

# MATERIALS AND METHODS

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## CHAPTER III

### MATERIALS AND METHODS

The materials and methods pertaining to study entitled “**Adsorption Behaviour and Corrosion Inhibitive Potential of Imidazoline Derivatives on Mild Steel/Acid Interface**” are presented below.

In this chapter, the reasons for the selection of mild steel sample, imidazoline derivatives as corrosion inhibitor in acid media and synthesis and characterization of inhibitors, techniques adopted are discussed.

In recent years, scientists have been concerned with the use of certain organic compounds as corrosion inhibitors in metal-corrodent system. Most well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms.

It is well known that imidazolines are N-heterocyclic compounds and therefore it can be used as inhibitor for corrosion of mild steel.

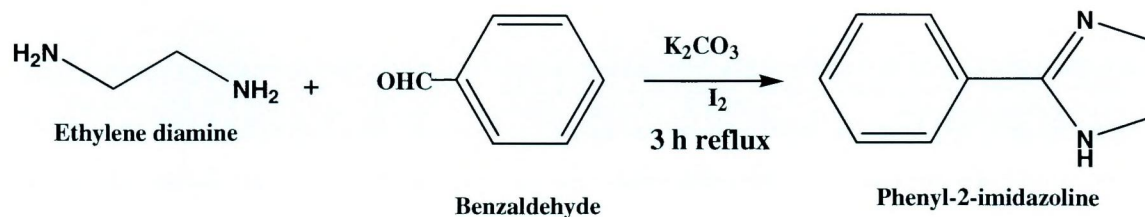
#### 3.1 Synthesis of Imidazoline Derivatives

In the present work the imidazoline derivatives are synthesized in the laboratory following the procedure reported earlier (**Midori Ishihara *et al.*, 2006**).

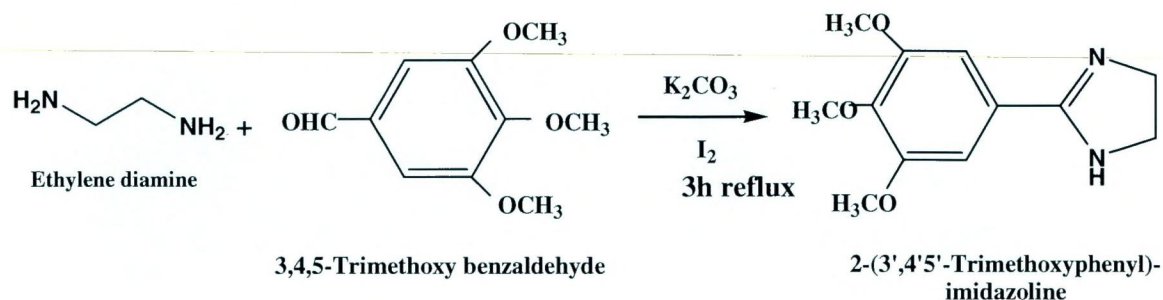
2-imidazolines derivatives were easily prepared in good yield from the reaction of aldehydes and ethylene diamine with iodine in the presence of Potassium carbonate.

To a solution of aldehyde (1mmol) and ethylene diamine (1 mmol) were added potassium carbonate and iodine. The reaction mixture was stirred for 3 hrs at reflux. The solvent was evaporated and the crude sample was recrystallised from ethanol to give the desired product.

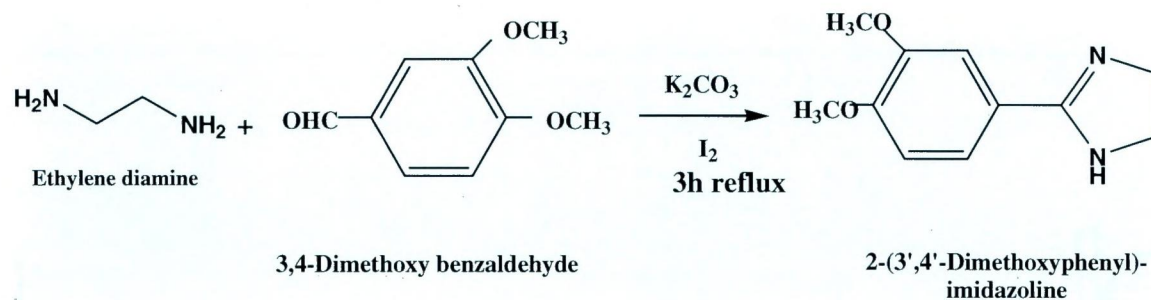
#### Synthesis of Phenyl-2-imidazoline (P2I):



