CHAPTER-II
MATERIALS AND THE
EXPERIMENTAL PROCEDURES
2.1 METAL SPECIMEN SELECTED FOR THE STUDY

The mild steel (MS) selected for corrosion inhibition experiments was procured commercially. The chemical composition of MS (in weight %), as analyzed by optical emission spectrometer, is given in Table 2.1. For gravimetric studies, rectangular coupons of dimension $2.5 \times 2.0 \times 0.1$ cm (exposed surface area of 10.27 cm$^2$) and for electrochemical measurements circular coupons of exposed surface area 1 cm$^2$ were press cut from the MS sheet and used. The specimens were machined and abraded with a series of emery papers, grade 320-1200, degreased with acetone or 1:1 ethanol/water mixture, rinsed with double distilled water and finally dried in warm air and used with no further storage.

Table 2.1 Chemical composition of the MS.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>Cr</th>
<th>Mo</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>0.1611</td>
<td>0.1815</td>
<td>0.0178</td>
<td>0.0351</td>
<td>0.0539</td>
<td>0.0174</td>
<td>0.0336</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2.2 INHIBITORS SELECTED FOR THE STUDY

In the present work, the amino acids, L-Cysteine (CYS) [2-amino-3-sulphydryl propanoic acid, Sigma-Aldrich 97%], L-Tyrosine (TYR) [2-amino-3-(4-hydroxyphenyl) propanoic acid, Sigma-Aldrich ≥98%], amino acid derivative, L-Phenylalanine methyl ester hydrochloride (PMEH) [(s)-methyl-2-amino-3-phenyl propanoate hydrochloride, Sigma-Aldrich ≥98%] and surfactants, sodium dodecyl sulphate (SDS, Sigma-Aldrich 98%), cetyl pyridinium chloride (CPC, Sigma-Aldrich 98%) and Triton X-100 (TX, Sigma-Aldrich 98%) were used as received. The amino acid, glycine derivative [N-benzylidine-2((2-oxo-2-(10H-phenothiazine-10yl)ethyl)amino) acetohydrazide (BPAA)] and amino acids, glycine and glutamic acid (Sigma-Aldrich ≥99%) based Ionic liquid surfactants, Glycine propyl ester lauryl sulphate (GlyC$_3$LS) and Glutamic acid propyl ester lauryl sulphate (GluC$_3$LS) were synthesized according to a procedure reported earlier [138,169,170].
2.2.1 Synthesis and characterization of Glycine Derivative, N-benzyldiene-2((2-oxo-2-(10H-phenothiazine-10yl)ethyl) amino) acetohydrazide (BPAA)

The starting material phenothiazine was prepared by fusion of 0.05 M diphenylamine with powdered sulphur via the classical condensation in 90% yield. After this, 2-chloro-1-(10H-phenothiazine-10-yl) ethan-1-one was synthesized by mixing the solution of freshly prepared phenothiazine in 50 ml dry benzene and 0.01 M chloroacetyl chloride at 0–5°C. Followed by the mixing of reagents, the reaction mixture was refluxed for 4 h at 50–60°C and resulting mixture was distilled off and the mixture was poured on ice cold water to get solid phase, which is further recrystallized in ether. After that, the resultant product was treated with glycine in the presence of K₂CO₃ and refluxed for 4 h at 50–60°C and further re-crystallized in acetone. The obtained compound was then treated with hydrazine hydrate, and subsequently with benzaldehyde to yield the final product, N-benzyldiene-2((2-oxo-2-(10H-phenothiazine-10yl)ethyl)amino) acetohydrazide. The synthesized compound was characterized by FT-IR and elemental analysis. Its purity was checked by thin layer chromatography and. The scheme for synthesis of BPAA is represented in scheme 2.1.

Scheme 2.1 Scheme for the preparation of BPAA.
Structure confirmation of BPAA

IR (KBr), cm⁻¹: 1680 cm⁻¹ (Phenothiazine ring), 1638 cm⁻¹ (C=O), 2939 cm⁻¹ (-CH₂), 2925.46 cm⁻¹ (-NH), 1407.5 cm⁻¹ (-CN), 1588.89 cm⁻¹ (Ar-C=C), 3433.11 cm⁻¹ (Ar-phenyl ring).

Elemental Analysis, %: Cal.: C (67.54), H (5.44), N (12.60), O (7.95), S (7.97), Found: C (64.98), H (4.85), N (11.96), O (9.58), S (8.99).

