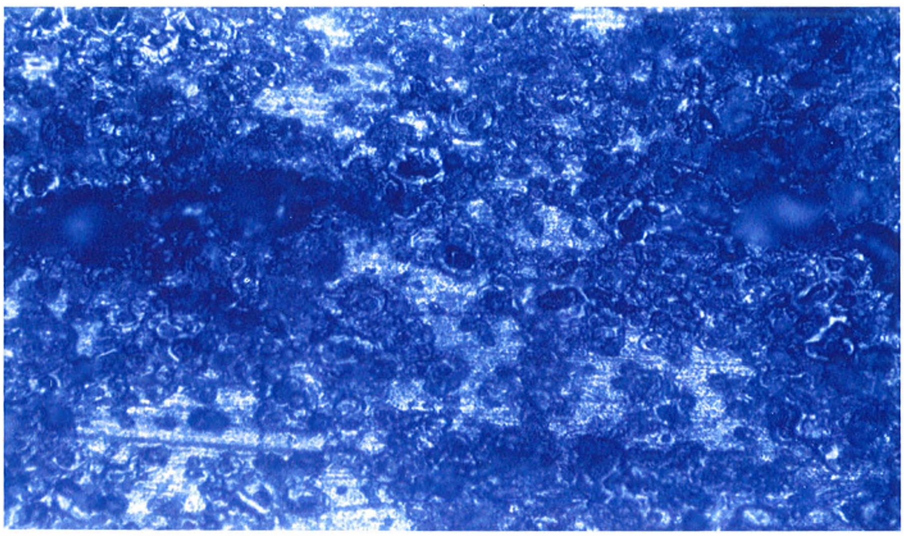
FIGURE – 38
OPTICAL MICROGRAPH OF MS EXPOSED FOR 6 hrs IN 1M HCl



**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**