PART IV

CORROSION INHIBITION STUDIES OF SCHIFF BASES ON MILD STEEL
CHAPTER 1
INTRODUCTION

Aggressive acid solutions are extensively used in the industries for manufacturing processes and other applications like acid pickling, acid cleaning, acid de-scaling and oil well cleaning\(^1\). Metals which are subjected to painting, enameling, galvanizing, electroplating, phosphate coating, cold rolling etc. must have a clean surface free from salt or oxide scaling. To remove unwanted scale such as mill scale rust, the metal is immersed in an acid solution known as acid pickling bath. The most commonly used acids in industrial process are hydrochloric acid, sulphuric acid, nitric acid, hydrofluoric acid, citric acid, formic acid, acetic acid etc. Hydrochloric acid is extensively used in the pickling baths because of its easy economic regeneration from the depleted pickling solution. The use of acids makes the industrial pipe lines and metal vessels to corrode and there by reducing the production and causing economical loss.

Corrosion inhibitor

A corrosion inhibitor is a substance which when added in small quantities to a corroding medium brings about an appreciable reduction of the corrosive action. Corrosion inhibitors are commonly added in small amounts to acids, cooling waters, steam and other environments, either continuously or intermittently to prevent serious corrosion. The selection of suitable inhibitor
depends on the type of acid, its concentration, temperature, flow velocity, the presence of dissolved inorganic or organic substance and type of metallic material exposed to the acid solution.

Corrosion is an electrochemical phenomenon and inhibitors decrease the velocity of electrochemical electrode reactions\(^2,3\). Depending upon the mechanism of their action corrosion inhibitors are classified as anodic inhibitors, cathodic inhibitors and organic or mixed type inhibitors. Anodic inhibitors are substances, which reduce the anode area by acting on the anodic sites and polarize the anodic reaction and displace the corrosion potential in the positive direction. Chromates, nitrates, tungstate, molybdates are some examples of anodic inhibitors.

Cathodic inhibitors reduce the cathode area by acting on the cathodic sites and polarize the cathode reaction and displace the corrosion potential in the negative direction. They reduce corrosion current and thereby retard the cathodic reaction and suppress corrosion rate. Examples for cathodic inhibitors are phosphates, silicates and borates.

Substances which affect both cathodic and anodic reaction are called mixed inhibitors. In general these are organic compounds, which are also known as organic or adsorption type inhibitors, which absorb on the metal surface and suppress metal dissolution and reduction reaction. Organic inhibitors affect the entire surface of the corroding metal when present in sufficient concentration. Both the anodic and cathodic areas are probably
Schiff bases as corrosion inhibitors in acid solutions – A review

Compounds containing functional groups with hetero atoms, which can donate lone pair of electrons, are found to be very efficient as inhibitors against metal corrosion in many environments. Many N-heterocyclic compounds with polar groups and/or π electrons are also acting as efficient corrosion inhibitors in acidic solutions. Schiff base, an organic compound which has both these features combined in one molecule, will be a potential inhibitor. Schiff bases have been previously reported as effective corrosion inhibitors for steel, copper and aluminum in acid medium like hydrochloric acid, sulphuric acid, acetic acid, formic acid etc.\textsuperscript{4-26}.

Emregul and Atakol\textsuperscript{4} studied the corrosion inhibition efficiency of Schiff base compounds N-(2-hydroxyphenyl)salicyaldimine, N,N'-bis-(salicyaldehyde)-1,3-diaminopropane, N,N'-bis-(2-hydroxybenzyl)1,3-diaminopropane on iron in 1M HCl using weight loss, polarization and electrochemical impedance spectroscopy (EIS) techniques. All these Schiff bases act as good inhibitors and among the three compounds N,N'-bis-(2-hydroxybenzyl) 1,3-diaminopropane showed maximum inhibition efficiency. Sorkhabi et al.\textsuperscript{5} determined the inhibition efficiency of pyridinimic Schiff bases, benzilidene-pyrimidine-2-yl-amine, (4-methyl-benzilidene)–pyrimidine-2-yl-amine, (4-
chloro-benzilydene)-pyrimidine-2-y1-amine towards mild steel (MS) in 1M HCl medium by weight loss and electrochemical polarization methods. These results reveal that these compounds act as good corrosion inhibitors even at very low concentrations and adsorption followed Langmuir isotherm.

In terms of molecular parameters, Lukovits\(^6\) explained the variation in the inhibition efficiency of thiosemicarbazide and thiosemicarbazones derivatives using quantitative structure activity relationships (QSAR). It was found that in the studied series of thiosemicarbazide and thiosemicarbazone derivative corrosion inhibition efficiency depends on the \(E_{HOMO}\) and the dipole moment, or alternatively, on the minimal electronic excitation energy. Rehim et al.\(^7\) have tested 4-amino antipyrine (AAP) for the corrosion inhibition of MS in 2M HCl using weight loss, potentiodynamic polarization and EIS methods. The results showed that AAP is an inhibitor for MS and the inhibition was assumed to take place via adsorption of the inhibitor molecule on the metal surface.

Quraishi and co-workers\(^8\) investigated the influence of three macrocyclic compounds on corrosion of MS in HCl using weight loss method, potentiodynamic polarization, AC impedance and hydrogen permeation techniques. All the investigated compounds showed significant efficiencies and reduced permeation of hydrogen through MS in HCl. Potentiodynamic polarization results reveal that macrocyclic compounds acted as mixed inhibitors.
The influence of pyridinium chloride (PC) and n-hexadecylpyridinium chloride (HDPC) on the corrosion of MS in 5N HCl and 5N H$_2$SO$_4$ has been studied using weight loss, gasometric, linear polarization, potentiodynamic polarization, and small amplitude cyclic voltametric techniques. It was found that HDPC is more inhibitive than PC and both compounds perform better in H$_2$SO$_4$. The corrosion inhibition on SS 400 by Schiff base compounds derived from diamines and o-hydroxy, o-methoxy aromatic aldehyde was investigated by weight loss, electrochemical measurements and surface analysis in various aqueous solutions such as tap water, concentrated tap water and HCl solutions by Shokry. It was found that 93% inhibition efficiency was achieved for N,N'-bis(salicyladehyde)-1,12-diaminododecane and adsorption obeyed Langmuir isotherm.

Dadgarnezhad et al. synthesized new tetradendate Schiff base, bis-(2-hydroxy-1-naphthaldehyde)1,6-hexadiamine and studied its corrosion inhibition on carbon steel in 1M HCl and 0.5M H$_2$SO$_4$ using EIS, polarization curves and weight loss techniques. Potentiodynamic polarization tests showed that this inhibitor act as both cathodic and anodic inhibitor and efficiency of 95% was achieved for a 100 ppm concentration. The inhibitor effect of Schiff base compounds N,N'-bis-(salicylidene)-2-hydroxy-1,3-propanediamine and N,N'-bis-(2-hydroxyacetophenlidene)-2-hydroxy-1,3-propane diimine on MS in 2M HCl medium were studied using weight loss, polarization and impedance methods. The results revealed that the latter
Schiff base showed better inhibition property than the former one and both the inhibitors appear to function through the Langmuir adsorption isotherm.

Sorkhabi et al.\textsuperscript{13} have carried out the corrosion inhibition studies on MS in 1M HCl medium using the Schiff bases benzylidine-pyridine-2-yl-amine, (4-benzylidene)-pyridine-2-yl-amine and (4-chloro-benzidilene)-pyridine-2-yl-amine by weight loss measurements and electro chemical methods. Results showed that these compounds were excellent inhibitors and inhibition efficiency increased with increase in inhibitor concentration and varied with the type of functional groups substituted on benzene ring. The polarization curves reveal that compounds are mixed type inhibitors and experimentally obtained adsorption isotherms follow the Langmuir equation.

The inhibition efficiency of Schiff bases, 2-((1E)-2-aza-2-pyrimidine-2-ylvinyl)thiophene, 2-((1Z)-1-aza-2-(2-pyridyl)vinyl)pyrimidine, 2-((1E)-2-aza-2-(1,3-thiazol-2-yl)vinyl)thiophene, 2-((1Z)-1-aza-2-(2-thienyl)(vinyl)benzothiazole containing hetero aromatic substituents on carbon steel in 0.1 M HCl, using potentiodynamic polarization and EIS studies have been carried out by Yurt et al.\textsuperscript{14} Polarization studies reveal that studied Schiff bases act as anodic inhibitors. The variation of inhibition efficiency mainly depends on the type and nature of the substituents present in the inhibitor molecule and these compounds are adsorbed on the steel surface and the adsorption obeys Temkin’s isotherm. Desai et al.\textsuperscript{15} studied seven Schiff bases as corrosion inhibitors for MS in HCl solutions by weight loss and electrochemical
methods. Polarization data indicate that all these compounds act as predominantly cathodic inhibitors.

Quraishi and Sardar\textsuperscript{16} have synthesised organic compounds like 5-mercapto-3-butyl-4-salicylidine-1,2,4-triazole (MBST), 5-mercapto-3-butyl-4-benzilidineiminio-1,2,4-triazole (MBBT) and 5-mercapto-3-butyl-4-cinnamylidineiminio-1,2,4-triazole (MBCT) and investigated their corrosion inhibition capacity on MS in 1N HCl and 1N H\textsubscript{2}SO\textsubscript{4} by weight loss and potentiodynamic polarization techniques. Inhibition efficiency was found to vary with respect to temperature, concentration and immersion time. The adsorption of these compounds on the steel surface for both acids was found to obey Temkin’s adsorption isotherm. The potentiodynamic polarization data have shown that compounds studied are mixed type inhibitors.