2.2.2 Synthesis and characterization of Amino Acid Based Ionic Liquid Surfactants

It involve two steps, first is the synthesis of amino acid ester hydrochlorides and the second step is the preparation of amino acid Ionic liquid surfactants (AAILSs).

2.2.2.1 Preparation of amino acid ester hydrochloride

Thionyl chloride (16.02 g, 0.13 mol) was added slowly to iso-propanol (50 mL) at 0°C followed by slow addition of amino acids (10g, 0.11 mol). Solution was refluxed for 4 hours. The progress of reaction was monitored by TLC. After completion of reaction, solution was concentrated in a rota-evaporator. Crude amino acid isopropyl ester hydrochlorides, was triturated with hexane at 0°C. During washing colored impurities were removed. The resulting white solid product was collected and dried under vacuum to obtain amino acid propyl ester hydrochloride (89.90% yields). Product was re-crystallized using methanol: hexane and dried under vacuum. Obtained hydrochloride salt was highly hygroscopic and was stored under vacuum.

2.2.2.2 Preparation of amino acid Ionic liquid surfactants [AAILSs]

For the synthesis of amino acid propyl ester lauryl sulfate, freshly synthesized and dried amino acid ester hydrochloride and sodium lauryl sulfate CH₃(CH₂)₁₁OSO₃Na (purchased from Aldrich) were dissolved in equimolar amounts in 100 ml of hot water (60°C). The reaction was monitored through TLC. After the completion of reaction, water was slowly removed under vacuum at 70–80°C and a white solid precipitate was collected. Crude solid was dissolved in 100 ml of CH₂Cl₂
(purchased from SD fine chemicals) to extract the pure product from the mixture. The solid sodium chloride was filtered and filtrate was washed with water. Washing was repeated until it became chloride free. Two to three drops of 0.1 M AgNO₃ were added to the washings to confirm the presence/absence of chloride ions. The clear but slightly yellow viscous extract was then washed several times with water and the white solid (accounted for NaCl as by-product) was separated out. The extract was distilled to get rid of the CH₂Cl₂ solvent and finally dried under N₂ and vacuum for 5–7 h to afford the viscous product (Yield: 92%).

The schematic representation for the preparation of AAILSs is given in scheme 2.2.

![Scheme 2.2](image)

**Scheme 2.2** Scheme for the preparation of AAILSs.

*Structure confirmation of AAILSs*

(a) GlyC₃LS

**IR (KBr), cm⁻¹:** 664 (–SO₄), 1256.2 (-CN), 1725.2 (-C=O), 2850.9 (-CH), 2921.2 (-CO), 3437.2 (-NH) cm⁻¹.

**Elemental Analysis, %:** Cal.: C (53.24), H (9.72), N (3.65), O (25.03), S (8.36). Found: C (53.05), H (9.47), O (25.69), N (3.54), S(8.25).
(b) GluC3LS

**IR (KBr), cm⁻¹:** 664 (–SO₄⁻), 1235.2 (-CN), 1742.8 (C=O), 2924.2 (-OH), 2853.8 (-CH), 3443 (-NH) cm⁻¹.

**Elemental Analysis, %:** Cal.: C (52.73), H (9.07), N (3.07), O (28.09), S (7.04). Found: C (52.85), H (8.97), N (3.40), O (27.93), S (6.85).

The molecular structure of amino acids, amino acid derivatives and surfactants used during the present study has been listed in Table 2.3.

