Chapter 3

Materials and Methods
CHAPTER – 3

MATERIALS AND METHODS

3.1 Synthesis of inhibitors

The condensation products of 1,2-diaminoethane / 1,3-diaminopropane with various aldehydes are synthesised as follows [1].

The diamine and the respective aldehydes are taken in 1:2 molar ratio in a round bottomed flask. About thrice the volume of this mixture, ethanol is added and the contents are refluxed for about an hour. Then the contents are cooled and passed in a thin stream into crushed ice. Compound A is a semisolid while compounds B to L are viscous liquids. They were separated and purified.

3.2 Characterisation of the Compounds

3.2.1 U.V. Spectrum

The U.V – Visible absorption spectra were recorded in methanol in a Shimadzu UV 1601 PC UV- Visible recording spectrometer. The spectra were recorded in the range 190-900nm. The spectra for the precursors were also run to ensure the formation of the compounds.

3.2.2 Infrared spectrum

The IR spectra were recorded, for the synthesised compounds to confirm the formation of aldimines using a PERKIN ELMER - Model 598 IR spectrometer. Based on the above studies, the most likely structures for the compounds synthesised along with their abbreviations used in the text are given below.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Structure and Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \text{CH}_2=\text{N-CH}_2-\text{CH}_2-\text{N}=\text{CH}_2 )  \    N,N'- bis (formaldehyde)-1,2-diaminoethane</td>
<td>A</td>
</tr>
<tr>
<td>2.</td>
<td>( \text{CH}_3\text{CH}=\text{N-CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{CH}_3 )  \    N,N'- bis (acetaldehyde)-1,2-diaminoethane</td>
<td>B</td>
</tr>
<tr>
<td>3.</td>
<td>( \text{CH}_3-\text{CH}_2-\text{CH}=\text{N-CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{CH}_3 )  \    N,N'- bis (propionaldehyde)-1,2-diaminoethane</td>
<td>C</td>
</tr>
<tr>
<td>4.</td>
<td>( \text{CH}_3-\text{CH}_2-\text{CH}=\text{N-CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{CH}_3 )  \    N,N'- bis (butyraldehyde)-1,2-diaminoethane</td>
<td>D</td>
</tr>
<tr>
<td>5.</td>
<td>( \text{C}_6\text{H}_5\text{CH}=\text{N-CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{C}_6\text{H}_5 )  \    N,N'- bis (benzaldehyde)-1,2-diaminoethane</td>
<td>E</td>
</tr>
<tr>
<td>6.</td>
<td>( \text{C}_6\text{H}_5\text{CH}=\text{CH-CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{CH}_3 )  \    N,N'- bis (cinnamaldehyde)-1,2-diaminoethane</td>
<td>F</td>
</tr>
<tr>
<td>7.</td>
<td>( \text{CH}_2=\text{N-CH}_2-\text{CH}_2-\text{CH}_2-\text{N}=\text{CH}_2 )  \    N,N'- bis (formaldehyde)-1,3-diaminopropane</td>
<td>G</td>
</tr>
<tr>
<td>8.</td>
<td>( \text{CH}_3\text{CH}=\text{N-CH}_2-\text{CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{CH}_3 )  \    N,N'- bis (acetaldehyde)-1,3-diaminopropane</td>
<td>H</td>
</tr>
<tr>
<td>9.</td>
<td>( \text{CH}_3-\text{CH}_2-\text{CH}=\text{N-CH}_2-\text{CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{CH}_3 )  \    N,N'- bis (propionaldehyde)-1,3-diaminopropane</td>
<td>I</td>
</tr>
<tr>
<td>10.</td>
<td>( \text{CH}_3-\text{CH}_2-\text{CH}=\text{N-CH}_2-\text{CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{CH}_3 )  \    N,N'- bis (butyraldehyde)-1,3-diaminopropane</td>
<td>J</td>
</tr>
<tr>
<td>11.</td>
<td>( \text{C}_6\text{H}_5\text{CH}=\text{N-CH}_2-\text{CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{C}_6\text{H}_5 )  \    N,N'- bis (benzaldehyde)-1,3-diaminopropane</td>
<td>K</td>
</tr>
<tr>
<td>12.</td>
<td>( \text{C}_6\text{H}_5\text{CH}=\text{CH-CH}_2-\text{CH}_2-\text{CH}_2-\text{N}=\text{CH}_2\text{CH}_3 )  \    N,N'- bis (cinnamaldehyde)-1,3-diaminopropane</td>
<td>L</td>
</tr>
</tbody>
</table>

