3.1. Preparation of the mild steel specimens

The mild steel specimens were chosen from the same sheet of the following composition:

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>0.1</td>
<td>0.026</td>
<td>0.06</td>
<td>0.4</td>
<td>99.36</td>
</tr>
</tbody>
</table>

Mild steel specimens of the dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish, degreased with acetone and used for weight loss and surface examination studies. Mild steel rod encapsulated in teflon with an exposed cross section of 1 cm² area was used as the working electrode in electrochemical studies. The surface of the electrode was polished to mirror finish and degreased with acetone.

3.2. Chemicals used

The chemicals used in the present study are given in Table 3.1.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Chemicals</th>
<th>Grade</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Poly (acrylic acid) (PAA)</td>
<td>Analar</td>
<td>Sigma-Aldrich, USA</td>
</tr>
<tr>
<td>2.</td>
<td>Sodium gluconate (SG)</td>
<td>Analar</td>
<td>Merck, Mumbai</td>
</tr>
<tr>
<td>3.</td>
<td>Potassium sodium tartrate (SPT)</td>
<td>Analar</td>
<td>Merck, Mumbai</td>
</tr>
<tr>
<td>4.</td>
<td>Trisodium citrate dehydrate (TSC)</td>
<td>Analar</td>
<td>Merck, Mumbai</td>
</tr>
<tr>
<td>5.</td>
<td>Sodium lauryl sulphate (SLS)</td>
<td>Analar</td>
<td>Sigma-Aldrich, USA</td>
</tr>
<tr>
<td>6.</td>
<td>Benzyl triethylammonium chloride (BEC)</td>
<td>Analar</td>
<td>Sigma-Aldrich, USA</td>
</tr>
<tr>
<td>7.</td>
<td>Zinc sulphate hepta hydrate</td>
<td>Analar</td>
<td>S.D. Fine chem. Ltd, India</td>
</tr>
<tr>
<td>8.</td>
<td>Nickel sulphate hexahydrate</td>
<td>Analar</td>
<td>S.D. Fine chem. Ltd, India</td>
</tr>
<tr>
<td>9.</td>
<td>Sodium hydroxide</td>
<td>Analar</td>
<td>Merck specialities (P) Ltd., India</td>
</tr>
<tr>
<td>10.</td>
<td>Sodium chloride</td>
<td>Analar</td>
<td>Merck specialities (P) Ltd., India</td>
</tr>
<tr>
<td>11.</td>
<td>Sulphuric acid</td>
<td>Analar</td>
<td>Merck specialities (P) Ltd., India</td>
</tr>
<tr>
<td>12.</td>
<td>Acetone</td>
<td>Analar</td>
<td>Merck specialities (P) Ltd., India</td>
</tr>
<tr>
<td>13.</td>
<td>Yeast extract powder</td>
<td>Analar</td>
<td>Merck specialities (P) Ltd., India</td>
</tr>
<tr>
<td>14.</td>
<td>Agar - Agar</td>
<td>Analar</td>
<td>Merck specialities (P) Ltd., India</td>
</tr>
<tr>
<td>15.</td>
<td>Peptone</td>
<td>Analar</td>
<td>Merck specialities (P) Ltd., India</td>
</tr>
</tbody>
</table>
3.3. Properties of the inhibitors used in the present study

3.3.1. Poly (acrylic) acid (PAA)

The selected properties are listed below:

- **Molecular formula**: \((C_3H_4O_2)_n\)
- **Molecular Weight**: 1800 g/mol
- **Solubility**: soluble in water
- **Appearance**: liquid
- **Colour**: white

3.3.2. Sodium gluconate (SG)

The selected properties are listed below:

- **Molecular formula**: \(C_6H_{11}NaO_7\)
- **Molecular Weight**: 218.14 g/mol
- **Solubility**: soluble in water
- **Appearance**: powder
- **Colour**: white

3.3.3. Potassium Sodium Tartrate (SPT)

The selected properties are listed below:

- **Molecular formula**: \(C_4H_4KNaO_6\cdot4H_2O\)
- **Molecular Weight**: 282.22 g/mol
- **Solubility**: soluble in water
- **Appearance**: powder
- **Colour**: white
3.3.4. **Trisodium citrate dehydrate (TSC)**

The selected properties are listed below:

- Molecular formula: \((\text{HOC(COONa)(CH}_2\text{COONa)}_2 \cdot \text{2H}_2\text{O})\)
- Molecular Weight: 294.10 g/mol
- Solubility: soluble in water
- Appearance: powder
- Colour: white

3.3.5. **Sodium lauryl sulphate (SLS)**

The selected properties are listed below:

- Molecular formula: \(\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}\)
- Molecular Weight: 288.38 g/mol
- Solubility: soluble in water
- Appearance: powder
- Colour: white

3.3.6. **Benzyl triethylammonium chloride (BEC)**

The selected properties are listed below:

- Molecular formula: \(\text{C}_6\text{H}_5\text{CH}_2\text{N(Cl)(C}_2\text{H}_5)_3\)
- Molecular Weight: 227.77 g/mol
- Solubility: soluble in water
- Appearance: powder
- Colour: white
3.4. Preparation of the stock solution

3.4.1. Poly (acrylic acid)

1 g of PAA was dissolved in double distilled water, neutralized and then made up to 100 mL in a standard measuring flask. 1 mL of this solution was diluted to 100 mL, which yields exactly 100ppm of PAA.