The inhibition capacity of Schiff bases, 2-hydroxyacetophenone-etansulphonylhydrazone, salicyldehyde-etansulphonylhydrazone, 5-bromo salicyldehyde-etansulphonylhydrazone and 5-chlorosalicylaldehyde-etansulphonylhydrazone on AA3102 aluminum in 0.1M HCl by means of hydrogen evolution tests and EIS technique have been carried out in 2004\textsuperscript{17}. Maximum efficiencies were obtained for third and fourth Schiff bases because they have electronegative atoms like chlorine and bromine as para substituents on phenol ring.

Bansiwal et al.\textsuperscript{18} conducted weight loss and thermometric methods to study the inhibition of aluminum corrosion in HCl solution by four Schiff
bases such as 2-anisalidine-pyridine, 2-anisalidine-pyrimidine, 2-salicylidine-
pyridine, 2-salicylidine-pyrimidine and have shown that they are effective
inhibitors for the corrosion of aluminum in HCl. Desai et al.\textsuperscript{19} carried out the
corrosion inhibition testing of Schiff bases derived from benzaldehyde,
aliphatic and aromatic primary amines on aluminium alloy 51S in HCl.
Schiff bases showed fairly good inhibition efficiency and conversion of an
amine into its Schiff base improved its inhibitive action.

The corrosion inhibition of copper in 0.5 M HCl by 1,3,4-thiadiazole-
2,5-dithiol(bismuthiol) using potentiodynamic polarization technique has
been reported\textsuperscript{20}. It was found that bismuthiol was chemically adsorbed on
the copper surface and follows Langmuir isotherm. Li and co-workers\textsuperscript{21}
examined inhibiting effect of Schiff base N, N'-O-phenylen-bis(3-methoxy
salicyaldenimine) on corrosion of copper in 1.0 M HCl and NaCl solutions
using potentiostatic polarization and EIS techniques. The results show a
remarkable decrease in the corrosion rate in the presence of Schiff base.

Fouda\textsuperscript{22} investigated the inhibition action of semicarbazide, thiosemi-
carbazide and diphenylcarbazide towards corrosion of zinc in HCl using
weight loss, thermometric and polarization techniques. From the weight loss
measurements it was observed that the rate of corrosion depends on the nature
of inhibitor and its concentration. The polarization studies reveal that these
inhibitors act as mixed type inhibitors. The increase in adsorption is due to
electron density at the reactive C=S and C=O groups and N atoms.
Corrosion inhibition of Zinc on HCl using *Nypa Fruticans Wurmb* extract and 1,5 Diphenylcarbazone were tested by Okorosaye et al.\textsuperscript{23} using weight loss technique. Maximum inhibition efficiency was obtained at an optimum concentration. The corrosive behaviour of Zinc in HCl solution containing various concentrations of glutaraldehyde, glycine, methionine and their condensation products formed between was examined using chemical and electrochemical methods by Rajappa et al.\textsuperscript{24}. The condensation product of glutaraldehyde and methionine acted as cathodic inhibitor showing an efficiency of 92.5\% and adsorption followed Temkin isotherm.

Hosseini et al.\textsuperscript{25} have synthesised and studied corrosion inhibition efficiency of Schiff bases N,N'-ortho-phenylene(salicylaldimine-acetyl acetoneimine) and N,N'-ortho-phenylene(salicylaldimine-2-hydroxy-1-napth aldime) on MS in 0.5M H\textsubscript{2}SO\textsubscript{4} using weight loss, polarization and EIS techniques. These compounds achieved 95\% efficiency at a concentration of 400 ppm and identified both compounds as good inhibitors.

Quraishi et al.\textsuperscript{26} have investigated the inhibition efficiency of three Schiff bases 1-vanillinthiosemicarbazone, 1-salicyaldehyde thiocarbazone, 1-dimethyl aminobenzaldehyde thiosemicarbazone towards MS in aqueous solutions containing 20\% formic and 20\% acetic acid media by weight loss and potentiodynamic polarization methods. These compounds acted as mixed inhibitors and shown good inhibition efficiency in formic acid solutions.
**Scope of present investigation**

Organic compounds are used to control the corrosion of MS in acid solutions. Due to the presence of the -C=N group, an electron cloud on the aromatic ring, the electronegative N,O and S atoms in the molecule, Schiff bases may be good corrosion inhibitors. As part of our study four new Schiff bases have been synthesised. The corrosion inhibition studies of these Schiff bases on MS in HCl are not yet reported. Taking into consideration of above factors, the inhibition efficiency studies of four Schiff bases towards MS in 1M HCl are investigated using weight loss and electrochemical methods. An adsorption isotherm which describes the adsorptive behaviour of a corrosion inhibitor provides important clues to the nature of metal inhibitor interaction for the inhibition process. Assignment of suitable adsorption isotherms for the corrosion inhibition of MS in the presence of Schiff bases is also attempted.
The corrosion inhibition efficiency of Schiff bases was determined using weight loss measurements and electrochemical methods like potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The method of determining the weight loss of metal coupons exposed to the corrosive environment using laboratory immersion corrosion testing method is the traditional and most widely used method for in situ corrosion monitoring\textsuperscript{3,27}. As a classical corrosion test method, the weight loss coupon method has provided a great deal of useful information.

**Materials**

**Preparation of inhibitor solution**

Schiff bases FTSC, FATP, FAP and FSC were prepared by the methods described in the Part I and employed for the corrosion inhibition studies. The molecular structures of the Schiff bases FTSC, FSC, FAP and FATP are also given in the Part I. 1M HCl solution is used as the test solution (corrodent) and is prepared from the reagent grade HCl (E-Merck) using deionised water. 0.0001M, 0.0002M, 0.0004M, 0.001M, 0.002M, 0.003M, 0.004M and 0.008M solutions of inhibitor solution were employed for inhibition studies and were prepared by dissolving the required amount of the FTSC, FATP, FAP and FSC in 50 ml of 1M HCl by stirring at room
temperature. 50 ml of 1 M HCl without inhibitor is considered as blank test solution.

**Preparation of test specimens**

The MS having 99.22% Fe, 0.019% Mn, 0.28% Ni and 0.30% carbon as determined by the chemical analysis using Philips PW 2400 model X-ray fluorescence spectrophotometer were selected as test samples for corrosion studies. These MS sheets were cut into coupons having 1cm x 1cm x 0.1cm size using a LeCo VC-50 diamond wheel cutting machine and polished with different grade emery papers (120, 220, 400, 600, 800, 1500 and 2000 grade) to mirror polish. Then these coupons were washed with methanol, acetone and distilled water, dried and weighed using electronic balance having 0.0001g accuracy. The exposed area of the MS coupons was found out using Vernier calipers.

**Methods**

In laboratory immersion corrosion testing method, the metal coupons are exposed to the corrosive environment like acid solutions and weight loss of the metal coupons are measured at regular time intervals and corrosion rate is calculated from the weight loss measurements. The inhibition capacity of the inhibitor is calculated from the corrosion rates. In the present investigation, American Society for Testing and Materials (ASTM) G31-72 standard procedure for laboratory immersion corrosion testing published in
the year 1990 was adopted for the determination of weight loss and corrosion rate of MS coupons in HCl$^{28,29}$

The polished MS coupons were immersed in hanging position in 50 ml of test solution taken in stoppered glass bottles with the help of a fishing line at room temperature (30°C). The specimens were taken out in 24 hours interval, cleaned with acetone and water, dried and weighed. The weight loss of these coupons immersed in the 1M HCl was recorded for a consecutive seven days period.

The corrosion rate (CR), expressed in millimeter per year (mmY$^{-1}$), is calculated using the equation (1)

$$CR(\text{mmY}^{-1}) = \left[ \frac{(87600)(\text{Weight loss in grams})}{(\text{Area in cm}^2)(\text{Time in hours})(\text{Density of coupon in g/cc})} \right]$$ (1)

The density of the coupon is substituted with density value of iron i.e. 7.88g/cc. The percentage inhibition efficiency (\(\eta W_L \%)\) of a corrosion inhibitor is calculated from the corrosion rate values using the equation (2)

$$\eta W_L = \left[ \frac{(W - W')}{W} \times 100 \right]$$ (2)

where $W$ and $W'$ is the corrosion rate of the MS coupons in the absence and presence of inhibitor respectively$^4$. The surfaces of the MS coupons were examined using Olympus Japan make BX 51 model optical microscope.
Electrochemical methods for corrosion rate measurement

Most corrosion phenomena are of electrochemical nature and consist of reactions on the surface of the corroding metal. Therefore electrochemical test methods can be used to characterise corrosion mechanism and predict corrosion rates. Electrochemical methods are used routinely for the evaluation of the efficiency of corrosion inhibitors\textsuperscript{30,31}. The advantages of electrochemical methods are short measurement time and mechanistic information that they provide which help not only in the design of corrosion protection strategies but also in the design of new inhibitors.

