CHAPTER III
EXPERIMENTAL DETAILS

In any research work the materials and methods adopted are the aspects which decide and determine qualitatively and quantitatively the outcome of the research. The aim of the present work is “Synthesis of Poly (ethylene glycol- substituted aniline) water soluble composites and its inhibitive action on the corrosion of MS in acid medium”.

Design of the present investigation consists of the following steps.

- Analysis of composition of mild steel
- Synthesis of polymer composites
- Characterization of the polymer composites
- Different parameters studied
- Different techniques used
- Surface analysis

3.1 ANALYSIS OF COMPOSITION OF MILD STEEL

The composition of the sample has been analysed by using ARL 3460 metal analyzer (Optical emission spectrometer). The composition of the specimen was found to be

<table>
<thead>
<tr>
<th>ELEMENTS</th>
<th>PERCENTAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>99.677</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.035</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.196</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.003</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.011</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.030</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.010</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.014</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.024</td>
</tr>
</tbody>
</table>
3.2 PREPARATION OF THE SPECIMENS

Cold rolled MS sheet was cut into pieces of 1 x 5 cm\(^2\) area. These samples were polished with emery papers of different grit size, degreased with trichloroethylene, washed thoroughly with triply distilled water, dried, stored in desiccators and used for all studies. Prior to each experiment, the specimens were treated as described and freshly used.

3.3 SYNTHESIS OF POLYMER COMPOSITES

Ammonium peroxy disulphate (2% aqueous solution in oxalic acid) was added dropwise to a stirred solution of 2% polyethyleneglycol (PG) and 2% aniline derivative in aqueous solution of oxalic acid, precooled to 3 – 5 °C. Ammonium peroxy disulphate solution was added very slowly to prevent the warming of the solution. Stirring was continued for 6 h to ensure completion of the reaction. The solution was then treated with NH\(_4\)OH to maintain pH of the solution around 9. Precipitates collected by adding acetone were filtered and dried (adopted from Trivedi – Handbook 1993).

![Figure 3.1 Magnetic stirrer and polymer composite solutions](image)

3.4 CHARACTERIZATION OF POLYMER COMPOSITES

The polymer composites and the surface of mild steel exposed with composites were characterized by FTIR spectroscopic techniques. The FTIR spectrum of the polymer composites were recorded with a Nicolet- spectrometer (Madison, WI) in the 4000 – 500 cm\(^{-1}\).
range. Morphological studies of composite samples were performed by Scanning Electron Microscopy (SEM) technique with JEOL scanning electron microscope (model JSM-840).

3.5 EVALUATION OF CORROSION INHIBITION

The efficiency of the inhibitor was evaluated using the techniques such as physicochemical method (weight loss method) and electrochemical method (potentiodynamic polarization and A.C.Impedance method).

3.5a Preparation of inhibitor solution

Two percent solution of the inhibitor was prepared by dissolving two grams of the inhibitor in 100 ml of water. This solution was further diluted to 0.01, 0.03, 0.05, 0.07, 0.09, 0.13, 0.17 and 0.19 % by diluting it with the desired volume of 1 N hydrochloric acid.

3.5.1 Weight loss method

Mild steel specimens were accurately weighed and fully immersed in 100 ml of 1M HCl without and with different concentrations of the inhibitor and at different time intervals. After the correct intervals of time, test specimens were washed with distilled water, dried and reweighed. The loss in weight was determined in triplicate. The experiments were conducted to optimize the concentration of the inhibitor (100 ppm to 1900 ppm), time of exposure (1/2h, 1h, 3h, 6h, 12h and 24h) and temperature of the medium (303K, 313K, 323K, 333K and 343K) for the best performance of the inhibitor.

3.5.1.a Determination of corrosion rate

The corrosion rate expressed as mills per year was calculated using the formula.

$$\text{Corrosion rate (mpy)} = \frac{543 \times w}{D \times AT} \times 1000$$

where

w - Weight loss in g

D - Density of specimen in gm/cm².

A - Area of the Specimen in cm².

T - Exposure time in hours.
3.5.1.b Determination of percentage of Inhibition Efficiency

Inhibitor efficiency was calculated using the following formula

\[ IE (\%) = \left( \frac{CR_o - CR_i}{CR_o} \right) \times 100 \]  

where

IE – Inhibitor efficiency

CR_o – corrosion rate (without inhibitor).

CR_i – corrosion rate (with inhibitor).

3.5.1.c Surface Coverage (Θ)

The degree of surface coverage for different concentrations of the inhibitor on acid media was evaluated from weight loss experiments using the equation.

\[ \theta = \left( \frac{W_o - W_i}{W_o} \right) \]  

Where

\( \theta \) – Surface Coverage

W_o – Weight loss without inhibitor in gm.

W_i – Weight loses with inhibitor in gm.

