CHAPTER-II

EXPERIMENTAL WORK
Chapter II

EXPERIMENTAL

2.1. Introduction

Since metallic corrosion is highly diverse in its occurrence, no universal testing procedure is found satisfactory to cover all aspects of corrosion. But for reproducible and informative evaluation, it is very essential to select a relevant method to correlate laboratory test with actual service conditions. Detailed information regarding the appropriate method to be adopted in corrosion testing is available from several reports including those of Ailor [1], Champion [2], ASTM [3], Uhling [4], Lague [5], Speller [6], Shreir [7] and Evans [8]. Though absolute reproducibility is rather impossible to achieve due to several factors, reproducibility within a reasonable error is of considerable importance. According to Evans and Champion, this is possible by taking precautionary measures regarding the size and shape of the specimen, design of the setup, time of exposure and a careful control of experimental conditions such as temperature and stirring of the medium. It is also desirable to perform the tests at least in duplicate or triplicate to minimize the error. Prior to corrosion tests, the treatment of the surface is another important factor. The exposed surface should be free from oxides, grease, etc., for unambiguous results.

2.2. Materials and methods

Materials

2.2.1. Preparation of electrode surface

The specimens used for corrosion tests were mild steel (MS) coupons with a dimension of 1 cm long × 1 cm breadth × 0.1 cm thickness. The chemical composition (wt %) of the MS used in the experiment is given in Table 2.1. Before gravimetric and electrochemical measurements, the surface of the specimens was polished under running tap water using emery paper (SiC, grade 200 - 1200), rinsed with distilled water, dried on a clean tissue paper, immersed in benzene for 5 s, dried and immersed in acetone for 5 s, and dried with clean tissue paper. Finally, the specimens were kept in desiccators until use. At the end of the gravimetric experiment, the specimens were carefully washed with acetone and benzene, dried and then weighed. For potentiodynamic polarization and
electrochemical impedance studies, the MS specimen was embedded in epoxy resin to expose a geometrical surface area of 1cm$^2$ to the electrolyte.

Table 2.1. Chemical composition of mild steel specimen

<table>
<thead>
<tr>
<th>Elements</th>
<th>Chemical composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.051</td>
</tr>
<tr>
<td>Mn</td>
<td>0.179</td>
</tr>
<tr>
<td>Si</td>
<td>0.006</td>
</tr>
<tr>
<td>P</td>
<td>0.005</td>
</tr>
<tr>
<td>S</td>
<td>0.023</td>
</tr>
<tr>
<td>Cr</td>
<td>0.051</td>
</tr>
<tr>
<td>Ni</td>
<td>0.05</td>
</tr>
<tr>
<td>Mo</td>
<td>0.013</td>
</tr>
<tr>
<td>Ti</td>
<td>0.004</td>
</tr>
<tr>
<td>Al</td>
<td>0.103</td>
</tr>
<tr>
<td>Cu</td>
<td>0.050</td>
</tr>
<tr>
<td>Co</td>
<td>0.017</td>
</tr>
<tr>
<td>Fe</td>
<td>99.419</td>
</tr>
</tbody>
</table>

2.2.2. Preparation of solutions

Approximately 1 M HCl was prepared by diluting the appropriate amount of concentrated acid (AR grade) with double distilled water. The concentration of acid is checked by titrating an appropriately diluted portion with standard solution of sodium hydroxide and which was titrated in turn against standard solution of oxalic acid. From the stock solution, required concentrations were prepared by dilution with double distilled water which was used throughout the experiment.

Stock solutions of 2 mM (BDTC, BMTC, BHTC, FMPPTS, FMPPDS, FMPPMS, FMPPDBS, FMPPNBS and FMPPMBS in chapter III, chapter V and chapter VI), 1.5 mM (MOMMBD and MOMMDP in chapter IV) and 3000 ppm (PH, CA, PR and AA in chapter VII and VIII) were prepared by weighing appropriate amount of it and dissolved in aggressive medium, and series of concentrations were prepared from these stock solutions. The test solution was industrial water collected from heat exchangers and reboilers of the
chemical industries in and around Mysore city, India. The chemical composition of the industrial water (ppm) obtained from ionic chromato graph was: 7500 $\text{Cl}^{-}$; 64 $\text{Ca}^{2+}$; 3440 $\text{SO}_4^{2-}$; 23 $\text{Mg}^{2+}$; 140 $\text{Na}^{+}$; 0.28 $\text{PO}_4^{3-}$.