**Table 2.2** Name and molecular structures of the investigated compounds.

<table>
<thead>
<tr>
<th>S.NO</th>
<th>NAME</th>
<th>STRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>L-Cysteine (CYS)</td>
<td><img src="image1.png" alt="Structure of L-Cysteine" /></td>
</tr>
<tr>
<td>2.</td>
<td>L-Phenylalanine Methyl Ester Hydrochloride (PMEH)</td>
<td><img src="image2.png" alt="Structure of L-Phenylalanine Methyl Ester Hydrochloride" /></td>
</tr>
<tr>
<td>3.</td>
<td>L-Tyrosine (TYR)</td>
<td><img src="image3.png" alt="Structure of L-Tyrosine" /></td>
</tr>
<tr>
<td>4.</td>
<td>N-benzylidine-2((2-oxo-2-(10H-phenothiazine-10yl)ethyl)amino) acetohydrazide (BPAA)</td>
<td><img src="image4.png" alt="Structure of N-benzylidine-2((2-oxo-2-(10H-phenothiazine-10yl)ethyl)amino) acetohydrazide" /></td>
</tr>
<tr>
<td>5.</td>
<td>Glycine propyl ester lauryl sulphate (GlyC₃LS)</td>
<td><img src="image5.png" alt="Structure of Glycine propyl ester lauryl sulphate" /></td>
</tr>
<tr>
<td>6.</td>
<td>Glutamic acid propyl ester lauryl sulphate (GluC₃LS)</td>
<td><img src="image6.png" alt="Structure of Glutamic acid propyl ester lauryl sulphate" /></td>
</tr>
<tr>
<td>7.</td>
<td>Sodium Dodecyl Sulphate (SDS)</td>
<td><img src="image7.png" alt="Structure of Sodium Dodecyl Sulphate" /></td>
</tr>
<tr>
<td>8.</td>
<td>Cetyl Pyridinium Chloride (CPC)</td>
<td><img src="image8.png" alt="Structure of Cetyl Pyridinium Chloride" /></td>
</tr>
<tr>
<td>9.</td>
<td>Triton X-100 (TX)</td>
<td><img src="image9.png" alt="Structure of Triton X-100" /></td>
</tr>
</tbody>
</table>
2.3 TEST SOLUTION SELECTED FOR THE STUDY

The corrosion inhibition experiments were performed in unstirred, aerated 1 M HCl solution, which was obtained by diluting 37% HCl (analytical grade) with double distilled water.

A stock solution of 1000 ppm of inhibitors was prepared in 1 M HCl solution and the desired concentrations were obtained by appropriate dilution. The concentration of the inhibitors used for the study ranges from 1 to 1000 ppm. All solutions were made using double distilled water.

2.4 CORROSION INHIBITION STUDIES

2.4.1 Gravimetric Study

The gravimetric experiments were performed for duration of 6 h, as per ASTM designation G1-90 [171]. The clean and dry MS specimen was measured for the total surface area with utmost accuracy. The weight of the specimen was determined on digital balance (with a sensitivity of 0.001g). After taking the initial weight and dimensions, the freshly prepared MS specimens were suspended in 250-mL beakers containing 200 mL of test solution maintained at 30, 40, 50 and 60°C. The volume of the test solution was kept at about 20 mL cm⁻² of steel sample, which was found to be sufficient to avoid any appreciable change in its corrosivity during the period of immersion of test specimens. The temperature was maintained using a thermo-stated water bath. To avoid crevice corrosion the specimens were hanged in the test solution with the help of nylon thread. After the duration of 6 hours, the coupons were retrieved, rinsed with distilled water. The resultant corrosion products were removed mechanically by scrubbing with a bristle brush, washed with water, dried and reweighed. The specimens were immersed in triplicate and the average corrosion rate was calculated, the uncertainty in the results was less than 5%. The corrosion rate ($\nu$ in mpy) was calculated from the following eq.:

$$\nu = \frac{534W}{\rho A t}$$  \hspace{1cm} (2.1)

where, $W$ is the weight loss in mg, $A$ is the total area of the specimen in cm² and $t$ is the immersion time in h. From the corrosion rate thus obtained, the inhibition
efficiency, $\eta_{\text{grav}}$ (%) and values of surface coverage ($\theta$) were calculated by the following eq.:

$$\eta_{\text{grav}}(\%) = \frac{V_o - V_i}{V_o} \times 100$$

(2.2)

$$\theta = \frac{V_o - V_i}{V_o}$$

(2.3)

where, $V_o$ is the corrosion rate in the absence of inhibitor and $V_i$ is the corrosion rate in the presence of inhibitor.

2.4.2 Synergistic Inhibition Effect of Surfactant Additives

Synergistic inhibition, which is an enhanced performance of a combination of inhibitors compared with the individual inhibitors in preventing the metals from corrosion, has proved to be an effective method to enhance the inhibition performance or to reduce the required dosage of the inhibitors. The synergism parameter, $S_1$ was estimated using the relation actually proposed by Aramaki and Hackerman [172]:

$$S_1 = \frac{1 - \theta_{1+2}}{1 - \theta_1' + \theta_2'}$$

(2.4)

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$$

(2.5)

where, $\theta_1$ and $\theta_2$ are surface coverage by inhibitor and surfactant additives, respectively and $\theta_{1+2}'$ is assessed surface coverage by the mixture of studied inhibitor and surfactant additives. Usually, $S_1$ more than unity signifies synergistic effect while $S_1$ less than unity signifies that antagonistic behavior prevails.