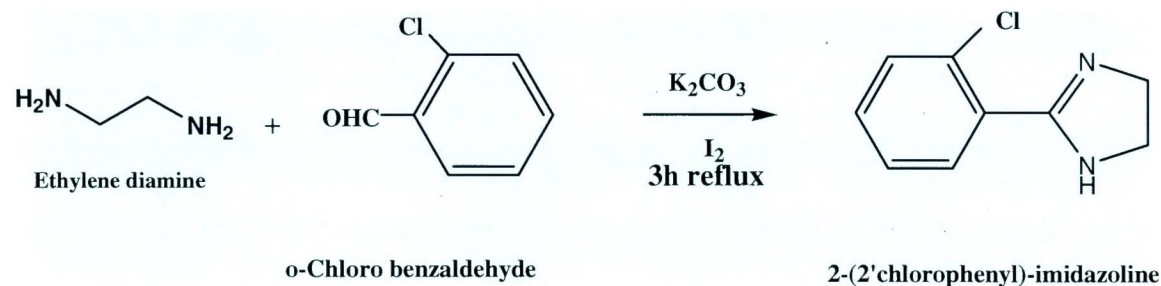
### Synthesis of 2-(3',4',5'-Trimethoxyphenyl)-imidazoline (TMP2I):



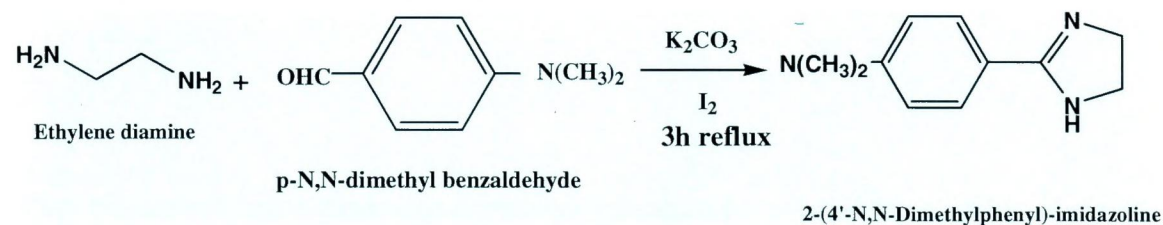
### Synthesis of 2-(3',4'-Dimethoxyphenyl)-imidazoline (DMP2I):



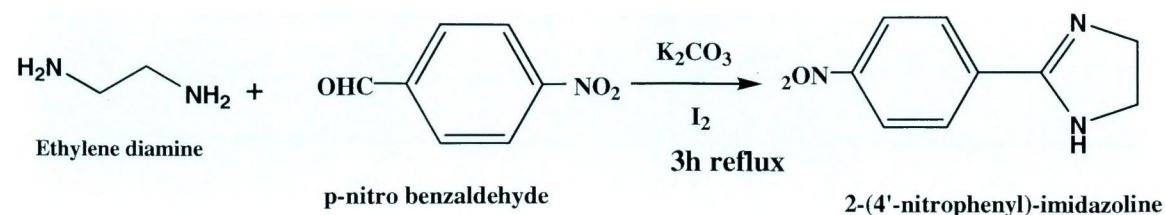
### Synthesis of 2-(2'-Chlorophenyl)-imidazoline (OCP2I):



### Synthesis of 2-(4'-N,N-Dimethylphenyl)-imidazoline (PNDMP2I):



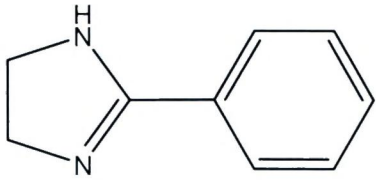
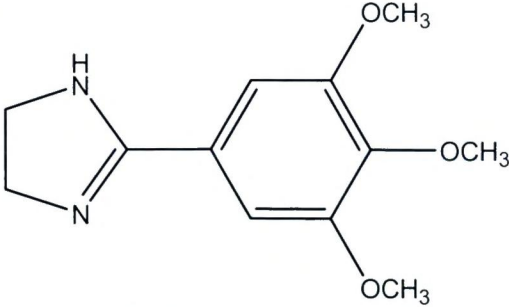
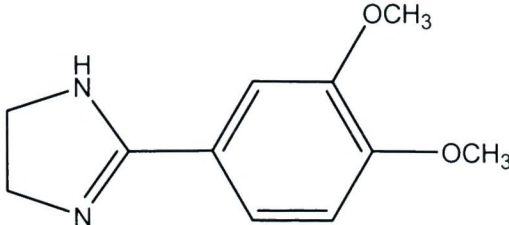
### Synthesis of 2-(4'-Nitrophenyl)-imidazoline (PNP2I):