When a metal is immersed in a given solution, electrochemical reactions characteristic of the metal solution interface occur at the surface of the metal, assuming the metal to corrode. These reactions create an electrochemical potential called the corrosion potential $E_{\text{corr}}$ or open circuit potential at the metal solution interface. At the $E_{\text{corr}}$ the rate of oxidation process is equal to rate of reduction. At $E_{\text{corr}}$ the system is electronically neutral and said to be at equilibrium. The value of either the anodic or cathodic current at $E_{\text{corr}}$ is called corrosion current $i_{\text{corr}}$.

Calculation of corrosion rates requires determination of corrosion currents. The corrosion rate is decided by the current produced in the oxidation and reduction reactions. The amount of current is controlled by the kinetics of the reactions and the diffusion of reactants both towards and away from the electrode. The measurement of corrosion rate is actually equivalent
to the determination of kinetics of the corrosion electrochemical process. The common electrochemical techniques used for the determination of corrosion rates and the characterisation of corrosion systems are potentiodynamic polarization and electrochemical impedance spectroscopy.

**Potentiodynamic polarization method**

The theoretical model used for the corrosion process assumes that the electrochemical corrosion is an activation controlled process. In activation controlled process, an activation controlled reaction is involved for which the rate of reaction is controlled solely by the rate of the electrochemical charge transfer process at the metal surface.

**The Butler-Volmer equation**

The fundamental formula describing the kinetics of an electrochemical reaction is the Butler-Volmer equation developed by Butler and Volmer\(^{30,31}\). The relationship between current density and potential of anodic and cathodic electrode reactions under charge transfer control is given by the Butler–Volmer equation as shown in the equation (3)

\[
\eta = \frac{RT}{nF} \left( \exp \left( \frac{\alpha n F}{RT} \eta \right) - \exp \left( - \frac{\beta n F}{RT} \eta \right) \right)
\]

\[i = i_{\text{corr}} \left[ \exp \left( \frac{\alpha n F}{RT} \eta \right) - \exp \left( - \frac{\beta n F}{RT} \eta \right) \right]
\]

where \(\eta\) is the over potential defined as the difference between applied potential \(E\) and corrosion potential \(E_{\text{corr}}\), \(\eta = E - E_{\text{corr}}\), \(i\) is the measured current density, \(i_{\text{corr}}\) is the corrosion current density, \(F\) is Faraday’s constant, \(R\) is the
Universal gas constant, T is the absolute temperature, n and n' are the number of electron transferred in the anodic and cathodic reactions, and $\alpha$ and $\beta$ are coefficients related to the potential drop through the electrochemical double layer. While the Butler-Volmer equation is valid over the full potential range, for practical applications to calculate the electrochemical corrosion current, it has to be simplified for more restricted ranges of potential. The two most commonly used simplified forms of the Butler–Volmer equation are Tafel equation and the Stern–Geary equation.

### The Tafel Equation and Tafel plots

The Tafel equation was first found empirically by Tafel in 1905. This can be deduced from the equation (3) for sufficiently high values of applied potential. As over potentials, either positive or negative, become larger than about $5 \times 10^{-2} \text{V}$, the second or the first term of Butler-Volmer equation becomes negligible, respectively.

For anodic polarization, when $\eta >> \frac{RT}{\beta n'F}$, the following equation are obtained.

$$i = i_{\text{corr}} \left[ \exp \left( \frac{\alpha nF}{RT} \eta \right) \right]$$

or, for cathodic polarization, when $-\eta >> \frac{RT}{\alpha nF}$
\[ i = i_{\text{corr}} \left[ \exp \left( \frac{-\beta n F}{RT} \eta \right) \right] \]  
\hspace{1cm} (6)

\[ i.e., -\eta = -\frac{2.303RT}{\beta F} \log i_{\text{corr}} + \frac{2.303RT}{\beta F} \log i \]  
\hspace{1cm} (7)

The equations (5) and (7) have the form of Tafel equation as shown in the equation (8)

\[ |\eta| = a + b \log i \]  
\hspace{1cm} (8)

where \( a \) and \( b \) are constants, \( a = -\frac{2.303RT}{\alpha F} \log i_{\text{corr}} \) and \( b = \frac{2.303RT}{\alpha F} \) for anodic polarization or \( a = -\frac{2.303RT}{\beta F} \log i_{\text{corr}} \) and \( b = \frac{2.303RT}{\beta F} \) for cathodic polarization.

Hence, simple exponential relationships between current i.e. rate and over potential are obtained, or the over potential can be considered as logarithmically dependent on the current density.

A plot of electrode potential versus the logarithm of current density is called the "Tafel plot" and the resulting straight line the "Tafel line". The slope of a Tafel plot, “b”, provides information about the mechanism of the reaction. The intercept “a” at \( \eta = 0 \) gives the exchange current density \( i_0 \) and provides information about the rate constant of the reaction. This type of analysis is referred to as Tafel slope analysis. The percentage inhibition efficiency is calculated using the corrosion current densities using the relation,
where \( i_{\text{corr}} \) and \( i'_{\text{corr}} \) are uninhibited and inhibited corrosion current densities respectively\(^{5,25}\).

**Electrochemical impedance spectroscopy (EIS)**

Electrochemical impedance spectroscopy is a powerful technique for the characterisation of electrochemical systems and provides a wealth of kinetic and mechanistic information. For this reason this technique is being applied to an increasing extent to understand corrosion process in solution, to study rate determination, inhibitor performance, coating performance and passive layer characteristics\(^{33-39}\).

Impedance, \( Z \), is a measure of a circuit’s tendency to resist (or impede) the flow of an alternating electrical current. The EIS instrument records the real (resistance) and imaginary (capacitance) components of the impedance response of the system. In EIS measurements, frequency dependent impedance \( Z(\omega) \) is obtained by applying a sinusoidal alternating potential signal to test system in a range of frequencies. The expression for \( Z(\omega) \) is as follows

\[
Z(\omega) = \frac{V(t)}{I(t)} = \frac{V_0 \sin \omega t}{I_0 \sin(\omega t + \theta)} = Z'(\omega) + jZ''(\omega) \tag{10}
\]
where \( \omega = \) frequency, \( t= \) time, \( V(t) = \) sinusoidal alternating potential signal, \( V_0 \sin \omega t \), \( t = \) time dependent current response, \( I_0 \sin (\omega t + \theta) \), and \( \theta = \) phase angle between \( V(t) \) and \( I(t) \).

Impedance is given by a complex number with real \( Z'(\omega) \) and imaginary \( Z''(\omega) \) component as given in the equation (11)

\[
Z(\omega) = Z'(\omega) + jZ''(\omega)
\]  

(11)

where \( j = \sqrt{-1} \).

EIS applies very small voltages generally in the range of 5 to 10mV between a specimen and a reference electrode. A typical electrochemical impedance experimental set up consists of an electrochemical cell (the system under investigation), a potentiostat/galvanostat, and a frequency response analyzer (FRA). The FRA applies the sine wave and analyses the response of the system to determine the impedance of the system.

When the impedance is measured at a number of frequencies and is plotted on the Cartesian axes, the resulting plot is called a Nyquist plot some time referred as Cole–Cole plot or a Complex plane plot with \( Z'(\omega) \) versus \( Z''(\omega) \) is obtained as shown in the figure 4.2.1. In the figure 4.2.1 \( R_\Omega \) is the uncompensated resistance between the working electrode and reference electrode or solution resistance, \( R_p \) is the polarization resistance at the electrode/solution interface. At high frequencies, the impedance of the system is almost entirely created by the ohmic resistance (solution resistance) \( R_\Omega \). The frequency reaches its high limit at the leftmost end of the semicircle,
where the semicircle touches the x axis. The frequency reaches its low limit at the rightmost end of the semicircle.

**Figure 4.2.1 A typical Nyquist plot for a simple corrosion of metal**

Polarization resistance is correlated unequivocally to the corrosion current density in the relatively simple corrosion systems characterised by a charge transfer controlled process\(^4\). Since \(R_p\) is inversely proportional to the corrosion current it can be used to calculate the inhibitor efficiency from the relation

\[
\eta_{\text{EIS}} \, \% = \frac{R_p - R_p'}{R_p} \times 100 \tag{12}
\]

where \(R_p\) and \(R_p'\) denote polarization resistance of electrode with and without inhibitor respectively\(^4\).
Equivalent circuit model

The characterisation of electrochemical systems with impedance spectroscopy requires the interpretation of the data with the help of suitable models. These models can be divided into two broad categories, equivalent circuit model and process model. These models are regressed to experimental data to estimate parameters that can describe the experimental data adequately and can be used to predict the behaviour of the system under various conditions. Electrochemical systems such as coated surfaces or corroding metals often behave like simple electronic circuits. The equivalent circuit is a simple circuit which can be built from electronic parts which behaves exactly in the same manner of an electrochemical system built from electrodes and electrolytes when an alternating current is applied. These models are built with the help of well-known passive elements such as resistors, capacitors, and inductors and distributed elements such as constant phase element and Warburg impedance. These elements can be combined in series and parallel to give complex equivalent circuits and certain physical meaning is then assigned to the various elements of the equivalent circuit.37,38

Experimental set up for electrochemical measurements

The electrochemical experiments potentiodynamic and EIS were carried out using a computer controlled Autolab make Metro Ohm PGSTAT 30 model potentiostat/galvanostat having a frequency response analyzer set
up. A three electrode cell consisting of a working electrode, a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode were used for the measurements.