### 3.3 Specimen Composition

Cold rolled mild steel used for the present investigation, has been found to have the following percentage composition.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.0125</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.0060</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.1690</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.0519</td>
</tr>
</tbody>
</table>

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The composition of the mild steel sample was analysed using Spertivac model ARL-3460-433, Applied Research Laboratory, Switzerland.

3.4 Size of the Specimen

Mild steel specimens of thickness 0.017cm and size 5cm x 2.5cm with a hole near the upper edge were used for non-electrochemical studies. For electrochemical measurements, the working electrode was fabricated by fixing the mild steel specimen of size 1cm x 1cm to a mild steel rod of diameter 1mm with araldite. Then the working electrode was lacquered to expose 1cm² of it to the experimental solution.

3.5 Preparation of Metal Surface

3.5.1 Preparation of metal surface for non-electrochemical methods

The mild steel specimens were numbered, pickled in 5% HCl, mechanically polished, degreased with trichloroethylene and stored in a desiccator.

3.5.2 Preparation of metal surface for electrochemical methods

Before immersing the working electrode in the corrosive medium, each specimen was polished with different grades of emery paper, degreased with acetone and stored in a desiccator.

3.6 Chemicals used

Analar Grades of the following chemicals were used in the studies.

3. 1,2-diaminoethane(Loba)
4. 1,3-diaminopropane (Lanchaster)
5. Formaldehyde (S.D.Fine Chemicals) (40% aqueous solution)
6. Acetaldehyde (E.Merck)
7. Propanaldehyde (E.Merck)
8. Butyraldehyde (Fluka)
9. Benzaldehyde (S.D Fine)
10. Cinnamaldehyde (E.Merck)
11. Ethyl alcohol (BDH).
Triple distilled water was used for preparing stock solutions.

3.7 Evaluation of inhibitors
3.7.1 Non–Electrochemical Methods

3.7.1.1 Weight loss studies
Mild steel specimens of size 5 cm x 2.5 cm x 0.017 cm were employed for the determination of corrosion rate. The pre-treated specimens were weighed and immersed completely in 100 ml of the experimental solution in a glass beaker with the help of glass hooks without touching the sides of the beaker. The duration of the experiment was two hours. After two hours the specimens were taken out, washed thoroughly with distilled water, dried and weighed. From the initial and final weights the loss in weight was calculated for each specimen. The experimental solutions used were 1M HCl and 0.5M H₂SO₄. Weight loss measurements were made with and without the inhibitors. For both the media, the experiment was carried out in triplicate. Inhibition efficiency was calculated using the formula,

\[
\text{Inhibition efficiency} = \left(\frac{W_1 - W_2}{W_1}\right) \times 100
\]

Where \(W_1\) and \(W_2\) are weight losses in acids without and with the inhibitor respectively.

The loss in weight is expressed in milligrams per square decimeter per day (mdd). This value can be converted into the equivalent corrosion current by using Faraday’s laws. The conversion factor for iron corroding to Fe²⁺ [2] is \(1\text{mdd} = 4 \times 10^{-7}\text{ Amp cm}^2\).

3.7.1.2 Gasometry
The size of the specimen used was identical with that used for weight loss method. This technique gives accurate results compared to that of conventional weight loss method provided,

- The inhibitor does not react with hydrogen
- The hydrogen penetration into the metal is small compared to the total volume of hydrogen gas.