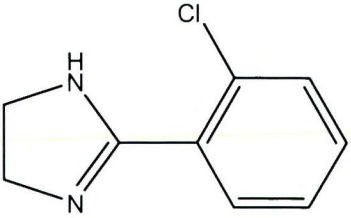
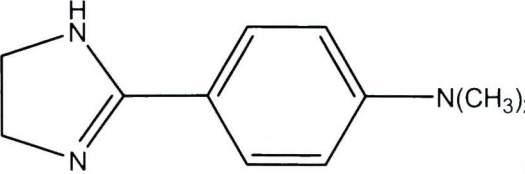
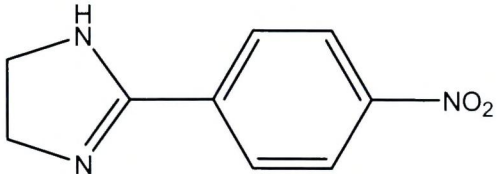


### 3.2 Characterisation of the Synthesized compounds

The formation of imidazoline derivatives was confirmed by Melting point, Colour and IR Spectral Data ( Figure- 13).

Table - 1 Characterisation of Synthesized compounds

Structure & Name of the compound	Colour	Melting Point °C	Yield	IR Frequencies $\text{cm}^{-1}$
 <p>Phenyl-2-imidazoline - P2I</p>	Pale Yellow	98-101	90	i) -C=N - 1677 ii) C-N-C 1563,1477, 1376 iii) N-H - 3330 iv) Aromatic & Aliphatic C-H stretching 2914, 2842
 <p>2-(3',4',5'-Trimethoxyphenyl)-imidazoline - TMP2I</p>	Orange	112-116	87	i) -C=N - 1636 ii) C-N-C 1577,1498, 1367 iii) N-H - 3370 iv) Aromatic & Aliphatic C-H stretching 3005, 2919, 2827 v) Ar-OCH <sub>3</sub> 1227
 <p>2-(3',4'-Dimethoxyphenyl)-imidazoline - DMP2I</p>	Dark Yellow	129-131	95	i) -C=N - 1634 ii) C-N-C 1504,1452, 1378 iii) N-H - 3352 iv) Aromatic & Aliphatic C-H stretching 2995, 2941, 2898 v) Ar-OCH <sub>3</sub> 1260

 <p><b>2-(2'-Chlorophenyl)-imidazoline - OCP2I</b></p>	<p><b>Shiny Yellow</b></p>	<p><b>98-100</b></p>	<p><b>90</b></p>	<p>i) -C=N - 1622  ii) C-N-C 1575, 1430, 1366  iii) N-H - 3346  iv) Aromatic &amp; Aliphatic C-H stretching 2903, 2852  v) Ar-Cl 750</p>
 <p><b>2-(4'-N,N-Dimethylphenyl)-imidazoline - PNDMP2I</b></p>	<p><b>Dark Brown</b></p>	<p><b>258-260</b></p>	<p><b>81</b></p>	<p>i) -C=N - 1631  ii) C-N-C 1519, 1440  iii) N-H - 3412  iv) Aromatic &amp; Aliphatic C-H stretching 3034, 2849  v) -N(CH<sub>3</sub>) 1351</p>
 <p><b>2-(4'-Nitrophenyl)-imidazoline - PNP2I</b></p>	<p><b>Dark Brown</b></p>	<p><b>231</b></p>	<p><b>80</b></p>	<p>i) -C=N - 1571  ii) C-N-C 1488, 1410  iii) N-H - 3340  iv) Aromatic &amp; Aliphatic C-H stretching 3100, 2903, 2852  v) Ar-NO<sub>2</sub> 1370</p>

( IR: Deana Wahyuningrum *et al.*, 2008)