3.4.2. Sodium Chloride Solution

Exactly 1 g of sodium chloride was dissolved in double distilled water and made up to 100 ml in a standard measuring flask. A hundred - fold dilution yields exactly 60 ppm of chloride ion concentration.

3.4.3. Zinc sulphate solution

Exactly 1.09 g of zinc sulphate was dissolved in double distilled water and made up to 250 ml in a standard measuring flask. A hundred fold dilution yields exactly 10 ppm of Zn$^{2+}$ ion concentration.

3.4.4. Nickel sulphate solution

Exactly 1.11 g of nickel sulphate was dissolved in double distilled water and made up to 250 ml in a standard measuring flask. A hundred fold dilution yields exactly 10 ppm of Ni$^{2+}$ ion concentration.

3.4.5. Sodium Gluconate (SG) / Sodium Potassium Tartrate (SPT) / Trisodium Citrate (TSC)

1 g of SG/SPT and TSC were dissolved in double distilled water and then made up to 100 ml in a standard measuring flask separately. 1 ml of this solution was diluted to 100 ml, which yield exactly 100 ppm of SG/SPT and TSC.
3.4.6. Sodium lauryl sulphate (SLS) / Benzyl triethyl ammonium chloride (BEC)

A stock solution of SLS and BEC were prepared by dissolving 1g of SLS/BEC in a 100 ml of standard measuring flask with double distilled water. 1 ml of this solution was diluted to 100 ml, which yields 100 ppm of SLS/BEC.

3.4.7. Zobell medium

Zobell medium was prepared by dissolving 5 g of peptone, 1 g of yeast extract, 0.1 g of potassium dehydrate phosphate and 15 g of agar-agar in 1 liter of double distilled water. The medium was sterilized by applying 15 pounds per square inch for 15 minutes in an autoclave.

3.5. Weight - Loss Method

3.5.1 Determination of surface area of the specimens

The length, breadth and the thickness of mild steel specimens and the radius of the holes were determined with the help of Vernier Calipers of high precision (least count = 0.02 cm). The surface area of the specimens was measured.

3.5.2. Weighing the specimens before and after corrosion

The weights of the mild steel specimens before and after immersion were determined using a Denver balance, TP 214 model, with a readability of 0.1 mg in 210 g range. This balance has reproducibility (standard deviation) of 0.1 mg in 210 g range and was supplied by Denver instruments, Germany.
3.5.3. Determination of corrosion rates (CR) and inhibition efficiencies (IE)

The weighed specimens, in triplicate were suspended by means of glass hooks in 100 mL beakers containing 100 mL of the test solutions. The test solutions consisted of blank (60 ppm chloride ion) and inhibitor solution containing 60 ppm chloride ion in presence of different inhibitor combinations. After seven days of immersion, the mild steel specimens were taken out from the beakers, scrubbed with cotton and a mild cleaning solution, washed with distilled water, treated with acetone to remove traces of moisture, grease and dried with an air drier. The mild steel specimens were then re-weighed. From the change in weights of the specimens, corrosion rates were calculated using the following relationship [1-2].

\[
\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the Specimen (dm}^2\text{)} \times \text{Period of Immersion (days)}} \text{ (mld)}
\]

The corrosion rate is expressed in mdd units

Where,

\begin{align*}
m & \text{ - Loss in weight (mg)} \\
d & \text{ - Surface area of the specimen (dm}^2\text{)} \\
d & \text{ - Period of immersion (days)}
\end{align*}

Corrosion inhibition efficiency (IE) was then calculated using the equation [3-7].

\[
\text{IE} = \left[ 1 - \frac{W_2}{W_1} \right] \times 100
\]

Where, \( W_1 \) = Corrosion rate in the absence of the inhibitor.

\( W_2 \) = Corrosion rate in the presence of the inhibitor.
3.6. Potentiodynamic polarization study

Polarization study was carried out in Electrochemical impedance Analyzer model CHI 660A (USA) using a three electrode cell assembly. The working electrode was used as a rectangular specimen of mild steel with one face of the electrode of constant 1 cm² area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrode. A time interval of about 5 to 10 min was given for the system to attain a steady state open circuit potential [8-11].