The polished MS coupon with an exposed area of 1cm$^2$ was used as the working electrode. 1M HCl acid was taken as electrolyte. The working electrode was immersed in the test solution for 2 hours prior to the measurements to establish a steady state open circuit potential.

The potentiodynamic polarization (Tafel plot method) curves were obtained with a scan rate of 5 mV/Sec in the potential range from -250mV to +250mV relative to the open circuit potential. All the potentials reported versus that of the SCE. Corrosion current density values were obtained by Tafel extrapolation method. The percentage inhibition efficiency is calculated using the corrosion current densities using the relation (9).

The three electrode cell and other setup used for potentiodynamic polarization were used for the EIS measurements along with a Frequency response analyzer. EIS measurements were performed at open circuit potential in the frequency range from 20 kHz to 20 mHz with a 5 mV sine wave as excitation signal.

From impedance measurements, the percentage inhibition efficiency is calculated using the expression (12).
Adsorption isotherm studies

Adsorption plays an important role in the inhibition of metallic corrosion by organic inhibitors. Adsorption isotherms are often shown to demonstrate the performance of organic adsorbent type inhibitors and important in determining the mechanisms of organic electrochemical reactions. Establishment of isotherms that describe the adsorptive behaviour of a corrosion inhibitor is an important part of its study as they can provide important clues to the nature of metal inhibitor interaction. Three types of adsorption isotherms are usually cover all the data relating to adsorption isotherms. The most frequently used adsorption isotherms are Langmuir, Temkin and Frumkin isotherms having the following surface coverage–bulk concentration relationships:

\[
\frac{\theta}{1-\theta} = KC \quad (13)
\]

\[
\frac{\theta}{1-\theta} e^{\beta} = KC \quad (14)
\]

\[
e^{\beta} = KC \quad (15)
\]

where \(\theta\) is the degree of surface coverage, \(C\) is the inhibitor concentration in the solution and \(K\) is the equilibrium constant or the molecular interaction constant, a coefficient expressing interaction between adsorbed and adsorbing molecule. The plots are usually given as \(\log \frac{\theta}{1-\theta}\) versus \(\log C\) for Langmuir.
isotherm, \( \log \frac{\theta}{C(1-\theta)} \) versus \( \theta \) for Frumkin isotherm and \( \theta \) versus \( \log C \) for Temkin isotherm. The plots which give straight line will be best suitable adsorption isotherm. The values of \( \theta \) can be calculated from the percentage inhibition efficiency values obtained from weight loss method using the following relation 25.

\[
\theta = \frac{\text{Percentage inhibition efficiency}}{100} \tag{16}
\]

**Calculation of thermodynamic parameters**

The values of activation energy for steel corrosion reaction \( (E_a) \) were obtained from Arrhenius equation. The activation energy values were calculated from the slopes of the log(corrosion rate) vs 1/T plots\(^{26,42,43} \). The equilibrium constant for adsorption process is related to the free energy of adsorption, \( \Delta G_{ads} \) by the relation

\[
\Delta G_{ads} = -RT \ln (55.5K_{ads}) \tag{17}
\]

where \( R \) is universal gas constant, \( T \) temperature in absolute scale, \( K \) is the equilibrium constant for adsorption process and 55.5 concentration of water in the solution\(^5,41 \). The \( K_{ads} \) is given by the relation

\[
K_{ads} = \frac{\theta}{(1-\theta)C_{inh}} \tag{18}
\]

where \( \theta \) is the degree of coverage on the metal surface and \( C_{inh} \) the concentration of inhibitor in mol L\(^{-1} \).
Instruments

The following instruments are used for this study.

1. Philps Netherlands make PW 2400 model X-ray fluorescence (XRF) spectrophotometer
2. LeCo VC -50 USA make diamond wheel cutting machine
3. Olympus Japan make BX 51 model optical microscope
4. Autolab make MetroOhm PGSTAT 30 model Potentiostat/Galvanostat having a frequency response analyzer set up with computer control.
CHAPTER 3
CORROSION INHIBITION STUDIES OF SCHIFF BASES ON MILD STEEL IN 1M HCl

The results of weight loss experiments and electrochemical analysis carried out to find the corrosion inhibition efficiencies of Schiff bases FTSC, FATP, FAP and FSC on MS in HCl are presented in this chapter.

Weight loss method

The weight loss occurred for the MS coupons immersed in blank, 0.0001M, 0.0002M, 0.0004M, 0.001M, 0.002M, 0.003M, 0.004M and 0.008M inhibitor solutions of Schiff bases FTSC, FATP, FAP and FSC prepared in 1M HCl solution, after 24 hours are given in table 4.3.1. The figure 4.3.1 is the photograph of MS coupons after 48 hours immersion in blank and different concentrations of FTSC inhibitor solutions. It is clear from the photograph that the coupons immersed in the inhibitor solutions were least corroded while the coupon in blank solution was severely corroded. With increase in concentration a film formation on the surface of coupons were observed. The optical microscopic images of the immersed MS coupons for 24 hours in the blank solution and 0.003M solution of FATP are given in the figure 4.3.2. The surface of the MS coupons immersed in the blank solution was completely corroded as visible in the picture 4.3.2 (a). The surface of the MS coupon immersed in the 0.003M FATP solution was
less corroded as observed in the figure 4.3.2(b) showing the inhibition capacity of the inhibitor used. The weight loss recorded in 24 hours interval for MS coupons immersed in the above eight concentrations of inhibitor solutions of FTSC, FATP, FAP, FSC and blank for seven days duration were plotted against immersion time and given in the figures 4.3.3 to 4.3.6.

<table>
<thead>
<tr>
<th>Concentration [M]</th>
<th>FTSC</th>
<th>FATP</th>
<th>FAP</th>
<th>FSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>162.66</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0001</td>
<td>35.42</td>
<td>48.47</td>
<td>63.27</td>
<td>158.53</td>
</tr>
<tr>
<td>0.0002</td>
<td>20.77</td>
<td>31.86</td>
<td>47.49</td>
<td>154.10</td>
</tr>
<tr>
<td>0.0004</td>
<td>8.77</td>
<td>24.07</td>
<td>40.48</td>
<td>149.68</td>
</tr>
<tr>
<td>0.001</td>
<td>4.55</td>
<td>12.16</td>
<td>27.43</td>
<td>74.05</td>
</tr>
<tr>
<td>0.002</td>
<td>3.48</td>
<td>12.91</td>
<td>20.32</td>
<td>54.53</td>
</tr>
<tr>
<td>0.003</td>
<td>2.14</td>
<td>5.39</td>
<td>16.77</td>
<td>39.89</td>
</tr>
<tr>
<td>0.004</td>
<td>3.27</td>
<td>3.57</td>
<td>9.76</td>
<td>38.88</td>
</tr>
<tr>
<td>0.008</td>
<td>2.36</td>
<td>2.14</td>
<td>5.23</td>
<td>26.36</td>
</tr>
</tbody>
</table>
Figure 4.3.1 Photograph of MS coupons taken out after 48 hours immersion in blank and FTSC inhibitor solutions. From left to right-blank, 0.0001M, 0.0002M, 0.0004M, 0.001M, 0.002M, 0.003M of FTSC

Figure 4.3.2 Optical microscope images of MS coupons after 24 hours immersion (a) blank and (b) 0.003 M FATP inhibitor solution
Figure 4.3.3 Comparison of weight loss occurred for MS coupons immersed in different concentrations of FTSC and blank for seven days. (The weight loss for the Blank and 0.0001M are given as insert graph)

Figure 4.3.4 Comparison of weight loss occurred for MS coupons immersed in different concentrations of FATP and blank for seven days
Figure 4.3.5 Comparison of weight loss occurred for MS coupons immersed in different concentrations of FAP and blank for seven days

Figure 4.3.6 Comparison of weight loss occurred for MS coupons immersed in different concentrations of FSC and blank for seven days
Figure 4.3.7 Comparison of weight loss of MS immersed in FTSC, FATP, FAP and FSC inhibitor solutions for 24 hours time.

Minimum weight loss was occurred for the coupons immersed in the inhibitor solution with high concentrations. Similar trends of decreasing the weight loss with increase in inhibitor concentration were noticed for all Schiff base studied. The loss of weight of the coupons in acid solutions was more in the case of FSC and least in the case of FTSC. Among the studied Schiff bases weight loss was decreasing in the order FTSC<FATP<FAP<FSC as shown in the figure 4.3.7. It is clear from figures 4.3.3 to 4.3.6 that, the weight loss of Schiff bases containing systems fall below, with respect to Schiff bases free system indicating the inhibitive properties of the four Schiff bases.
Corrosion rates and percentage inhibition efficiency

The corrosion rates expressed in mm/year of the MS specimens in 1M HCl with and without the presence of different concentrations are calculated from the weight loss values recorded at room temperature. The corrosion rates of FTSC, FATP, FAP and FSC for the first 24 hours are given in the table 4.3.2.