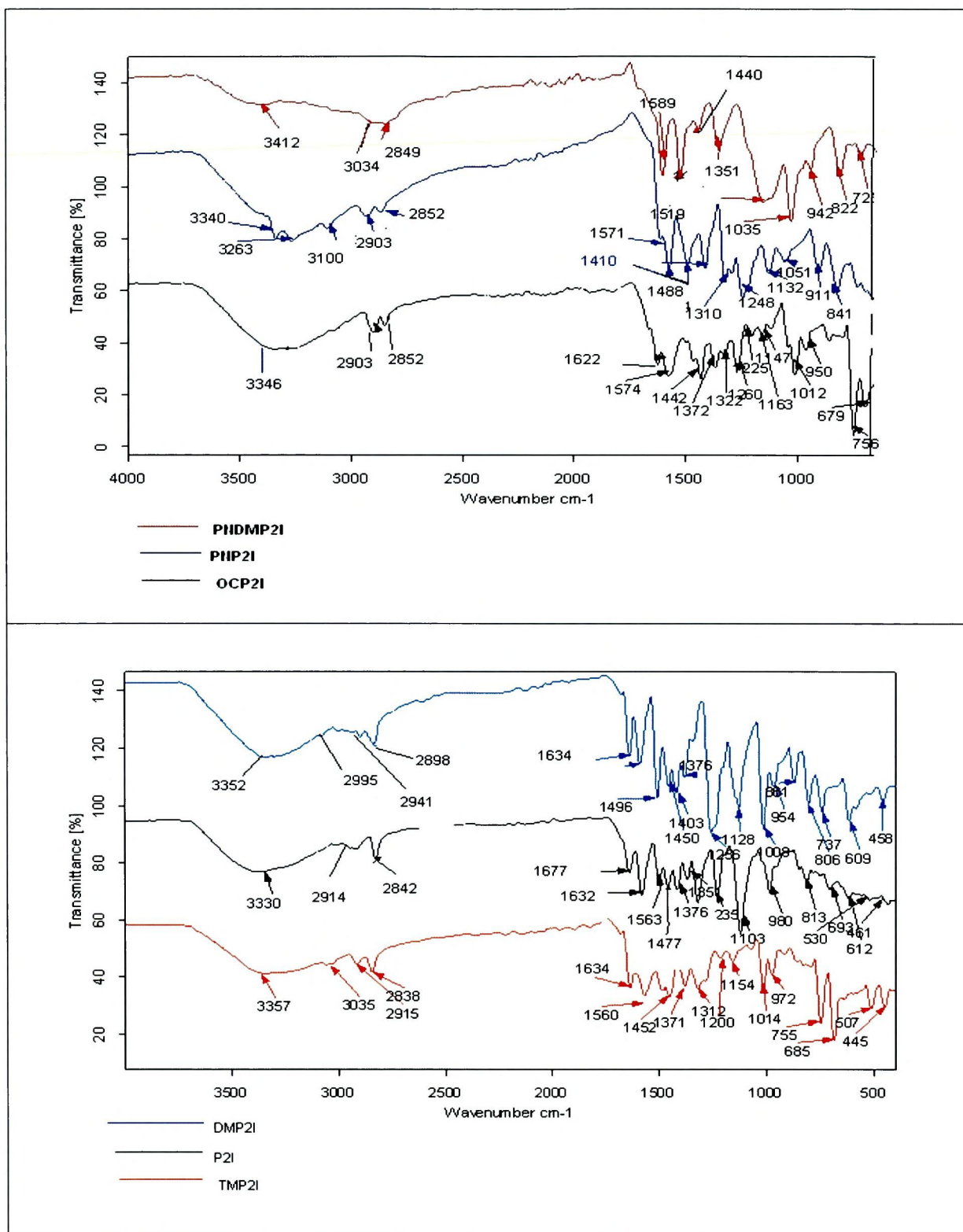


Figure - 13 FT IR Spectra for the studied Inhibitors

### 3.3 Selection of Mild Steel Sample

Mild steel is a structural material of choice to fabricate various reaction vessels, pipes and so on in sugar, petrochemical, textile, food, paper and marine industries due to its excellent mechanical properties and low cost. Mild steel suffers from severe corrosion in aggressive environment which needs to be protected.