Polarization curves were recorded after doing iR compensation. The corrosion parameters such as Tafel slopes (anodic slope $\beta_a$ and cathodic slope $\beta_c$), corrosion current ($I_{corr}$) and corrosion potential ($E_{corr}$) values were calculated. During the polarization study, the scan rate (V/s) was 0.005; Hold time at $E_f$ (s) was zero and quiet time (s) was 2. The values of inhibition efficiencies (IEp) were calculated from $I_{corr}$ values using the equation [12].

$$IE_p (\%) = \left[ \frac{I_{corr} - I'_{corr}}{I_{corr}} \right] \times 100$$

Where, $I_{corr}$ and $I'_{corr}$ are the corrosion current densities in case of blank and inhibited solutions respectively.

3.7. AC impedance measurements

AC Impedance study was carried out in Electrochemical Impedance Analyzer model CHI 660A (USA) using a three electrode cell assembly. The working electrode was used as rectangular specimen of mild steel with one face of the electrode of
constant 1 cm$^2$ area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrode. AC impedance spectra were recorded after doing iR compensation. The real part ($Z'$) and imaginary part ($Z''$) of the cell impedance were measured in ohms for various frequencies. The corrosion parameters such as charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$) values were calculated. During the AC impedance spectra, the scan rate (V/s) was 0.005; Hold time at Ef (s) was zero and quiet time (s) was 2. The inhibition efficiencies (IEi) using $R_{ct}$ were calculated using the equation [13].

$$\text{IE}_1 \, (\%) = \left[ \frac{R_{ct(b)} - R_{ct(i)}}{R_{ct(i)}} \right] \times 100$$

Where, $R_{ct(b)}$ and $R_{ct(i)}$ are the charge transfer resistance values in the absence and presence of the inhibitor.

3.8. Surface characterization studies

The mild steel specimens were immersed in blank, as well as in inhibitor solutions for a period of seven days. After seven days, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analyzed by various surface analysis techniques.

3.8.1. Surface analysis by FTIR spectra

After the immersion period of seven days in various environments, the specimens were taken out of the test solutions and dried. The film formed on the
surface was scratched carefully and it was thoroughly mixed so as to make it uniform throughout. FTIR spectrum of the powder (KBr pellet) \([14-21]\) was recorded using Perkin-Elmer 1600 FTIR spectrophotometer with a resolving power of 4 cm\(^{-1}\).

3.8.2. **Scanning Electron Microscopy studies (SEM)**

The mild steel specimen immersed in blank and in the inhibitor solution for a period of seven days was removed, rinsed with double distilled water, dried and observed in a Scanning Electron Microscopy to examine the surface morphology. The surface morphology measurements of the mild steel were examined using VEGA3-TESCAN computer controlled scanning electron microscopy.

3.8.3. **Energy Dispersive X-ray Analysis (EDX)**

EDX (Model: VEGA3-TESCAN) system attached with Scanning Electron Microscopy was used for elemental analysis or chemical characterization of the film formed on the mild steel surface. As a type of spectroscopy, it relies on the investigation of sample through interaction between electromagnetic radiation and the matter. So that, a detector was used to convert X-ray energy into voltage signals. This information is sent to a pulse processor, which measures the signals and passed them into an analyzer for data display on the analysis.

3.8.4. **Atomic Force Microscopy (AFM)**

The atomic force microscopy was used for surface morphology studies. The protective films were examined with atomic force microscopy (AFM) using A100 model (A.P.E Research, Italy). The topography of the entire samples from a scanned area of 20 µm x 20 µm is evaluated for a set point of 20 nm and a scan speed of 10
mm/s. The three dimensional topography of surface films gave various roughness parameters of the film.

3.9. Determination of biocidal efficiency of the system

Inhibitor (PAA) - Zn\(^{2+}\) and Ni\(^{2+}\) formulation that offered the best corrosion inhibition efficiency was selected. The biocidal efficiency of biocides such as Sodium lauryl sulphate (SLS) and Benzyl triethylammonium chloride (BEC) was determined.

Various concentrations of SLS and BEC namely 10 ppm, 25 ppm, 50 ppm, 75 ppm, 100 ppm were added to the formulation consisting of the inhibitor system. Polished and degreased mild steel specimens in duplicate were immersed in these environments for a period of seven days. After seven days 1 mL each of test solutions from the environments was pipetted out into sterile petri dishes containing about 20 ml of the sterilized Zobell medium and kept in a sterilized environment inside the Laminar flow system. Then the Petri dishes were kept in an incubator at 30\(^{\circ}\)C in an inverted position for two days. Distinct colonies of bacteria were developed. Such colonies may be easily isolated. The numbers of colony forming units (CFU/ml) present in the above formulations were determined by Step dilution technique [22]. Each organism grows and reproduces itself. To determine the number of colonies, plate count technique [23] was applied.
Chapter - III

Materials and Methods

REFERENCES