<table>
<thead>
<tr>
<th>Concentration [M]</th>
<th>FTSC</th>
<th>FATP</th>
<th>FAP</th>
<th>FSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>75.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0001</td>
<td>16.41</td>
<td>22.45</td>
<td>29.31</td>
<td>73.43</td>
</tr>
<tr>
<td>0.0002</td>
<td>9.62</td>
<td>14.76</td>
<td>22.0</td>
<td>71.37</td>
</tr>
<tr>
<td>0.0004</td>
<td>4.06</td>
<td>11.15</td>
<td>18.75</td>
<td>69.33</td>
</tr>
<tr>
<td>0.001</td>
<td>2.10</td>
<td>5.63</td>
<td>12.71</td>
<td>34.30</td>
</tr>
<tr>
<td>0.002</td>
<td>1.61</td>
<td>5.98</td>
<td>9.41</td>
<td>25.29</td>
</tr>
<tr>
<td>0.003</td>
<td>0.99</td>
<td>2.50</td>
<td>7.77</td>
<td>18.48</td>
</tr>
<tr>
<td>0.004</td>
<td>1.52</td>
<td>1.66</td>
<td>4.52</td>
<td>18.00</td>
</tr>
<tr>
<td>0.008</td>
<td>1.09</td>
<td>0.99</td>
<td>2.42</td>
<td>12.23</td>
</tr>
</tbody>
</table>
It was observed that the corrosion rate was decreasing with increase in concentration of the Schiff base inhibitor used. The lowest corrosion rates were observed for the higher concentrations of inhibitor solutions. FTSC has shown least corrosion rates among the four Schiff bases studied.

The percentage inhibition efficiencies of the Schiff base inhibitors towards the MS in 1M HCl were found out from the corrosion rates obtained for 24 hours and are given in the table 4.3.3.

Table 4.3.3 Corrosion inhibition efficiencies obtained for FTSC, FATP, FAP and FSC inhibitors

<table>
<thead>
<tr>
<th>Concentration [M]</th>
<th>FTSC η W_L%</th>
<th>FATP η W_L%</th>
<th>FAP η W_L%</th>
<th>FSC η W_L%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>78.82</td>
<td>70.2</td>
<td>61.00</td>
<td>2.53</td>
</tr>
<tr>
<td>0.0002</td>
<td>87.23</td>
<td>80.4</td>
<td>70.80</td>
<td>5.28</td>
</tr>
<tr>
<td>0.0004</td>
<td>94.61</td>
<td>85.2</td>
<td>75.11</td>
<td>7.98</td>
</tr>
<tr>
<td>0.001</td>
<td>97.21</td>
<td>92.52</td>
<td>83.12</td>
<td>54.47</td>
</tr>
<tr>
<td>0.002</td>
<td>97.86</td>
<td>92.06</td>
<td>87.51</td>
<td>66.47</td>
</tr>
<tr>
<td>0.003</td>
<td>98.68</td>
<td>96.68</td>
<td>89.69</td>
<td>75.47</td>
</tr>
<tr>
<td>0.004</td>
<td>97.98</td>
<td>97.80</td>
<td>94.00</td>
<td>76.00</td>
</tr>
<tr>
<td>0.008</td>
<td>98.55</td>
<td>98.68</td>
<td>96.79</td>
<td>83.80</td>
</tr>
</tbody>
</table>
In the case of FTSC an efficiency of \( \approx 95\% \) was achieved for a comparatively lower concentration of 0.0004M equivalent to 106ppm (0.016\%) and a maximum efficiency of 98.68\% at concentration of 0.003M corresponding to 796ppm (0.0796\%). It is also observed that the inhibition efficiency of the FTSC was not further increased after 0.003M. 0.003 M is found to be the optimum concentration for FTSC. In the case of FATP more than 90\% efficiency was obtained for 0.001M corresponding to 300ppm (0.03\%) and maximum of 98.68\% for 0.008M corresponding to 2400 ppm (0.12\%). In the case of FAP 90\% efficiency attained for a concentration of 0.003M corresponding to 850ppm (0.085\%) and a maximum of 96\% at 0.008M. Among the four Schiff bases studied the lowest inhibition efficiency was observed in the case of FSC with a maximum efficiency of 83.5\% achieved at the highest concentration of 0.008M corresponding to 2286ppm (0.2286\%).

To compare the performance of the Schiff bases, the percentage inhibition efficiencies obtained were plotted against the concentrations of inhibitor solutions used and are shown in the figure 4.3.8. It has been found that all these Schiff bases inhibit the corrosion of MS in HCl solution at all concentrations used in this study except in the case of few lower concentrations of FSC. It is also noticed that the inhibition efficiency for all these compounds increase with increase in the concentration of inhibitor.
Among the four Schiff bases studied the FTSC shows maximum inhibition efficiency and follows the order FTSC>FATP>FAP>FSC.

**Figure 4.3.8** Plot of percentage inhibition efficiencies against the concentration of Schiff bases FTSC, FATP, FAP and FSC.

**Effect of Temperature on the performance of Schiff base inhibitors**

To study the effect of temperature on the inhibition efficiency, weight loss measurements of MS specimens were carried at three different temperatures 30°C, 40°C and 50°C with 0.003 M inhibitor solution of the Schiff bases FTSC, FATP, FAP and FSC. The weight loss recorded, corrosion rate and percentage inhibition efficiency are given in the table 4.3.4. The percentage inhibition efficiencies obtained for four Schiff bases at different temperatures are plotted and shown in the figure 4.3.9. Inhibition efficiencies found to decrease with increase in temperature.
<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Temp. (°C)</th>
<th>Weight loss (mg/cm²)</th>
<th>Corrosion rate (mm/year)</th>
<th>Per. inhibition efficiency (η WL%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>30</td>
<td>162.66</td>
<td>75.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>207.80</td>
<td>96.25</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>319.18</td>
<td>147.84</td>
<td></td>
</tr>
<tr>
<td>FTSC</td>
<td>30</td>
<td>2.14</td>
<td>0.99</td>
<td>98.68</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>7.59</td>
<td>3.51</td>
<td>96.35</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>13.76</td>
<td>6.37</td>
<td>95.68</td>
</tr>
<tr>
<td>FATP</td>
<td>30</td>
<td>5.39</td>
<td>2.50</td>
<td>96.68</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>16.52</td>
<td>7.65</td>
<td>92.05</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>31.58</td>
<td>14.63</td>
<td>90.10</td>
</tr>
<tr>
<td>FAP</td>
<td>30</td>
<td>16.77</td>
<td>7.77</td>
<td>89.69</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>28.46</td>
<td>13.18</td>
<td>86.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>58.37</td>
<td>27.04</td>
<td>71.90</td>
</tr>
<tr>
<td>FSC</td>
<td>30</td>
<td>39.89</td>
<td>18.48</td>
<td>75.47</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>72.66</td>
<td>33.65</td>
<td>65.03</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>162.58</td>
<td>75.31</td>
<td>49.06</td>
</tr>
</tbody>
</table>
Comparison of inhibition efficiency of Schiff base and its parent amine

To compare the inhibition efficiency of the Schiff base furoin thiosemicarbazone and its parent amine, the weight loss measurements of the MS specimens in 1M HCl containing various concentrations of furoin thiosemicarbazone and thiosemicarbazide inhibitor solutions were carried out at room temperature (30°C). The percentage inhibition efficiencies obtained are plotted against concentration and given in the figure 4.3.10. It was found that inhibition efficiency of the Schiff base FTSC was more than the corresponding amine, thiosemicarbazide.
Potentiodynamic polarization studies

Typical Tafel polarization curves obtained for MS in 1M HCl with and without the presence of different concentrations of FTSC are shown in the figure 4.3.11. Various corrosion parameters such as corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$) and percentage inhibition efficiency, ($\eta_{pol \%}$) are given in table 4.3.5.

It is observed that the presence of Schiff base inhibitor lowers $i_{corr}$ values. The corrosion current obtained for MS coupons tested in the FTSC inhibitor solutions are lower than solution without FTSC i.e. blank. This shows that the presence of FTSC lowers $i_{corr}$ values. A lowest $i_{corr}$ value was observed for a FTSC concentration of 0.002M. The percentage inhibition
efficiency increases with increase in the inhibitor concentrations and a maximum efficiency of 97.68 % was obtained for a low concentration of 0.002M corresponding to 531ppm (0.0053%). The inhibition efficiency was found to remain constant after achieving maximum efficiency at 0.002M. This trend was also noticed in the case of weight loss measurements. It is also observed from the table that there is no significant change in $E_{corr}$ values of inhibited and uninhibited systems.