#### Composition of Mild Steel Specimen:

C= 0.098 %	Mn = 0.201 %	P= 0,020 %
S=0.016 %	Fe= 99.653 %	Ni=0.012 %

Rectangular specimens of working surface area  $5 \times 1 \text{cm}^2$  were used for weight loss measurements and  $1 \times 1 \text{cm}^2$  with 5cm long stem (isolated with Teflon tape) for the electrochemical methods. The specimens were polished mechanically using emery papers and washed thoroughly with triple distilled water, degreased with acetone and dried using air flow at room temperature and kept in a moisture free desiccator for further studies.

### 3.4 Selection of Acid media

Hydrochloric acid and Sulphuric acid are widely used as pickling agents for the removal of rust and scale in several industrial processes like cleaning of boilers and heat exchangers. Aqueous solutions of the acids are among the corrosive media. Hence HCl and  $\text{H}_2\text{SO}_4$  were used for the present study (1M HCl and 0.5M  $\text{H}_2\text{SO}_4$ ). 1M HCl and 0.5M  $\text{H}_2\text{SO}_4$  were prepared by dilution of analytical grade 37% HCl and 96%  $\text{H}_2\text{SO}_4$  with double distilled water, respectively.

### 3.5 Techniques Adopted

The use of inhibitors is the most economical and practical method in reducing corrosive attack on metals.

#### 3.5.1 Weight Loss Methods

#### 3.5.2 Electrochemical Methods

- ❖ Potentiometric Polarisation Method
- ❖ Linear Polarisation Resistance Method
- ❖ Electrochemical Impedance Spectroscopic Techniques

### 3.5.3 Surface Analytical Techniques

FTIR

Scanning Electron Microscope

### 3.5.4 Molecular Modelling/ Quantum Chemical approach/Computational details

### 3.5.5 Software Tools

- Origin 8
- SPSS 17
- MS Excel
- Gaussian 03W code of programs using 6-311G (d,p)

### 3.5.1 Weight Loss Method:

Weight loss measurements were performed with dried rectangular strips following ASTM Standard Procedure.

The mild steel for weight loss method coupons were immersed in 100 ml of inhibited and uninhibited solutions and are allowed to stand for time intervals of 1/2h, 1h, 3h, 6h, 12h, 24h at 30°C and for 1/2h for various temperature range of 303K, 313K, 323 K, 333 K, 343 K. Concentration of the inhibitors range from 40ppm to 200ppm in 0.5M H<sub>2</sub>SO<sub>4</sub> and 1M HCl. The specimens were abraded with abrasive papers 320, 400 and 600 grit, washed in absolute ethanol and acetone, dried in room temperature and stored in a moisture free desiccator before their use in corrosion studies.

The specimens were weighed before immersion in the test solutions and reweighed after immersion. From the initial and final masses of the specimen, the weight loss was calculated.

From the weight loss, Corrosion rate, Inhibition Efficiency and surface coverage were determined using the following relationship.

$$\text{Corrosion rate (mpy)} = \frac{534 \times W}{D A T} \times 100 \text{ ----(1)}$$

where,

W is the weight loss in milligram

D is the density in g/cm<sup>3</sup>

A is the area of the specimen in square inches

T is the time of exposure in hours

$$\text{Inhibition efficiency (\%)} = \frac{\text{Weight loss}_{\text{blank}} - \text{Weight loss}_{\text{inhibitor}}}{\text{Weight loss}_{\text{blank}}} \times 100 \text{ ----(2)}$$

$$\text{Surface Coverage } (\theta) = \frac{\text{Weight loss}_{\text{blank}} - \text{Weight loss}_{\text{inhibitor}}}{\text{Weight loss}_{\text{blank}}} \text{ ----- (3)}$$

### Adsorption isotherms:

Various adsorption isotherms were tested graphically to fit a suitable adsorption model for the inhibitor. Data were tested graphically by fitting various isotherms and statistical estimation of correlation for the curve fitting of isotherms have been used to investigate the goodness of fit of the isotherms using **SPSS 17 Package**.

$$\text{Langmuir – Plot of } \log \theta / (1 - \theta) \text{ Vs } \log C \text{ ----- (4)}$$

$$\text{Temkin - Plot of } \log C \text{ Vs } \log \theta \text{ ----- (5)}$$

$$\text{Freundlich – Plot of } \log C \text{ Vs } \log \theta \text{ ----- (6)}$$

$$\text{Frumkin _ Plot of IE Vs } \log C. \text{ ----- (7)}$$

$$\text{El – awady } et al., \text{ Thermodynamic – kinetic model ----- (8)}$$

A straight line will indicate that the inhibitor adsorbed through Langmuir and Freundlich adsorption isotherms whereas ‘S’ shaped curve in the case of Frumkin indicate the inhibitor adsorbed through Frumkin isotherm.