2.4.3 Adsorption Isotherm

Adsorption of organic inhibitors onto metal surfaces is usually described by adsorption isotherms. It is widely acknowledged that adsorption isotherms provide useful insights into the mechanism of corrosion inhibition and provide important clues on the nature of metal-inhibitor interactions. Various adsorption isotherms (eq. 2.6-2.11) that have been tested in the research work, are presented in Table 2.2 [173,174].
Table 2.3 Adsorption isotherm models that can be used to describe the adsorption of inhibitor on the metal surface.

<table>
<thead>
<tr>
<th>Name</th>
<th>Isotherm</th>
<th>Verification Plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$C/\theta = 1/K_{ads} + C$</td>
<td>(2.6) $C/\theta$ vs. $1/C$</td>
</tr>
<tr>
<td>Frumkin</td>
<td>$[\theta(1-\theta)e^{-2f\theta}$</td>
<td>(2.7) $\theta$ vs. log $C$</td>
</tr>
<tr>
<td>Temkin</td>
<td>$\exp(f\theta) = K_{ads}C$</td>
<td>(2.8) $\theta$ vs. log $C$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\theta = K_{ads}C$</td>
<td>(2.9) $\theta$ vs. $C$</td>
</tr>
<tr>
<td>Bockris-Swinkels</td>
<td>$\theta(1-\theta)[\theta + n(1-\theta)^{n-1}/n^n = C e^{-K_{ads}/55.5}$</td>
<td>(2.10) $\theta(1-\theta)$ vs. log$C$</td>
</tr>
<tr>
<td>Virial Parson</td>
<td>$\theta e^{2f\theta} = K_{ads}\theta$</td>
<td>(2.11) $\theta$ vs. log$(\theta/C)$</td>
</tr>
</tbody>
</table>

where, $\theta$ is the fraction of the metal surface covered with the inhibitor as a result of adsorption, $C$ is inhibitor concentration, $n$ is the number of water molecules replaced per inhibitor molecule, $f$ is the inhibitor interaction parameter and $K_{ads}$ is the equilibrium constant of the adsorption-desorption process.

2.4.4 Computation of Thermodynamic and Activation Parameters

The mechanism of inhibition was also investigated by calculating the thermodynamic and activation parameters like free energy of adsorption ($\Delta G^°_{ads}$), apparent activation energy ($E_a$), enthalpy of activation ($\Delta H$) and apparent entropy of activation ($\Delta S$) from the gravimetric data. The free energy of adsorption ($\Delta G^°_{ads}$) of the inhibitor on MS surface can be determined using the following eq. [175]:

$$K_{ads}=(1\times10^6)\exp(-\Delta G^°_{ads}/RT)$$

(2.12)

where, $K_{ads} =$ equilibrium constant (values were computed from the intercept of the graphs of adsorption isotherms), $1\times10^6 =$ molar concentration of water (ppm), $R =$ universal gas constant and $T =$ thermodynamic temperature. Generally, for the values of $\Delta G^°_{ads}$ around -20 kJ mol$^{-1}$ or more negative, the adsorption is regarded as physical adsorption where the inhibition occurs due to the electrostatic interactions between the charged molecules and the charged metal and those around -40 kJ mol$^{-1}$ or more negative are associated with chemical adsorptions, which is due to the transfer or charge sharing from the inhibitor molecules to the MS surface to form a co-ordinate type of bond.
The temperature dependence of corrosion rate can be best represented by calculating the values of apparent activation energy \((E_a)\). The value of apparent activation energy was calculated by using the Arrhenius rate eq., where the natural logarithm of \(\nu\) is a function of \(1/T\) [176]:

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

(2.13)

where, \(\nu\) = corrosion rate, \(E_a\) = apparent effective activation energy, \(R\) = molar gas constant, \(T\) = absolute temperature, and \(A\) = Arrhenius constant. The activation energy for metallic corrosion is the minimum amount of energy that is required in order to produce the corrosion products. The natural logarithm of \(\nu\) behaves as linear function with \(1/T\). Therefore, the value of \(E_a\) could be obtained by calculating the linear slope \((-E_a/R)\) of eq. 2.13.