Table 4.3.5 Electrochemical polarization parameters for MS in 1M HCl containing different concentrations of FTSC

<table>
<thead>
<tr>
<th>Concentration [M]</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (A/cm²)</th>
<th>Per. inhibition efficiency ($\eta_{pol}$ %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-0.461</td>
<td>4.747 x 10^{-3}</td>
<td>-</td>
</tr>
<tr>
<td>FTSC 0.0001</td>
<td>-0.464</td>
<td>1.373 x 10^{-3}</td>
<td>71.08</td>
</tr>
<tr>
<td>FTSC 0.0002</td>
<td>-0.478</td>
<td>1.42 x 10^{-3}</td>
<td>70.09</td>
</tr>
<tr>
<td>FTSC 0.0004</td>
<td>-0.469</td>
<td>1.44 x 10^{-3}</td>
<td>69.67</td>
</tr>
<tr>
<td>FTSC 0.001</td>
<td>-0.469</td>
<td>9.755 x 10^{-4}</td>
<td>79.41</td>
</tr>
<tr>
<td>FTSC 0.002</td>
<td>-0.476</td>
<td>1.102 x 10^{-4}</td>
<td>97.68</td>
</tr>
<tr>
<td>FTSC 0.003</td>
<td>-0.457</td>
<td>4.361 x 10^{-4}</td>
<td>90.81</td>
</tr>
<tr>
<td>FTSC 0.004</td>
<td>-0.445</td>
<td>4.149 x 10^{-4}</td>
<td>91.26</td>
</tr>
<tr>
<td>FTSC 0.008</td>
<td>-0.476</td>
<td>3.992 x 10^{-4}</td>
<td>91.59</td>
</tr>
</tbody>
</table>
Figure 4.3.11 Tafel plots of MS in 1M HCl in presence of different concentrations of FTSC

The potentiodynamic polarization curves obtained for the other three Schiff bases FATP, FAP and FSC for an inhibitor concentration of 0.008M are shown in figure 4.3.12, to 4.3.14 and the electrochemical parameters obtained are summerised in table 4.3.6. The corrosion current densities for the 0.008 M solutions of the four Schiff bases are found to decrease in the order FSC>FATP>FAP>FTSC. The variation of percentage inhibition efficiencies achieved at 0.008 M were found to follow the order FTSC>FAP>FATP>FSC.
Table 4.3.6 Electrochemical polarization parameters for MS in 1M HCl containing 0.008 M of FTSC, FATP, FAP and FSC

<table>
<thead>
<tr>
<th>Concentration of inhibitor [M]</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (A/cm$^2$)</th>
<th>Per. inhibition efficiency ($\eta_{pol} %$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-0.461</td>
<td>$4.747 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>FTSC 0.008</td>
<td>-0.476</td>
<td>$3.992 \times 10^{-4}$</td>
<td>91.59</td>
</tr>
<tr>
<td>FATP 0.008</td>
<td>-0.425</td>
<td>$1.212 \times 10^{-3}$</td>
<td>74.47</td>
</tr>
<tr>
<td>FAP 0.008</td>
<td>-0.441</td>
<td>$3.953 \times 10^{-4}$</td>
<td>90.04</td>
</tr>
<tr>
<td>FSC 0.008</td>
<td>-0.456</td>
<td>$2.532 \times 10^{-3}$</td>
<td>44.13</td>
</tr>
</tbody>
</table>

Figure 4.3.12 Tafel plots of MS in 1M HCl with and without 0.008 M FATP
Figure 4.3.13  Tafel plots of MS in 1M HCl with and without 0.008 M FAP

Figure 4.3.14  Tafel plots of MS in 1M HCl with and without 0.008 M FSC
Electrochemical impedance spectroscopy

Nyquist plots of MS in 1M HCl in the presence and absence of different concentrations of FTSC are shown in the figure 4.3.15. The impedance parameters like polarization resistance ($R_p$), solution resistance ($R_s$), constant phase element or double layer capacitance (CPE), $n$ and percentage inhibition efficiency calculated from the $R_p$ values are given in the table 4.3.7.

Table 4.3.7 Impedance parameters and inhibition efficiency for the corrosion of MS with and without different concentrations of FTSC

<table>
<thead>
<tr>
<th>Con. [M]</th>
<th>$R_s$ (ohm)</th>
<th>$R_p$ (ohm)</th>
<th>CPE ($\mu$F/cm$^2$)</th>
<th>$n$</th>
<th>Per. inhibition efficiency ($\eta_{EIS} %$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.9523</td>
<td>4.69</td>
<td>279.53</td>
<td>0.8179</td>
<td></td>
</tr>
<tr>
<td>0.0001</td>
<td>0.7904</td>
<td>10.60</td>
<td>164.50</td>
<td>0.8018</td>
<td>55.72</td>
</tr>
<tr>
<td>0.0002</td>
<td>1.0470</td>
<td>16.47</td>
<td>157.05</td>
<td>0.7998</td>
<td>71.50</td>
</tr>
<tr>
<td>0.0004</td>
<td>1.0846</td>
<td>11.20</td>
<td>129.57</td>
<td>0.8065</td>
<td>58.06</td>
</tr>
<tr>
<td>0.001</td>
<td>0.8800</td>
<td>13.65</td>
<td>114.99</td>
<td>0.7790</td>
<td>65.61</td>
</tr>
<tr>
<td>0.002</td>
<td>0.9811</td>
<td>146.92</td>
<td>11.48</td>
<td>0.7996</td>
<td>96.80</td>
</tr>
<tr>
<td>0.003</td>
<td>0.7947</td>
<td>45.95</td>
<td>69.01</td>
<td>0.8195</td>
<td>89.78</td>
</tr>
<tr>
<td>0.004</td>
<td>0.7946</td>
<td>54.13</td>
<td>102.69</td>
<td>0.7984</td>
<td>91.33</td>
</tr>
<tr>
<td>0.008</td>
<td>0.9473</td>
<td>53.05</td>
<td>36.75</td>
<td>0.7192</td>
<td>91.15</td>
</tr>
</tbody>
</table>
All the Nyquist plots obtained were semicircle in nature and display a single capacitive loop as seen in the figure 4.3.15. The diameter of the semicircles was increased with increase in inhibitor concentration. The results also show that $R_p$ values were increased with increase in additive concentration. The percentage inhibition efficiencies calculated from the $R_p$ indicate that the inhibition efficiency increases with increase in FTSC concentration. A maximum inhibition efficiency of 96.80% was achieved for the 0.002M FTSC and for further increase in concentration, inhibition efficiency remained almost same as observed in the weight loss and Tafel methods.

![Figure 4.3.15 Nyquist plots for MS in 1M HCl in the presence and absence of different concentrations of FTSC](image)

**Figure 4.3.15** Nyquist plots for MS in 1M HCl in the presence and absence of different concentrations of FTSC
To study the inhibition efficiency of the other three Schiff bases FATP, FAP and FSC, EIS spectrum of the 0.008M solutions of these inhibitors were recorded as earlier. The Nyquist plot of the 0.008 M FTSC, FATP, FAP and FSC are given in the figure 4.3.16. The impedance parameters $R_p$, $R_s$, CPE, $n$ and percentage inhibition efficiency, $\eta_{\text{EIS}}$ % are given in the table 4.3.8. As in the case of FTSC, for other three Schiff bases also, the obtained Nyquist plots are semicircle shaped with one single capacitive loop. The diameter of semicircles and $R_p$ values were varied with respect to their inhibition efficiency.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$R_s$ (ohm)</th>
<th>$R_p$ (ohm)</th>
<th>CPE ($\mu$F/cm$^2$)</th>
<th>$n$</th>
<th>Per. inhibition efficiency ($\eta_{\text{EIS}}$ %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.9523</td>
<td>4.69</td>
<td>279.53</td>
<td>0.8179</td>
<td>-</td>
</tr>
<tr>
<td>FTSC</td>
<td>0.9473</td>
<td>53.05</td>
<td>36.75</td>
<td>0.7192</td>
<td>91.15</td>
</tr>
<tr>
<td>FATP</td>
<td>0.9668</td>
<td>26.85</td>
<td>46.39</td>
<td>0.6650</td>
<td>82.52</td>
</tr>
<tr>
<td>FAP</td>
<td>0.9932</td>
<td>47.15</td>
<td>67.41</td>
<td>0.7383</td>
<td>90.04</td>
</tr>
<tr>
<td>FSC</td>
<td>0.8317</td>
<td>8.08</td>
<td>267.86</td>
<td>0.8026</td>
<td>41.90</td>
</tr>
</tbody>
</table>
Figure 4.3.16 Nyquist plots for MS in 1M HCl in the presence of 0.008M FTSC, FATP, FAP and FSC

Adsorption isotherm studies

In order to understand the mechanism of corrosion inhibition, the adsorption behaviour of the organic adsorbate on the metal surface must be known. The degree of the surface coverage ($\theta$) was evaluated from the weight loss measurement results of MS in 1 M HCl in the presence and absence of the four Schiff bases conducted at 30°C using the equation (16) of chapter 2. The values of surface coverage ($\theta$) for four Schiff bases are given in the table 4.3.9. The data were tested graphically by fitting to various isotherms like Langmuir, Frumkin and Temkin isotherms. The Frumkin and Temkin isotherm did not yield a satisfactory description of the experimental adsorption behaviour. Among the three isotherms assessed Langmuir isotherm found to provide best description of the adsorption behaviour of the
investigated Schiff bases. The plots of $\log \frac{\theta}{1-\theta}$ versus logC give straight lines and shows that the adsorption of studied Schiff base obeys Langmuir adsorption isotherm. The Langmuir isotherm plots of FTSC, FATP, FAP and FSC are shown in the figures 4.3.17 to 4.3.20.