### Energy of Activation:

The activation energy in comparison with room temperature were calculated for different concentrations of the inhibitors by

$$\log K = \frac{-E_a}{2.303RT} + C \text{ ----- (9)}$$

Applying the formula  $E_a = -2.303 \times R \times \text{Slope}$

Slope is obtained by plotting  $\log CR$  Vs  $1/T$

## Thermodynamic Parameters:

### $\Delta G$ Adsorption:

Free energy values were obtained and calculated using the following equation

$$\log C = \log (\theta/1-\theta) - \log B \text{ ----- (10)}$$

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

“C” is the concentration of the system studied.

### $\Delta H$ and $\Delta S$ Adsorption:

The values of enthalpy of adsorption  $\Delta H$  and entropy of activation  $\Delta S$ , were obtained by plotting  $\Delta G$  (KJ/mol) Vs T (K). The slope of the straight line gives the value of  $\Delta S$  and the intercept gives the value of  $\Delta H$ .

### 3.5.2 Electrochemical Methods:

All the experiments were carried out in a double walled glass cell of capacity 200ml having provisions for the inlet of nitrogen gas, working electrode, counter platinum electrode and Luggin capillary. The potential of the working electrode was measured with respect to saturated calomel electrode (SCE) through luggin capillary. The experiments were carried out after the steady state attainment of corrosion potentials (15 mts) at  $30 \pm 1^\circ\text{C}$ .

For the electrochemical techniques, **SOLARTRON ELECTROCHEMICAL MEASUREMENT UNIT (1280B)** model interfaced with an IBM computer was used with a software package of ZPLOT 2 and CORR WARE 2. The polarization studies were made after the specimen attained a steady state potential. The potential was carried out from a cathodic potential of -0.2V to an anodic potential of +0.2V with respect to the corrosion potential at a sweep rate of 0.5mV/s. E versus log I curves were plotted. AC impedance measurements were done in the frequency range of 20 KHz to 0.1Hz

The charge transfer values were obtained from the plots of  $Z'$  and  $Z''$ . The values of  $(R_t+R_s)$  corresponds to the point where the plot cuts  $Z'$  axis at low frequency and  $R_s$  corresponds to the point where the plot cuts  $Z'$  axis at high frequency. The difference between  $R_t$  and  $R_s$  gives the charge transfer resistance ( $R_{ct}$ ) values. The  $C_{dl}$  values were obtained from the relationship

Where,

$C_{dl}$  = double layer capacitance

$R_{ct}$  = charge transfer resistance

$f_{\max}$  = frequency at  $Z'$  value maximum (Ross Macdonald, 1987).

### Measurement of Corrosion Current ( $I_{\text{corr}}$ )

Values of corrosion currents were obtained by Tafel extrapolation method. In Tafel extrapolation method, plots of  $\eta$  vs log current were made and on extrapolation gave the corrosion current and the slope of the linear portion of the anodic and cathodic curves gave  $b_a$  and  $b_c$  respectively.

### Determination of Inhibition Efficiency

The inhibition efficiency was obtained from the equation

$$\text{Inhibition efficiency (\%)} = \frac{I_{\text{corr (blank)}} - I_{\text{corr (inh)}}}{I_{\text{corr (blank)}}} \times 100 \text{ ----- (12)}$$

Where,

$I_{\text{corr (blank)}}$  = corrosion current in the absence of inhibitor

$I_{\text{corr (inh)}}$  = corrosion current in the presence of inhibitor

Besides the above method, the inhibition efficiencies were obtained from  $R_p$  and  $R_{ct}$  values as follows,

$$\text{Inhibition efficiency (\%)} = \frac{R_{P \text{ (inh)}} - R_{P \text{ (blank)}}}{R_{P \text{ (inh)}}} \times 100 \text{ -----(13)}$$

$$\text{Inhibition efficiency (\%)} = \frac{R_{ct \text{ (inh)}} - R_{ct \text{ (blank)}}}{R_{ct \text{ (inh)}}} \times 100 \text{ -----(14)}$$