3.5.1.d Corrosion Dynamics-Calculation of Activation Energy (Ea)

The corrosion reaction can be regarded as an Arrhenius type process the rate of which is given by

\[ CR = Ke^{Ea/RT} \]  

\[ \ln CR = \frac{-Ea}{RT} + \ln K \]  

Where

CR – corrosion rate

Ea – Apparent activation energy

T – Absolute temperature in Kelvin
K – Arrhenius pre exponential constant

R - Universal gas constant (8.314 J/mole)

From the slope of the plot log CR Vs 1/T the activation energy (Ea) was calculated using the following formula

\[ Ea = -2.303 \times R \times \text{slope of the Arrhenius plot} \]  

3.5.1. Determination of thermodynamics parameters

The changes in free energy (\( \Delta G_{\text{ads}} \)) of adsorption of the inhibitors are calculated using the following equation (Abdel and Saied, 1981).

\[ \log C = \log \theta / (1-\theta) - \log B \]  

where \( \log B = -1.74 - (\Delta G_{\text{ads}}/(2.303RT)) \)

\( R = \) Temperature in Kelvin

\( C = \) Concentration of the inhibitor in ppm (w/v)

\( \Theta = \) Surface coverage.

The change in heat of adsorption \( \Delta H_{\text{ads}} \) and change in enthalpy \( \Delta S_{\text{ads}} \) are calculated using Gibbs Helmholtz equation

\[ \Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T \Delta S_{\text{ads}} \]  

A plot of \( \Delta G_{\text{ads}} \) verses T will be a straight line with intercept \( \Delta H_{\text{ads}} \) and slope \( \Delta S_{\text{ads}} \).

3.5.1.f Adsorption Isotherms

Since corrosion inhibition involves the adsorption of the inhibitor on the surface of the metal, the phenomenon of interaction between the metal surface and inhibitor can better be understood in terms of adsorption isotherm. The degree of surface coverage \( \Theta \) for different concentrations of inhibitor in 1M HCl has been evaluated. The dependence of surface coverage on concentration was studied using the following isotherms.

Langmuir Isotherm : \( \log (\theta/1 - \theta) \) vs \( \log C \)

Temkin Isotherm : \( \theta \) vs \( \log C \)

Frendlich Isotherm : \( \theta \) vs \( \log \theta/C \)
The correlation co-efficient ($R^2$) values were used to determine to select the best fit Isotherm.

### 3.5.2 Potentiodynamic Polarization and Impedance Measurements

The experiments were performed in a classical three-electrode electrochemical cell. Mild steel specimen of one cm$^2$ area was used as the working electrode, platinum electrode as counter electrode and saturated calomel electrode as reference electrode. Prior to each experiment the working electrode surface was polished with emery paper.

Corrosion monitoring techniques like Potentiodynamic polarization (Tafel Polarisation) and electrochemical impedance spectroscopy (EIS) have been carried out using Solatron Electrochemical measurement unit (1284 Z) model with a software package of Z plot and corrware. For polarization and impedance studies the period of immersion was for 30 minutes. The potentiodynamic polarization studies were carried out over a potential range from -0.1 V of cathodic potential to -1 V of anodic potential with respect to corrosion potential at a sweep rate 2 mV sec$^{-1}$. These measurements were carried out at corrosion potential. The A.C. amplitude of 10 mV was applied and frequency was varied from 20 Hz to 0.1Hz. The real and imaginary parts of the impedance were plotted as Nyquist plot. From the Nyquist plots, the Charge Transfer Resistance (Rct) and Double Layer Capacitance (Cdl) values were derived. The charge transfer resistance values were obtained from the plots of $Z'$ Vs $Z''$.

#### 3.5.2.a Measurement of Corrosion Current (Icorr)

Applied potential vs current was plotted and on extrapolation of linear portion to the corrosion potential gives the corrosion current. In anodic and cathodic plot, the slope of the linear portion gives Tafel constants $b_a$ and $b_c$ respectively.

### Determination of Inhibition Efficiency

The inhibitor efficiency was obtained from all the parameters measured namely Icorr, Rp, Rct and surface coverage, $\theta$ calculated from Cdl using the following relationships
\[ IE (\%) = \frac{I_{corr}^{(blank)} - I_{corr}^{(inhibitor)}}{I_{corr}^{(blank)}} \times 100 \]

- \( I_{corr}^{(inhibitor)} \) - Corrosion current in the presence of inhibitor.

- \( I_{corr}^{(blank)} \) - Corrosion current in the absence of inhibitor.

Figure 3.2 Solartron 1280 B

Figure 3.3 Three Electrode Cell
\[ IE(\%) = \frac{R_P(\text{inhibitor}) - R_P(\text{blank})}{R_P(\text{inhibitor})} \times 100 \]  
\[ \theta = \frac{C_{dl}(\text{blank}) - C_{dl}(\text{inhibitor})}{C_{dl}(\text{blank})} \times 100 \]

**3.6 SURFACE ANALYSIS**

Mild steel specimens were fully immersed in 100 ml of 1M HCl without and with 0.19% concentration of the inhibitors for 3 h. The specimens were then taken out, dried and subjected to surface analysis.

Surface analysis of mild steel specimen was carried out before and after exposure to 1M HCl solution and in the presence of the inhibitors, using Optical microscope (OM) or Photo electron microscope (NIKOV – Model EPI – PHOT). Fourier transform Infrared spectroscopy was recorded for the mild steel exposed to polymer composites of optimum concentration.