To compute the enthalpy of activation \((\Delta H)\) and apparent entropy of activation \((\Delta S)\) for the formation of the activation complex a transition state formulation of Arrhenius eq. given below was used [177]:

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

(2.14)

where, \(\nu\) = corrosion rate, \(R\) = universal gas constant, \(N\) = Avogadro number, and \(h\) = Planck’s constant. From the slope \((-\Delta H/2.303R)\), and intercept \([\log(R/Nh) + (\Delta S/2.303R)]\) of the eq. the values of \(\Delta H\) and \(\Delta S\), respectively were computed.

### 2.4.5 Electrochemical Measurements

Electrochemical measurements were carried out by using Potentiostat/Galvanostat from Autolab, model 128N with inbuilt impedance analyzer FRA2. The 1L electrochemical cell supplied by Autolab (Fig. 2.1) consisted of a three electrode set up; MS specimens with exposed area of 1 cm\(^2\) as working electrode (WE), Ag/AgCl electrode (saturated KCl) as a reference electrode, and Pt wire as a counter electrode. A Luggin-Haber capillary was also included in the cell set up and the tip of the capillary was kept very close to the surface of the WE to minimize IR drop. Prior to the commencement of electrochemical experiments the specimens were allowed to stabilize in the test solution. In general, 30 min to 1 h immersion was
enough to stabilize the potential and establish a steady state open circuit potential (OCP). Each experiment was repeated at least three times to check the reproducibility of results, and acceptable reproducibility was obtained.

![Corrosion cell used in electrochemical technique.](image)

**Fig. 2.1** Corrosion cell used in electrochemical technique.

The EIS measurements were realized at corrosion potential ($E_{corr}$). The applied alternating-current perturbation signal was 10 mV within the frequency spectrum from $10^{-2}$ to $10^5$ Hz. The inhibition efficiency, $\eta_{EIS}$ (%), at various concentrations of tested inhibitors was calculated according the following relationship [176]:

$$
\eta_{EIS} (\%) = \frac{R_{ct}^o - R_{ct}}{R_{ct}} \times 100
$$

(2.15)

where $R_{ct}^o$ and $R_{ct}$ are the charge transfer resistance without and with inhibitors, respectively.

For the better approximation of the corrosion data the capacitance is replaced by a transfer function constant phase elements (CPE) and defined in term of impedance as:

$$
Z_{CPE} = \frac{1}{Y_o (j\omega)^n}
$$

(2.16)
where, $Y_0$ is the magnitude of CPE (in $\Omega^{-1}s^{n-1}cm^{-2}$), $j$ is the imaginary number and is equal to the square root of -1, $\omega$ is the angular frequency in rad s$^{-1}$ ($\omega = 2\pi f_{\text{max}}$) and $n$ corresponds to the phase shift, which can be used as a measure of surface irregularity. Generally, higher value of $n$ is associated with lower surface roughness and vice versa. Moreover, the nature of CPE can also be explained based on the values of $n$ and $Y_0$. For example $n = 0$ and $Y_0 = R$ represents the resistance, $n = 1$ and $Y_0 = C$ represents the capacitance, $n = -1$ and $Y_0 = 1/L$ represents the inductance, and $n = 1/2$ and $Y_0 = W$ represents the Warburg impedance. The values of double layer capacitance ($C_{\text{dl}}$), was calculated using Hsu and Mansfeld eq.:

$$C_{\text{dl}} = Y_0(\omega_{\text{max}})^{n-1}$$

(2.17)

For potentiodynamic polarization experiments, the WE was scanned in the potential range of 0.250 V below the corrosion potential to 0.250 V above the corrosion potential at a rate of 0.001 V/s. The electrochemical kinetic parameters such as corrosion potential ($E_{\text{corr}}$), corrosion current density ($i_{\text{corr}}$), anodic Tafel slope constant ($\beta_a$), and cathodic Tafel slope constant ($\beta_c$) were obtained from the extrapolation of the linear sections of anodic and cathodic branches of polarization curves. The inhibition efficiency, $\eta_{\text{PDP}}$ (%), at various concentrations of tested inhibitors was calculated according the following relationship:

$$\eta_{\text{PDP}} (%) = \frac{i_{\text{o,corr}} - i_{\text{corr}}}{i_{\text{o,corr}}} \times 100$$

(2.18)

where $i_{\text{o,corr}}$ and $i_{\text{corr}}$ are the corrosion current density without and with inhibitor, respectively.