2.2.3. Inhibitors

The inhibitors used are 4-(4-bromophenyl)-N'-(2,4-dimethoxybenzylidene)thiazole-2-carbohydrazide (BDTC), 4-(4-bromophenyl)-N'-(4-methoxybenzylidene)thiazole-2-carbohydrazide (BMTC), 4-(4-bromophenyl)-N'-(4-hydroxybenzylidene)thiazole-2-carbohydrazide (BHTC), 4-(((4-((5-Mercapto-1,3,4-oxadiazol-2-yl)methyl)-5-methylthiazol-2-yl)imino)methyl)benzene-1,2-diol (MOMMBD) and 4-(((4-((5-Mercapto-1,3,4-oxadiazol-2-yl)methyl)-5-methylthiazol-2yl)imino)methyl)-2,6-dimethoxyphenol (MOMMDP), N-(1-(5-fluoro-2-(methylthio)pyrimidin-4-yl)piperidin-4-yl)-2,4,6-trimethyl benzene sulfonamide (FMPPTS), N-(1-(5-fluoro-2-(methylthio)pyrimidin-4-yl)piperidin-4-yl)-3,4 dimethoxy benzene sulfonamide (FMPPDS), N-(1-(5-fluoro-2-(methylthio)pyrimidin-4-yl)piperidin-4-yl)-3-methoxybenzenesulfonamide (FMPPMS), N-(1-(5-fluoro-2-(methylthio)pyrimidin-4-yl)piperidin-4-yl)-2,5-dimethoxybenzene sulfonamide (FMPPDBS), N-(1-(5-fluoro-2-(methylthio)pyrimidin-4-yl)piperidin-4-yl)-4-nitrobenzene sulfonamide (FMPPNBS), N-(1-(5-fluoro-2-(methylthio)pyrimidin-4-yl)piperidin-4-yl)-3 methoxy benzene sulfonamide (FMPPMBS) and the extracts of *Pterolobium hexapetalum* (PH), *Celosia argentea* (CA), *Achyranthes aspera* (AA) and *Plumeria rubra* (PR) were used as environmentally friendly and cost effective inhibitors. PH, CA, PR and AA extracts are studied in industrial water medium and remaining inhibitors were studied in hydrochloric acid medium.

Procedures for the synthesis of BDTC, BMTC, BHTC, MOMMBD, MOMMDP, FMPPTS, FMPPDS, FMPPMS, FMPPDBS, FMPPMBS and FMPPNBS are explained in chapters III, IV and V. Mature leaves of PH, CA, AA and PR were collected from western ghats, Karnataka, India. Stock solutions of the plants extracts were obtained by drying the plants for 2 h in an oven at 80 °C. Thoroughly washed leaves were shade dried and then powdered with the help of a blender. The powdered leaves were extracted with methanol (10 g sample of the powder was refluxed into 250 mL methanol) using a Soxhelt extractor until they becomes almost color less (around 30 to 35 cycles). The extracts were concentrated using rotary flash evaporator. The refluxed solutions were filtered to remove any contamination.
For the synthesis of inhibitors, all solvents and reagents were purchased from Sigma Aldrich Chemicals Pvt Ltd. Melting range was determined by Veego Melting Point VMP III apparatus. Elemental analyses were recorded on VarioMICRO superuser V1.3.2 Elementar. The FT-IR spectra were recorded on FT-IR Jasco 4100 infrared spectrophotometer. Mass spectral data were obtained by LC/MSD Trap XCT. $^1$H NMR spectra were recorded on Bruker DRX-500 spectrometer at 400 MHz using DMSO-d$_6$ as solvent and TMS as an internal standard.

**Methods**

### 2.2.4. Mass loss measurements

Gravimetric experiments were carried out in a glass cell and the solution volume was 100 cm$^3$. The temperature of the environment was maintained by thermostatically controlled water bath (Weiber, India) with an accuracy of ± 0.2 °C under aerated condition. The square shaped MS specimens were used with a dimension of 1 cm × 1 cm × 0.1 cm. The initial weight of the specimen was recorded using an analytical balance (Seratorious, precision ± 0.1 mg). After the corrosion test in 0.5 M HCl with and without inhibitor, the specimens were carefully washed in double distilled water, dried and then weighed. The weight loss of the specimen was determined after an immersion period of 4 h, 45 h and 50 h at the temperature range of 303 - 333 K. Triplicate experiments were performed in each case and the average mass loss was reported. The corrosion rate ($C_R$) and inhibition efficiency ($E_{WL} \%$) are calculated using equations (2.1) and (2.2).

\[
C_R = \frac{\Delta W}{S \times t} \quad (2.1)
\]

\[
IE(\%) = \frac{(C_R)_a - (C_R)_p}{(C_R)_a} \times 100 \quad (2.2)
\]

where, $\Delta W$ is the weight loss, $S$ is the surface area of the specimen (cm$^2$), $t$ is the immersion time (h), and $(C_R)_a$ and $(C_R)_p$ are corrosion rates in the absence and presence of the inhibitor, respectively.