An improved design of the gasometric method is shown in Fig.6. It consists of three parts.
i. Reaction cell
ii. Vertical graduated burette
iii. Reservoir bulb

i. Reaction Cell

It consists of a cylindrical glass vessel of 150mL capacity with a central ground joint opening, through which the metal specimen can be inserted into the cell by means of a glass stopper provided with a hook.

The stopper exactly fits into the central ground glass joint so that there is no leakage of hydrogen gas. It is also provided with a gas release stopper on one side through which excess gas pressure over the atmospheric pressure, which builds up when the stopper carrying the metal strip is introduced, can be released.

ii. Vertical graduated burette

A 50 ml graduated burette with 0.1 ml accuracy is used to collect the gas evolved during the reaction. The top end of the burette is connected to the reaction cell through a side tube.

The vertical column tubes are filled with 20 – 25 % sodium chloride solution, acidified with HCl and coloured with methyl orange or methyl red. The gas is collected over this solution. The colour makes observation of the meniscus easy. The solubilities of gases like CO₂, H₂ etc., are very low in sodium chloride solution. Hence measurement is more accurate.

iii. Reservoir bulb

A reservoir bulb is attached to the other end of the graduated burette, to adjust the liquid level in the burette to be equal to that in the reservoir bulb so that the pressure of the gas inside the tube is the same as atmospheric pressure. As the liquid levels inside and outside the burette are kept the same from the beginning of the experiment, any pressure correction due to aqueous tension is not necessary.
The specimen was suspended from the hook of the glass stopper and was introduced into the cell containing 100ml of the experimental solution. The temperature was maintained constant throughout these experiments at $30^\circ C \pm 1^\circ C$ and at constant
atmospheric pressure. Volume measurements were made for a period of two hours in all the cases.

From the volume of hydrogen gas liberated, the inhibition efficiency was calculated using the formula,

\[
\text{Inhibition Efficiency (\%) } = \frac{V_0 - V_1}{V_0} \times 100
\]

where \( V_0 \) is the volume of hydrogen evolved in the absence of inhibitor, 
\( V_1 \) is the volume of hydrogen evolved in the presence of inhibitor.

3.7.1.3 Surface Characteristics Study

The mild steel specimens exposed to hydrochloric acid and sulphuric acid media without and with inhibitors in weight loss method and gasometric method were used for studying the surface characteristics. The surface of each of the exposed specimen were photomicrographed using an optical microscope (NIKON-Model EPI PHOT)

3.7.2 Electrochemical methods

3.7.2.1 Potentiostatic polarization studies

The polarization measurements were made to evaluate the corrosion current, corrosion potential and the Tafel slopes. The circuit used for the polarization studies is given in Fig. 7.

![FIGURE.7 Circuit Diagram For Potentiostatic Polarization studies](image-url)
The current was measured using Pico ammeter (Keithley Instrument, USA, Model 2001) and the voltage was followed using a digital multimeter (Philips Model PM2525). A ten turn potentiometer was used to vary the potential applied from a DC power source (Aplab Model L3202). The current was measured between the working electrode and a platinum electrode (counter electrode) and the rest potential was measured between the working electrode and a saturated calomel electrode (SCE).

Experiments were carried out in a conventional three-electrode cell assembly. The working electrode was mild steel specimen of 1 Sq.cm. exposed area, with the rest being covered with lacquer. A rectangular Pt foil was used as the counter electrode. To exert uniform potential field on the working electrode, it is designed in a way that the counter electrode is much larger in area compared to the working electrode [3]. The reference electrode used was SCE.