Where

$R_{p \text{ (blank)}}$  and  $R_{ct \text{ (blank)}}$  = polarization resistance and charge transfer resistance in the absence of inhibitor

$R_p$  and  $R_{ct \text{ (inh)}}$  = polarization resistance and charge transfer resistance in the presence of inhibitor

### Calculation of Surface Coverage

Surface coverage from impedance measurements was calculated using the formula,

$$\text{Surface Coverage } (\theta) = \frac{C_{dl(\text{blank})} - C_{dl(\text{inh})}}{C_{dl(\text{blank})}} \text{ ----- (15)}$$

Where,

$C_{dl(\text{blank})}$  is the double layer capacitance in the absence of inhibitor

$C_{dl(\text{inh})}$  is the double layer capacitance in the presence of inhibitor

### 3.5.3 Surface Analytical Techniques

#### 3.5.3.1 Scanning Electron Microscope:

To study the morphology of the iron substrate after corrosion in the absence and presence of the inhibitor the instrument **JEOL MODEL JSM 6360** was used.

#### 3.5.3.2 FTIR Spectral Analysis:

FTIR was recorded using Perkin Elmer FTIR spectrophotometer which extended from 4000 and 400  $\text{cm}^{-1}$  for P2I, TMP2I, DMP2I, OCP2I, PNDMP2I and PNP2I.

#### 3.5.3.3 UV-visible Spectrophotometric measurements:

The adsorption of monochromatic light is a suitable method for identification of complex ions. The adsorption of light is proportional to the concentration of the adsorbing species. For routine analysis, a simple conventional technique based on UV-Visible adsorption is the most sensitive direct spectrophotometric direction. Change in position of the absorbance maximum and change in the value of absorbance indicate the formation of a complex between two species in solution (**Obi-Egbedi 2010**).

UV-visible absorption spectrophotometric method was carried out on the prepared mild steel samples after immersion in 0.5M  $\text{H}_2\text{SO}_4$  and 1M HCl with and without addition of 200 ppm Imidazoline for three days. All the spectral measurements were carried out using UV-Visible Spectrophotometer.

### 3.5.4 Molecular Modelling/ Quantum Chemical approach/Computational details

Quantum-chemistry calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities. This is an useful approach to investigate the mechanism of reaction in the molecule and its electronic structure levels. The structure and electronic parameters can be obtained by means of theoretical calculations. (**Ebenso *et al.*, 2010**)

This QSAR approach is adequately sufficient to forecast the inhibitor effectiveness using the theoretical approach, it may be used to find out the optimal group of parameters for predicting a molecule's suitability to be a corrosion inhibitor. There is no doubt that the recent progress in DFT has provided a very useful tool for understanding molecular properties and for describing the behaviour of atoms in molecules. All the computations and calculations were carried out using **Gaussian 03 W code of programs using 6-311G(d,P)**. Exchange and correlation calculations were carried out with the functional hybrid B3LYP and the 6-311G (d,p) orbital basis sets for all the atoms. In all cases, total structure optimization together with the vibrational analysis of the optimized structures was carried out in order to determine whether they correspond to a maximum or a minimum in the potential energy curve. The frontier molecular orbitals, namely, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were evaluated for P2I, TMP2I and DMP2I using the following equations:

**Ionisation potential (IP)** and **electron affinity (EA)** were calculated from  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$

$$\text{Ionisation potential} = - E_{\text{HOMO}}$$

$$\text{Electron Affinity} = - E_{\text{LUMO}}$$

In DFT, the ground state energy  $E(\rho)$  of an atom/molecule can be expressed in terms of its electron density. Using the finite difference approximation, the **global softness S** can be evaluated. The **global hardness  $\eta$** , which is the inverse of the global softness can be evaluated using the following equations:

$$\text{Hardness } \eta = \frac{E_{\text{HOMO}} - E_{\text{LUMO}}}{2}; \quad \text{Softness } S = \frac{1}{2 \eta}$$

