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 set up, 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 the electrode surface

Corrosion studies were made on mild steel specimen cut from sheets with 1 cm long, 1 cm breadth and 0.3 cm thickness (used to study chapter 3 and 5) and 2 cm long, 2 cm breadth and 0.1 cm thickness (used to study Chapter 4, 6, 7 and 8). The chemical composition (wt %) of mild steels used for the experiment are given in Table 2.1. Prior to each experiment, the surface of the specimen was polished under running tap water using emery paper of grade numbers, 220, 320, 450, and 600, rinsed with distilled water, dried on a clean tissue paper, immersed in benzene for five seconds, dried and immersed in acetone for five seconds and dried with clean tissue paper. Finally, they are kept in a desiccator for one hour until use.
Table 2.1: Chemical composition of mild steel specimen

<table>
<thead>
<tr>
<th>Elements</th>
<th>Composition (% wt)</th>
<th>Mild steel(^1)</th>
<th>Mild steel(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.090</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.322</td>
<td>0.322</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.016</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.010</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.373</td>
<td>0.090</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.025</td>
<td></td>
<td>0.050</td>
</tr>
<tr>
<td>Cr</td>
<td>0.062</td>
<td>0.062</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>99.10</td>
<td>99.40</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)used to study chapters 3 and 5, \(^2\)used to study chapters 4, 6, 7 and 8

2.2.2. Preparation of the solutions

Approximately 1 M H\(_2\)SO\(_4\) and HCl solutions were prepared by diluting the appropriate volume of the concentrated acids (AR grade) with double distilled water. The concentration of the acids was checked by titrating an appropriately diluted portion with standard solution of sodium hydroxide which was titrated in turn against standard solution of oxalic acid. From this stock solution, required concentrations were prepared by dilution with double distilled water which was used throughout the experiment.

A stock solution of 10 mM (AA and AB), 1mM (SB\(_1\) and SB\(_2\)) and 3000 ppm (ZM, CZ, SP and CE) were prepared by weighing an appropriate amount of it and dissolved in aggressive medium, and series of concentrations were prepared from these stock solutions. The industrial water used for the experiment was actually taken from the some plants in and around Mysore city, India. The pH of the industrial water used was 5.65 and the chemical composition of industrial water was (ppm), 7500 Cl\(^-\), 64 Ca\(^{2+}\), 3440 SO\(_4^{2-}\), 23 Mg\(^{2+}\), 140 Na\(^+\), 0.28 PO\(_4^{3-}\).
2.2.3. Inhibitors

The inhibitors used are Imatinib mesylate (IMT), Azure A (AA), Azure B (AB), (E)-2-(3-nitrobenzylidene) hydrazine carbothioamide (SB1) and (E)-2-(4-(dimethylamino) benzylidene) hydrazine carbothioamide (SB2) and Spinacia oleracea (SP), Centella asiatica (CA), Ziziphus mauritiana (ZM), Cinnamomum zeylanicum (CZ) (Plant extracts) are also used as environmental friendly, inexpensive and efficient inhibitors. SB1 and SB2 are studied in industrial water medium and remaining inhibitors were studied in acid medium.

Azure A, Azure B, H$_2$SO$_4$, HCl, semicarbazide, aldehydes were purchased from Merck chemicals and Imatinib mesylate was procured from Intermed Labs, Bangalore, India. Fresh Spinacia oleracea, Centella asiatica, Ziziphus mauritiana and Cinnamomum zeylanicum leaves were collected in and around Mysore city, India.

Stock solution of the plants extracts was obtained by drying the plants for 2 h in an oven at 80 °C and ground to powder. The 10 g of the powder sample was refluxed in 250 mL ethyl alcohol for 5 h. The refluxed solution was filtered and the filtered liquor was evaporated to 100 mL dark green residue and then degreased with petroleum ether and extracted with separating funnel. The solution was evaporated and the solid residue obtained after complete drying was preserved in a desiccator. The residue so obtained was used in preparing different concentrations of the extracts in acid solution. [9].

Methods

2.2.4. Gravimetric measurements

The experiments were carried out using gravimetric method in 500 mL capacity round bottom glass flask placed in a thermostatically controlled water bath with accuracy of ± 0.2 °C (Weiber Ltd. Chennai, India). Experiment was performed in both static condition and the different rotational speed of the specimen. The desired speed of a specimen was set by using speed regulator motor (Eltek Ltd., Mumbai, India). This method is used to obtain well-defined diffusion conditions in solution. It permits the use of square electrode with area of (1 cm × 1 cm × 0.3 cm), embedded in epoxy resin. Only one face of the specimen was exposed to the solution and remaining faces were embedded in epoxy resin and it was rotated by shaft which is driven by a ¼ hp motor. Three specimens were used at each test, and the average was recorded. They were mounted axially on the lower part of the shaft which has washers to separate the specimens in order to prevent galvanic
contact. The initial weight of the specimen was recorded using an analytical balance (precision ± 0.1 mg) before immersion in the aggressive media. The corrosion rates \( CR \) of mild steel have been determined for desired immersion period at various rotational speed (1600 – 2200) rpm from mass loss using Eq. (2.1), where \( W \) is mass loss (mg), \( t \) is the immersion time (h), and \( A \) is the exposed surface area of the specimen (cm\(^2\)). \( CR \) is expressed in mg cm\(^{-2}\) h\(^{-1}\). Experiments were carried out in the temperature range of 30 - 80 °C.

\[
CR = \frac{W}{A \times t} \quad (2.1)
\]

The inhibition efficiency \( IE \) (%) of the inhibitors can be calculated by following equation:

\[
IE(\%) = \frac{CR_a - CR_p}{CR_a} \times 100 \quad (2.2)
\]

\( CR_a \) and \( CR_p \) represent the corrosion rate in the absence and presence of inhibitors, respectively.