The working electrode was polished and degreased with trichloroethylene. The reference, working and counter electrode were assembled in position and the electrical connections were given as shown in Fig. 7. A time interval of 10-20 minutes was given for each experiment to attain the steady state open circuit potential. The polarization was carried from a cathodic potential of \(-750 \text{ mV (Vs SCE)}\) to an anodic potential of \(-250 \text{ mV (Vs SCE)}\) at a sweep rate of 10mV per second. The experiments were carried out with 1M HCl and 0.5M H2SO4 and with various concentrations of the inhibitors in HCl and H2SO4. Graphs were drawn between potential \((\text{Vs SCE})\) and \(\log i\). The linear segments of the anodic and cathodic polarization curves were extrapolated to corrosion potential to obtain corrosion current \((i_{\text{corr}})\) and Tafel slopes \((b_a\) and \(b_c)\) were determined.

### 3.7.2.2 Impedance Measurements

Impedance measurements were made using a digital LCD meter (Chen Hova, Taiwan Model C 1060).

For the measurements of impedance, the cell used was the same as that used for potentiostatic polarization. An A.C. potential of 10mV was superimposed on the steady open circuit potential. The real part \((Z')\) and the imaginary part \((Z'')\) was measured at various frequencies. A plot of \(Z'\) Vs \(Z''\) was made. From the plot the charge transfer resistance, double layer capacity and the surface coverage were calculated.
Impedance measurements were carried out for mild steel in both 1M HCl and 0.5M H₂SO₄ in the absence and presence of different concentrations of inhibitors.

### 3.7.2.3 Hydrogen permeation measurement

The specimen used for the study was thin mild steel membrane. The specimens were given necessary pretreatment. AR grade sodium hydroxide and BDH grade palladium chloride were used. Triple distilled water was used for solution preparation.

The cell used for electropermeation study was similar to the one used earlier by Devanathan [4]. Lacquer was applied on to one side of the membrane and the specimen was cathodically cleaned. Then the membrane was electroplated with a thin layer of palladium from a solution of palladium chloride containing 98 gm / lit at 100A cm² current density for 90 minutes using stainless steel as anode [4]. Palladium is coated to catalyze the ionization of hydrogen, which is accounted as the permeation current. Then the specimens were washed many times with double distilled water, dried and kept in a desiccator after removing the lacquer.

#### 3.7.2.3.1 Cell setup

The cell used for electropermeation study contains two compartments and they are connected through teflon bushings, clamped between two stainless steel sheets, which are held intact. The teflon stoppers were provided with a hole of inner area 1 cm². Mild steel was used as working electrode, platinum as auxiliary electrode and Hg / HgO / 0.2 N NaOH as the reference electrode. Both compartments have provisions for inserting platinum auxiliary electrode. The glass cell has provision for circulation of water. The cell setup is given in Fig.8.

#### 3.7.2.3.2 Measurement of permeation current

The specimen was fixed in between teflon bushings and clamped tightly. The palladium coated side of the compartment was filled with 0.2N NaOH solution which was pre-electrolysed for a period of 12 hours at a current density of 2.5mA. The circuit was completed using Hg / HgO / 0.2N NaOH reference electrode and a platinum auxiliary electrode. The other compartment facing the mild steel was filled with the experimental solution. The cell is connected to a potentiostat and a constant potential of
-300mV was applied to the specimen on the anodic side. It has been shown earlier [5] that -300mV is the most suitable potential for ionizing the diffused hydrogen rapidly and efficiently at Pd / 0.2 N NaOH interface. The initial current gradually decreased and reached a steady value. The non-plated side was allowed to corrode with free hydrogen evolution. Some of the adsorbed hydrogen atoms find entry into the steel membrane and get trapped. These trapped hydrogen atoms are ionized and they are the measure of currents recorded.

The permeation current was measured both in HCl and H₂SO₄ solutions with and without inhibitors at the optimum concentration only for all the inhibitors.

1. Steel membrane
2. Teflon Bushings
3. PVC Coupling
4. Reference electrode (Hg/HgO/0.2N NaOH)
5. Counter electrode (Pt)
6. Tap
7. Water circulation
8. Anode

FIGURE.8 Hydrogen Permeation Cell set up.
REFERENCES