### 2.2.5. Potentiodynamic polarization measurements

The electrochemical character of MS sample in uninhibited and inhibited solutions was investigated by recording anodic and cathodic polarization curves in 0.5 M HCl solutions with different inhibitors concentrations with an exposed area of 1cm$^2$. A
conventional three electrode cell consisting of MS as working electrode, platinum foil as counter electrode and saturated calomel electrode as reference electrode was used. The schematic diagram of the polarization cell is shown in Fig. 2.1. Potentiodynamic polarization curves were recorded after immersion of the working electrode (MS) for 30 min in 0.5 M HCl solution containing different concentrations of the inhibitors in the potential range from +200 mV to -200 mV with a scan rate of 0.4 mV s\(^{-1}\). The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential (\(E_{\text{corr}}\)) to obtain corrosion current densities (\(I_{\text{corr}}\)). The \(C_R\) and \(IE\) (%) at different inhibitors concentrations are calculated using the following equation (2.3) and (2.4):

\[
C_R = 8.9548 \times 10^{-3} \times I_{\text{corr}} \times EW
\]  

(2.3)

\[
IE(\%) = \frac{(I_{\text{corr}})_a - (I_{\text{corr}})_p}{(I_{\text{corr}})_a} \times 100
\]  

(2.4)

where \(I_{\text{corr}}\) is the corrosion current density, \(EW\) is the equivalent weight of the specimen, \((I_{\text{corr}})_a\) and \((I_{\text{corr}})_p\) are the corrosion current densities (\(\mu\text{A cm}^{-2}\)) in the absence and presence of the inhibitors, respectively.

![Fig. 2.1: Polarization cell](image-url)
Fig. 2.2: CH instrument for electrochemical measurements.

Fig. 2.3: Polarization curves for measuring the Tafel slopes.
2.2.6. Electrochemical impedance spectroscopy (EIS)

The EIS tests were performed in a three electrode assembly CH1660D instrument (Fig. 2.2). CH Instruments software version 12.04 was used to fit impedance data. The cell arrangement used was a conventional three-electrode cell with platinum counter electrode, saturated calomel electrode (SCE) as reference electrode and test material (MS) as working electrode. All potentials were reported vs. SCE, and the measurements were done after 30 min of immersion in the test solution. EIS measurements were performed with a frequency range of 0.1 Hz to 10 kHz and amplitude of 0.005 V. The equivalent circuit is shown in the Figure 2.4. The $R_{ct}$ and $C_{dl}$ values are obtained from Nyquist plots, and the $I_{cor}$ can be calculated using the following expression:

$$I_{cor} = \frac{b_a b_c}{2.303(b + b_e) R_{ct}}$$

(2.5)

where $b_a$ and $b_e$ are Tafel slopes for the anodic and cathodic reactions, respectively and $R_{ct}$ is the charge transfer resistance. The inhibition efficiency IE (%) was then computed using the Eq. (2.6).

$$IE(\%) = \left(\frac{1}{R_{ct}}\right)_{a} - \left(\frac{1}{R_{ct}}\right)_{p} \times 100$$

(2.6)

where $R_{ct(a)}$ and $R_{ct(p)}$ are the charge transfer resistance in the absence and the presence of inhibitor, respectively. If the Randle equivalent circuit is assumed for the cell, the cell impedance, $Z$ can be shown to be:

$$Z = Z' - jZ''$$

(2.7)

$$Z' = R_s + \frac{R_{ct}}{1+(j C_{dl} \cdot R_{ct})^2}$$

(2.8)

$$Z'' = \frac{(j C_{dl} \cdot R_{ct})^2}{1+(j C_{dl} \cdot R_{ct})^2}$$

(2.9)

The cell impedance consists of a real ($Z'$) and an imaginary ($Z''$) parts, $R_s$ is the solution resistance, $R_{ct}$ is the charge transfer resistance and $C_{dl}$ is the double layer capacitance. The
double layer capacitance \( (C_{\text{dl}}) \) and the frequency at which the imaginary component of the impedance is maximal \( (-Z_{\text{max}}) \) are found as represented in Eq. (2.10).

\[
C_{\text{dl}} = \frac{1}{2\pi f_{\text{max}} R_{\text{ct}}} \quad (2.10)
\]

\[\begin{array}{c}
\mathcal{C}_{\text{dl}} \\
\hline
R_{\text{ct}} \\
\hline
R_s
\end{array}\]

**Fig. 2.4:** Equivalent circuit

### 2.2.7. FT-IR Spectroscopy

FT-IR studies (KBr pellet and Nujal) were made for mild steel exposed to corrosive media (0.5 M HCl and industrial water) in the presence of optimum concentration of inhibitors. A scratched powder from the metal surface after desired immersion time in different media under optimum conditions of inhibitors concentration and temperature was collected and left to dry. The resultant powder was mixed with KBr and Nujal, and prepared as pellets. The IR spectra were recorded using JASCO-4100 spectrophotometer in the spectral region between 4000 and 400 cm\(^{-1}\).