Table 4.3.9 The value of $\theta$ for the Schiff bases FTSC, FATP, FAP and FSC calculated from weight loss measurement results

<table>
<thead>
<tr>
<th>Con. [M]</th>
<th>Degree of surface coverage ($\theta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FTSC</td>
</tr>
<tr>
<td>0.0001</td>
<td>0.7822</td>
</tr>
<tr>
<td>0.0002</td>
<td>0.8723</td>
</tr>
<tr>
<td>0.0004</td>
<td>0.9461</td>
</tr>
<tr>
<td>0.001</td>
<td>0.9721</td>
</tr>
<tr>
<td>0.002</td>
<td>0.9798</td>
</tr>
<tr>
<td>0.003</td>
<td>0.9868</td>
</tr>
<tr>
<td>0.004</td>
<td>0.9798</td>
</tr>
<tr>
<td>0.008</td>
<td>0.9855</td>
</tr>
</tbody>
</table>
Figure 4.3.17 Langmuir adsorption isotherm of FTSC on MS in 1M HCl

Figure 4.3.18 Langmuir adsorption isotherm of FATP on MS in 1M HCl
Figure 4.3.19 Langmuir adsorption isotherm of FAP on MS in 1M HCl

Figure 4.3.20 Langmuir adsorption isotherm of FSC on MS in 1M HCl
The activation energy for the corrosion of MS in IM HCl in the presence and absence of 0.003M FTSC, 0.003M FATP, 0.003M FAP and 0.003M FSC solutions are calculated using the Arrhenius equation. The logarithmic values of corrosion rates obtained at temperatures 30°C, 40°C and 50°C for the blank and 0.003 M FTSC, FATP, FAP and FSC are plotted against 1000/T. From the slope of these Arrhenius plots activation energies are calculated. The Arrhenius plots of blank, 0.003 M FTSC, 0.003 M FATP, 0.003 M FAP and 0.003 M FSC are shown in the figure 4.3.21. The activation energy for the corrosion of MS in 1M HCl in the presence of 0.003M solutions is given in the table 4.3.10.

![Graph](image)

**Figure 4.3.21** Plots of log corrosion rate vs. 1000/T for blank and 0.003M solutions of FTSC, FATP, FAP and FSC
Table 4.3.10 The activation energy and enthalpy of adsorption obtained for the Schiff base inhibitors

<table>
<thead>
<tr>
<th>Schiff base</th>
<th>$E_a$ (kJmol$^{-1}$)</th>
<th>$\Delta H_{ads}$ (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>27.28</td>
<td>-</td>
</tr>
<tr>
<td>FTSC</td>
<td>76.01</td>
<td>-49.871</td>
</tr>
<tr>
<td>FATP</td>
<td>72.07</td>
<td>-47.61</td>
</tr>
<tr>
<td>FAP</td>
<td>50.65</td>
<td>-49.52</td>
</tr>
<tr>
<td>FSC</td>
<td>57.06</td>
<td>-47.18</td>
</tr>
</tbody>
</table>

The free energy of adsorption ($\Delta G_{ads}$) for the corrosion of MS in 1M HCl in the presence of four Schiff bases was calculated using the relation (17). The free energy of adsorption for the corrosion of MS in 1M HCl for the four Schiff bases is given in the table 4.3.11. The values for free energy of adsorption for the corrosion inhibition are negative.

The Langmuir adsorption isotherm may be expressed by the following equation$^{13}$

$$\log\frac{\theta}{1-\theta} = \log A + \log C - \frac{Q_{ads}}{2.303RT}$$  \ (19)

The heats of adsorption ($Q_{ads}$), obtained from the slopes of the linear portion of the log $K_{ads}$ vs 1000/T curves which are equal to $-Q'$ (2.303 R). In
this case, values of $Q_{ads}$ equal to enthalpy of adsorption ($\Delta H_{ads}$) with good approximation, because pressure is constant. The $\Delta H_{ads}$ values obtained for the four Schiff bases FTSC, FATP, FAP and FSC are given in table 4.3.10. Entropy of inhibitor adsorption ($\Delta S_{ads}$) is calculated using the equation\textsuperscript{13}

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$$ \hspace{1cm} (20)

The calculated $\Delta S_{ads}$ data at different temperature are given in table 4.3.11. It was found that all values are negative.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Temperature</th>
<th>$\Delta S$ (J/mol K)</th>
<th>$\Delta G_{ads}$ (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTSC</td>
<td>30</td>
<td>-47.03</td>
<td>-35.62</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-50.42</td>
<td>-34.08</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-46.97</td>
<td>-34.70</td>
</tr>
<tr>
<td>FATP</td>
<td>30</td>
<td>-47.40</td>
<td>-33.24</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-50.05</td>
<td>-31.94</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-47.34</td>
<td>-32.316</td>
</tr>
<tr>
<td>FAP</td>
<td>30</td>
<td>-63.77</td>
<td>-30.20</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-61.23</td>
<td>-30.36</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-63.82</td>
<td>-28.91</td>
</tr>
<tr>
<td>FSC</td>
<td>30</td>
<td>-64.68</td>
<td>-27.58</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-63.90</td>
<td>-27.18</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-64.69</td>
<td>-26.28</td>
</tr>
</tbody>
</table>
The percentage inhibition efficiencies obtained from weight loss, potentiodynamic polarization and EIS method are compared and given in the table 4.3.12. The percentage inhibition efficiencies obtained are showing similar trend of increase in inhibition efficiency with increasing concentration and are close to each other.

**Table 4.3.12 Percentage inhibition efficiencies obtained for MS in 1M HCl by weight loss, potentiodynamic polarization and EIS method.**

<table>
<thead>
<tr>
<th>Concentration [M]</th>
<th>(ηWL %)</th>
<th>(ηpol %)</th>
<th>(ηEIS %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTSC 0.0001</td>
<td>78.22</td>
<td>71.08</td>
<td>55.72</td>
</tr>
<tr>
<td>FTSC 0.0002</td>
<td>87.23</td>
<td>70.09</td>
<td>71.50</td>
</tr>
<tr>
<td>FTSC 0.0004</td>
<td>94.61</td>
<td>69.67</td>
<td>58.06</td>
</tr>
<tr>
<td>FTSC 0.001</td>
<td>97.21</td>
<td>79.41</td>
<td>65.61</td>
</tr>
<tr>
<td>FTSC 0.002</td>
<td>97.86</td>
<td>97.68</td>
<td>96.80</td>
</tr>
<tr>
<td>FTSC 0.003</td>
<td>98.68</td>
<td>90.81</td>
<td>89.78</td>
</tr>
<tr>
<td>FTSC 0.004</td>
<td>97.98</td>
<td>91.26</td>
<td>91.33</td>
</tr>
<tr>
<td>FTSC 0.008</td>
<td>98.55</td>
<td>91.59</td>
<td>91.15</td>
</tr>
</tbody>
</table>
Discussion

The basic action of an inhibitor is attributed to an increase in overvoltage of the hydrogen ion discharge as cathodic reaction of corrosion process or an increase in ohmic resistance of an inhibitor film at the metal electrolyte interface or due to some type of adsorption on the metal surface. The organic inhibitors like Schiff bases generally inhibit the corrosion process through adsorption of the inhibitor on the metal solution interface. The adsorption was considered either as physical adsorption or chemical adsorption. The physical adsorption may be due to the electrostatic attractive forces between ionic charges or dipoles on the adsorbed species and the electric charge on the metal at the metal/solution interface. The forces in electrostatic adsorption are generally weak. The inhibiting species adsorbed on the metal due to electrostatic force can also be desorbed easily. A main feature of the electrostatic adsorption is that the ions are not in direct physical contact with the metal. A layer of water molecule separates the metal from the ions. The physical adsorption process has low activation energy and is relatively independent of temperature.

In chemisorption the adsorbed species is in contact with the metal surface. A coordinate type of bond involving electron transfer from inhibitor to the metal is assumed to take place in the process. The chemisorption process is slower than the electrostatic sorption that has higher activation energy. The temperature dependency shows that higher inhibition efficiencies
at higher temperatures. Unlike electrostatic adsorption, it is specific for certain metals and is not completely reversible.

**Weight loss method**

In this study it has been found that all the four Schiff bases FTSC, FATP, FAP and FSC inhibit the corrosion of MS in HCl at all concentrations of Schiff bases used. It can be seen that inhibition efficiency increases with increase in inhibitor concentration. All the inhibitors reduce the corrosion rate to a significant extent showing higher inhibition efficiencies. The results of the corrosion inhibition studies of four Schiff bases on MS in 1M HCl by weight loss measurements clearly indicates that all studied Schiff bases act as efficient corrosion inhibitors for MS in HCl media as reported in the similar type of Schiff base materials\(^4,5,12,13\).

It was also observed that the corrosion inhibition efficiency is increasing with increase in Schiff base concentration. The increase in the inhibition efficiencies for MS corrosion in 1M HCl with increasing Schiff base concentration suggests that inhibition is a result of adsorption of inhibitor on the metal surface and these compounds act as adsorption inhibitors\(^5\).