The $R_p$ values are calculated from the Tafel plots according to the Stern-Geary eq.:

$$R_p = \frac{\beta_a\beta_c}{2.303(\beta_a + \beta_c)}i_{\text{corr}}$$

(2.19)

where $\beta_a$ and $\beta_c$ are anodic and cathodic Tafel slope constants, respectively.
2.4.6 Quantum Chemical Study

Quantum chemical calculations were conducted in order to describe the molecular properties of the inhibitors and understand the pattern in corrosion inhibition. The geometry optimization and several quantum chemical parameters of the studied inhibitors molecules were obtained by DFT calculations using the ORCA programme module (version 3.0.3) [178]. DFT is a most widely accepted \textit{ab initio} approach for modeling ground states of molecules and has been found to be successful in providing insights into the chemical reactivity and selectivity. Geometry optimizations and exchange correlations are treated using the Becke’s three parameter hybrid, B3LYP and full optimization was performed with SVP/SV(J) basis set [179, 180]. The molecule was optimized both in gas and aqueous phases. All the theoretical parameters are calculated in the solution phase because it is well known, that the electrochemical corrosion always occur in solution phase. Here, Conductor like screening model, abbreviated as COSMO model was applied in order to incorporate the effect of solvent (here, water) in this calculation. It is an efficient and elegant way to calculate the energies, structures and properties of molecules in solution [179]. The solvent is represented as a dielectric polarizable continuum. All the calculations were performed for the protonated form of the inhibitors. The calculated descriptors are the energy of highest occupied molecular orbital ($E_{HOMO}$), the energy of lowest unoccupied molecular orbital ($E_{LUMO}$), the separation energy ($\Delta E$), absolute electronegativity ($\chi$) and absolute hardness ($\eta$). According to Koopmen’s theorem, the values of $E_{HOMO}$ and $E_{LUMO}$ of the inhibitor molecule are associated with the ionization potential ($I$) and the electron affinity ($A$), respectively. The values of $I$ and $A$ are defined as $-E_{HOMO}$ and $-E_{LUMO}$, respectively. Absolute electronegativity ($\chi$) and absolute hardness ($\eta$) were obtained from eq.s [179]:

$$\chi = \frac{I+A}{2}$$

$$\eta = \frac{I-A}{2}$$

Fraction of electrons transferred from the inhibitor to MS surface ($\Delta N$) is calculated as follows [182]:

$$\Delta N = \frac{I + A}{2}$$
\[
\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})}
\]  

(2.22)

Following Pearson’s idea, to find out the fraction of electrons transferred, a theoretical value for the absolute electronegativity of bulk iron was used \(\chi_{\text{Fe}} = 7\) eV and a global hardness of \(\eta_{\text{Fe}} = 0\), by assuming that for a metallic bulk \(I = A\) because of their softer nature than neutral metallic atoms [183,184].

2.4.7 UV-Visible Spectroscopy

UV–Visible absorption spectroscopic studies was carried out for 1 M HCl solution containing optimum concentration of inhibitor before and after 6 h of MS immersion at 30°C. The studies were carried out in order to confirm the possibility of the formation of the inhibitor-metal complex. The UV-Visible spectra were obtained using a Perkin–Elmer UV–Visible Lambda 25 spectrophotometer and the data was analyzed using the Perkin Elmer UV Winlab Data Processor and viewer.

2.4.8 FT-IR Spectroscopy

FT-IR spectra of pure inhibitors and inhibitors adsorbed on the MS surface in 1 M HCl solution were obtained using FT-IR in the frequency range of 4000-500 cm\(^{-1}\). Perkin-Elmer ‘Spectrum Two’ Spectrophotometer (spectral resolution 0.5 cm\(^{-1}\)) was used to record the FT-IR spectra of pure inhibitor and inhibitor adsorbed on the MS surface employing the KBr disc technique. In order to record the spectrum of an inhibitor adsorbed on the MS surface, the specimen was first immersed in 1 M HCl solution containing optimum concentration of inhibitor at 30°C for a period of 6 h. After completion of immersion, the sample was taken out, corrosion product scrapped from the surface, dried in vacuum for 48 h, mixed with KBr, made into disc and subjected to FT-IR analysis.

2.4.9 Surface Morphological Studies

For the morphological studies and elemental analysis of the surface film, MS coupons obtained after gravimetric experiments in absence and presence of an optimum concentration of inhibitor were subjected to Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX). The samples were analyzed using JEOL (Japan) SEM (Model: JSM- 6510LV) attached with an Oxford
Instruments EDX Analysis System, INCA 300 (UK). The studies were done in order to visualize the extent of corrosion damage to the MS specimens in uninhibited/inhibited acid solution in terms of surface heterogeneity/roughness.