### 2.2.8. Scanning electron microscopy (SEM)

The SEM analysis was performed using a JSM-5800 electron microscope with the working voltage of 20 kV and the working distance 24 mm. In SEM micrographs, the specimens were exposed to the corrosive media in the absence and presence of inhibitors under optimum conditions after a desired period of immersion. The SEM images were taken for mild steel specimens immersed in solution without and with inhibitors.
2.2.9. Quantum chemical calculations

The molecular structures of inhibitors were fully geometrically optimized by AM1 semi empirical method with Spartan’ 08 V1.2.0. Three main related parameters such as the energy of the highest occupied molecular orbital \((E_{\text{HOMO}})\), the energy of the lowest unoccupied molecular orbital \((E_{\text{LUMO}})\) and dipole moment \((\mu)\) were gained.

2.2.10. Antioxidant activity

2.2.10.1. DPPH method

The free radical scavenging activity of the synthesized molecules was measured in terms of hydrogen donating or radical scavenging ability using the stable radical DPPH [10]. The test samples (10 - 100 µl) were mixed with 1.0 mL of DPPH solution and filled up with methanol to a final volume of 4 mL. Absorbance of the resulting solution was measured at 517 nm in a visible spectrophotometer. Ascorbic acid was used as the reference compound. Radical scavenging activity was expressed as the inhibition percentage of free radical by the sample, and was calculated using the following relation:

\[
\% \text{ Inhibition} = \left(\frac{A_0 - A_t}{A_0}\right) \times 100
\]  

(2.11)

where \(A_0\) is the absorbance of the control (blank) and \(A_t\) is the absorbance in the presence of the test samples. All tests were performed in triplicate and the results were expressed as mean values ± standard deviations.

2.2.10.2. Hydroxyl radical scavenging activity

The hydroxyl radical scavenging capacity was measured using modified method [11]. Stock solutions of EDTA (1 mM), FeCl₃ (10 mM), ascorbic acid (1 mM), H₂O₂ (10 mM) and deoxyribose (10 mM) were prepared in distilled water. The assay was performed by adding 0.1 ml EDTA, 0.01 ml of FeCl₃, 0.1 ml of H₂O₂, 0.36 ml of deoxyribose, 1.0 ml of sample (50 – 250 µg/ml) each dissolved in distilled water, 0.33 ml of phosphate buffer (50 mM, pH 7.4) and 0.1 ml of ascorbic acid in sequence. The mixture was then incubated at 37 °C for 1 h. About 1.0 ml portion of the incubated mixture was mixed with 1.0 ml of (10 %) TCA and 1.0 ml of (0.5 %) TBA containing 0.025 M NaOH and butylated hydroxyl anisole (BHA)) to develop the pink chromogen and measured at 532 nm. The
hydroxyl radical scavenging activity of the compound was reported as the percentage of inhibition of deoxyribose degradation and was calculated using Eq. (2.11).

2.2.10.3. Nitric oxide radical scavenging assay

The method of Garrat et al. [12] was adopted to determine the nitric oxide radical scavenging activity of the synthesized molecules. Sodium nitroprusside in aqueous solution at physiological pH spontaneously generate nitric oxide which interacts with oxygen to produce nitrite ions determined by the use of Griess reagents. To 2 mL of 10 mM sodium nitroprusside dissolved in 0.5 mL phosphate, buffer saline (pH 7.4) was mixed with 0.5 mL of sample solution at various concentrations (50 - 250 µg/mL). The mixture was incubated at 25 °C. After 150 min, 0.5 mL of the incubation solution was withdrawn and mixed with 0.5 mL of Griess reagent [(1.0 mL sulfanilic acid reagent (0.33 % in 20 % glacial acetic acid at room temperature for 5 min with 1 mL of naphthylethylenediamine dichloride (0.1% w/v)]. The mixture was incubated at room temperature for 30 min. The absorbance was measured at 540 nm. The amount of nitric oxide radical was calculated using Eq. (2.11).
Chapter II

Experimental

References