It was observed that corrosion inhibition efficiency of all the four Schiff bases towards MS in 1M HCl was found to decrease with increase of temperature. The decrease in inhibition efficiency with increasing
temperature, suggest a weak adsorption interaction between MS surface and the additives, which is physical in nature\textsuperscript{23}. This may due to desorption of some adsorbed molecule from the MS surface with increase of temperature\textsuperscript{5,23}. This observation reiterates that type of adsorption is physical in nature because if the adsorption was chemisorption type then the efficiency will be increased with increase in temperature\textsuperscript{26}. The inhibition efficiency of the Schiff base, furoin thiosemicarbazone was more than corresponding parent amine thiosemicarbazide. The presence of higher electron density of the -C=\textsuperscript{N}– group which is not present in the parent amine is responsible for the higher inhibition efficiency of the Schiff base than its corresponding amine. Thus conversion of an amine to Schiff base increases its inhibition capacity\textsuperscript{5,13,15,46}.

**Tafel plot analysis**

The typical Tafel polarization curves obtained for different concentrations of FTSC and blank shows the change in shape of the cathodic and anodic curves. The corrosion parameters like $i_{\text{corr}}$ values of the inhibited systems are lower than the uninhibited systems and $i_{\text{corr}}$ values decreases with increase in concentration of FTSC. Thus the inhibition efficiency was increasing with increasing concentration of the Schiff base as reported earlier\textsuperscript{4,5,13,15}. Increase in inhibition efficiency with increase of the concentration of the studied Schiff bases shows that inhibition actions are due
to the adsorption on steel surface\textsuperscript{13}. It is also observed from the polarization results that there is no significant change in $E_{\text{corr}}$ values of inhibited and uninhibited systems. This shows that the addition of studied Schiff bases affected both anodic and cathodic reaction suggesting that the Schiff base FTSC is a mixed type (anodic/cathodic) inhibitor\textsuperscript{13,26}.

The low values of the corrosion current obtained for the 0.008M solutions of FATP, FAP and FSC compared to the blank values also reveal the ability of these Schiff bases to inhibit the corrosion of MS in 1M HCl as proved by the weight loss method. The results obtained from the potentiodynamic polarization method are in agreement with weight loss measurement results.

**EIS method**

The electrochemical impedance results of different concentrations of FTSC in 1M HCl clearly showing semicircle shaped Nyquist plots with increasing radii with increasing concentration of Schiff base FTSC. The appearance of single semi circle in all the cases corresponds to one capacitive loop\textsuperscript{14}. It is apparent from these plots that the impedance response of MS in uninhibited HCl has significantly changed after the addition of Schiff bases in to the corrosive solutions. The semicircle shaped Nyquist plots indicate the formation of a barrier on the surface and a charge transfer process mainly controlling the corrosion of MS\textsuperscript{17,47}. The polarization resistance $R_p$ values
were found to increase with increasing Schiff base concentrations. The values of the constant phase element (CPE) are found to decrease with increase in concentration. This behaviour is generally seen for system where inhibition is the case and indicates the formation of a surface film by the adsorption of inhibitor on the metal surface\textsuperscript{4,12,48}. The nature of CPE can be derived from the values of the \( n \), which is purely resistive when \( n = 0 \), capacitive when \( n = 1 \) or inductive when \( n = -1 \). The values of \( n \) obtained for these systems are close to unity which shows that the interface behaves nearly capacitive\textsuperscript{25}. The increase in the \( R_p \) values with increase in the Schiff base concentration indicates that inhibition is due to the adsorption of Schiff base on the MS\textsuperscript{4,12}.

In simple case, when corrosion is uniform and corrosion reactions are strictly charge transfer controlled, the electrode impedance Nyquist will be semicircle. This type of impedance behaviour can be explained with the help of a simple and commonly used equivalent circuit diagram as shown in the figure 4.3.22 which is composed of a constant phase element CPE, in parallel with a resistor, \( R_p \), which corresponds to a single capacitive loop. The resistor \( R_s \) is in series to the CPE and \( R_p \). \( R_s \) is the uncompensated resistance between the working electrode and reference electrode or solution resistance, \( R_p \) is the polarization resistance at the electrode/solution interface, and CPE is the double layer capacitance at the interface. The double layer capacity is in parallel with the impedance due to the charge transfer reaction. These types of circuit have been used previously to model the iron /acid interface\textsuperscript{4,5,49}. 
The EIS studies clearly indicate that the Schiff base FTSC is a good corrosion inhibitor for MS in HCl medium. The efficiency of the inhibitor increases with increase in inhibitor concentration. Similar to the FTSC the other three Schiff bases also showing semicircle shaped Nyquist plots with higher radii and $R_p$ values and ascertains their capacity to inhibit the corrosion of MS. The percentage inhibition efficiency calculated from the EIS measurement almost matches with the percentage efficiency obtained from Tafel plot analysis.

![Figure 4.3.22](image)

**Figure 4.3.22** The equivalent circuit for the corrosion behaviour of MS in 1M HCl in the presence of Schiff base inhibitors

**Adsorption isotherm studies**

The adsorption of Schiff base was found to follow Langmuir adsorption isotherm in all the cases. The inhibiting effects deviate somewhat from the ideal Langmuir adsorption isotherm. It has been postulated in the derivation of the Langmuir equation that the adsorbed molecule do not interact with each other but this is not true in the case of organic molecule having polar atoms or groups which are adsorbed on the cathodic and anodic
sites of the metal surface. Such adsorbed species may interact by mutual repulsion or attraction\(^{18}\).

Thermodynamic parameters calculated with help of the adsorption isotherm plots also give indications of the type of adsorption process. The values of free energy of adsorption obtained for the four Schiff bases FTSC, FATP, FAP and FSC for the corrosion of MS in 1M HCl are -35.62, -33.24, -30.20 and -27.58 kJmol\(^{-1}\) respectively. The low values of \(\Delta G_{ads}\) below -40 kJmol\(^{-1}\) indicate that adsorption of Schiff base on the MS is physical in nature i.e. physisorption\(^{26,50}\). The chemisorption process is mainly characterised by the large interaction potentials, which leads to high heats of adsorption often approaching to the value of chemical bond. The low and negative values of \(\Delta G_{ads}\) indicate that the spontaneous adsorption of inhibitors on the surface of MS. The negative values of \(\Delta G_{ads}\) also suggest the strong interaction of the inhibitor molecule on the MS surface\(^{51,52}\). The decrease in inhibition efficiency with increasing temperature suggests weak adsorption interaction which is physical in nature.

It is found that the \(E_a\) values for inhibited systems are higher than \(E_a\) values for the uninhibited systems which propose the conclusion that physical adsorption occurs in the first stage, explains the nature of organic molecule-metal interactions. On the other hand the higher values of activation energy obtained in spite of the lower \(E_a\) values of physisorption (30-50kJmol\(^{-1}\)) may
be due to competitive adsorption of water whose removal from the surface requires some more activation energy\textsuperscript{13,22,53}.

The negative values of $Q_{\text{ads}}$ indicated the adsorption of used inhibitors on the MS surface is exothermic. The negative values also identify that the adsorption is a physisorption process\textsuperscript{13}. The obtained values of $\Delta S$ are negative indicating that the entropy of inhibitor molecules in the solution phase is higher than solid phase\textsuperscript{13}.

The reason for the high inhibition efficiencies of these studied Schiff bases towards MS in 1M HCl is due to the presence of azomethine (–C=N-) group, an electron cloud on the aromatic ring and presence of nitrogen, oxygen and sulphur atoms in the molecules. The Schiff bases are strongly adsorbed via the donation of the lone pair of electrons of O atom in the carbonyl group and S atom in the C=S group and N atoms to MS surface. The extent of percentage inhibition depends on the molecular size and electron density on the active groups and atoms\textsuperscript{22}.

The difference of inhibition efficiencies of the studied Schiff bases towards MS can be explained on the basis of the difference in molecular structure of the Schiff bases and the presence of substituents that increase or decrease electron density of azomethine (–C=N-) group. The higher inhibition efficiency of FTSC compared to the FSC and FATP than FAP may be due to the presence sulphur atom in FTSC and FATP in the place of oxygen atom in FSC and FAP. Adsorption capacity of S is higher than O. Adsorption
capacities of heteroatom present in the organic inhibitor molecules is in the order as reported earlier O<N<S<P.\(^{54,55,56,57}\)

The synthesised four Schiff bases FTSC, FATP, FAP and FSC are acting as good corrosion inhibitors of MS in 1M hydrochloric acid media. Among the four Schiff bases FTSC got maximum efficiency. The inhibition efficiency of the studied Schiff bases decrease in the order FTSC>FATP>FAP>FSC as evidenced from the weight loss measurements. The higher efficiency of the Schiff bases are due to the presence of azomethine group, atoms like sulphur or oxygen, and nitrogen in the Schiff bases molecule. The mechanism of the inhibition process is through the adsorption of the Schiff bases on the MS through physisorption. Thermodynamic parameters calculated and inhibition studies conducted at higher temperature also support the physical adsorption of the Schiff base over the MS. The conversion of an amine into its Schiff base increases the inhibition efficiency. All the Schiff bases are best suited to Langmuir adsorption isotherm behaviour. The results obtained by the weight loss, Tafel method and EIS find better agreement with each other. This shows that the results obtained for the weight loss method are acceptable in all the other cases.

Since all the Schiff bases studied exhibit corrosion inhibiting property on MS in HCl, they can be used as corrosion inhibitors for industrial applications.
REFERENCES