### 2.2.5. Potentiodynamic polarization measurements

For potentiodynamic polarization measurements, a three electrode cell was used. A rectangular specimen, a platinum wire and a saturated calomel electrode (SCE) were constituted as the working, counter and reference electrodes, respectively (Fig. 2.1). The specimen was pre-treated in the same way as in the gravimetric measurements. Experiments were carried out in different medium such as sulphuric acid, hydrochloric acid and industrial water medium at 30 °C using a thermostatically controlled water bath under aerated conditions at static condition. The measurements were performed by sweeping the potential between -900 and +300 mV from open circuit potential (OCP) at the scan rate of 0.4 mV s\(^{-1}\), using CHI660D electrochemical workstation. A rectangle with surface area of 24.2 cm\(^2\) was used as working electrode (WE), and only 1cm\(^2\) surface was exposed to the solution. Remaining surface of the specimens was embedded in epoxy resin. This is accomplished by measuring the voltage difference between the reference electrode and the metal using a CHI660D electrochemical workstation capable which is capable of measuring small voltages without drawing any appreciable current.
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The corrosion potential ($E_{\text{corr}}$) and corrosion current density ($I_{\text{corr}}$) were obtained from interaction of Tafel slopes of the polarization curves (Fig. 2.4). The $CR$ and the inhibition efficiency $IE\%$ can be calculated using the following equations:

$$CR = 8.9548 \times 10^{-3} \times I_{\text{corr}}EW$$

(2.3)

$$IE\% = \left(\frac{I_{\text{corr}}(a) - I_{\text{corr}}(p)}{I_{\text{corr}}(a)}\right) \times 100$$

(2.4)

where ($I_{\text{corr}}$) is the current density ($\mu A \text{ cm}^{-2}$), $EW$ is the equivalent weight of the specimen (g), ($I_{\text{corr}}(a)$ and ($I_{\text{corr}}(p)$ are the corrosion current density ($\mu A \text{ cm}^{-2}$) in absence and presence of the inhibitor, respectively.

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

Fig. 2.3: Experimental setup to measure the corrosion current and corrosion potential of the specimen.
2.2.6. Electrochemical impedance spectroscopy (EIS)

The EIS tests for mild steel specimens as working electrode in different aggressive media in the presence and the absence of inhibitors were carried out in a three necked cell (Fig. 2.1) with saturated calomel and platinum foil as reference and counter electrodes, respectively. The experiments were conducted using CHI660D electrochemical workstation. The A.C impedance measurements were performed at corrosion potential over a frequency range from 10 kHz to 0.05 Hz with signal amplitude of ±10 mV. The equivalent circuit is shown in Fig. 2.5. From Nyquist plots, $R_{ct}$ and $C_{dl}$ values were obtained, and by using Stern-Geary equation, $I_{corr}$ can be computed as follows:

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

(2.5)

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

$$IE(\%) = \frac{(1/R_{ct})_a - (1/R_{ct})_p}{(R_{ct})_a} \times 100$$

(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:
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\[ Z = Z' - jZ'' \]  \hspace{1cm} (2.7)

Where

\[ Z' = R_s + \frac{R_{ct}}{1 + (j C_{dl} R_{ct})^2} \]  \hspace{1cm} (2.8)

\[ Z'' = \frac{(j C_{dl} R_{ct})^2}{1 + (j C_{dl} R_{ct})^2} \]  \hspace{1cm} (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 \((C_{dl})\) and the frequency at which the imaginary component of the impedance is maximal \((-Z_{max})\) are found as represented in Eq. (2.10),

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

Fig. 2.5: Equivalent circuit

2.2.7. FT-IR spectroscopy

FT-IR spectra (KBr pellet) were recorded for pure and scrapped samples of the inhibitors from the metal surface. A scratched powder from the metal surface after desired immersion time in the aggressive media under optimum conditions of inhibitors concentration and temperature was collected and left to dry. The resultant powder was mixed with KBr and prepared as pellets. The IR spectra were recorded using JASCO-4100 spectrophotometer in the spectral region between 4000 and 400 cm\(^{-1}\).
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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 macrographs, the specimens were exposed to the corrosive medium in the absence and the presence of inhibitors under optimum conditions after a desired period of immersion. The SEM images were taken for pure 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. Four main related parameters such as the energy of the highest occupied molecular orbital ($E_{HOMO}$), the energy of the lowest unoccupied molecular orbital ($E_{LUMO}$), energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) and dipole moment ($\mu$) were gained. MOPAC calculations were carried out for four different Hamiltonians including parametric model 3 (PM3), Austin model 1 (AM1), Recief model 1 (RM1) and modified neglect of diatomic overlap model (MNDO). Mulliken charge population of atoms in the inhibitor was also calculated.
REFERENCES