$$\text{Electronegativity } \chi = \frac{\text{IP} + \text{EA}}{2}$$

$$\text{Electrophilic Index } \omega = \frac{\mu^2}{2 \eta}$$

### 3.5.5 List of Instruments used and Experimental plans.

**Sophisticated Instruments handled during the present investigations are listed in Figure – 14**

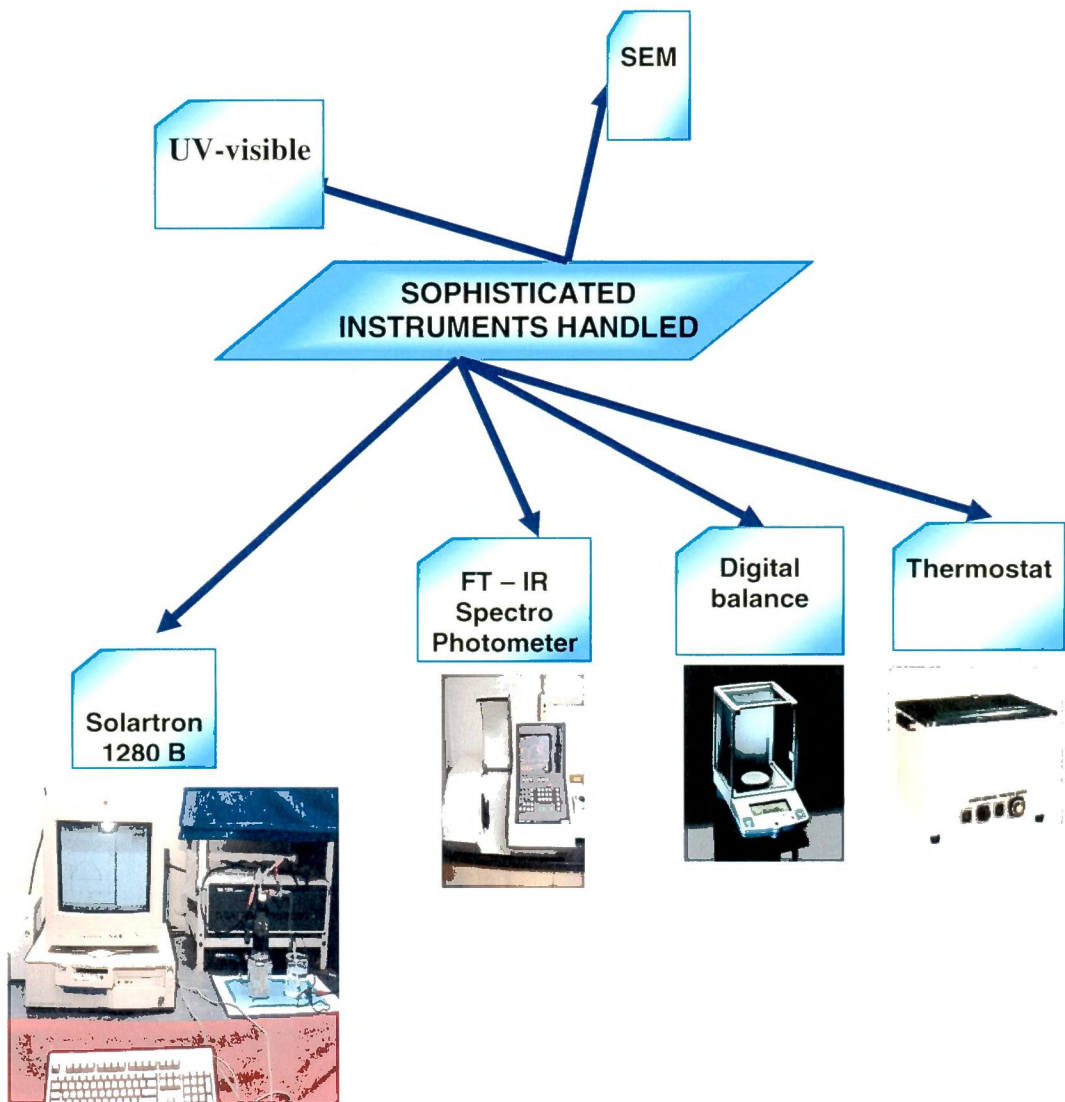
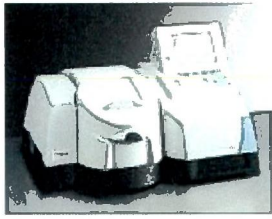


Figure - 14

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**Experimental plan for the current investigation is  
depicted in Figure - 14 a**

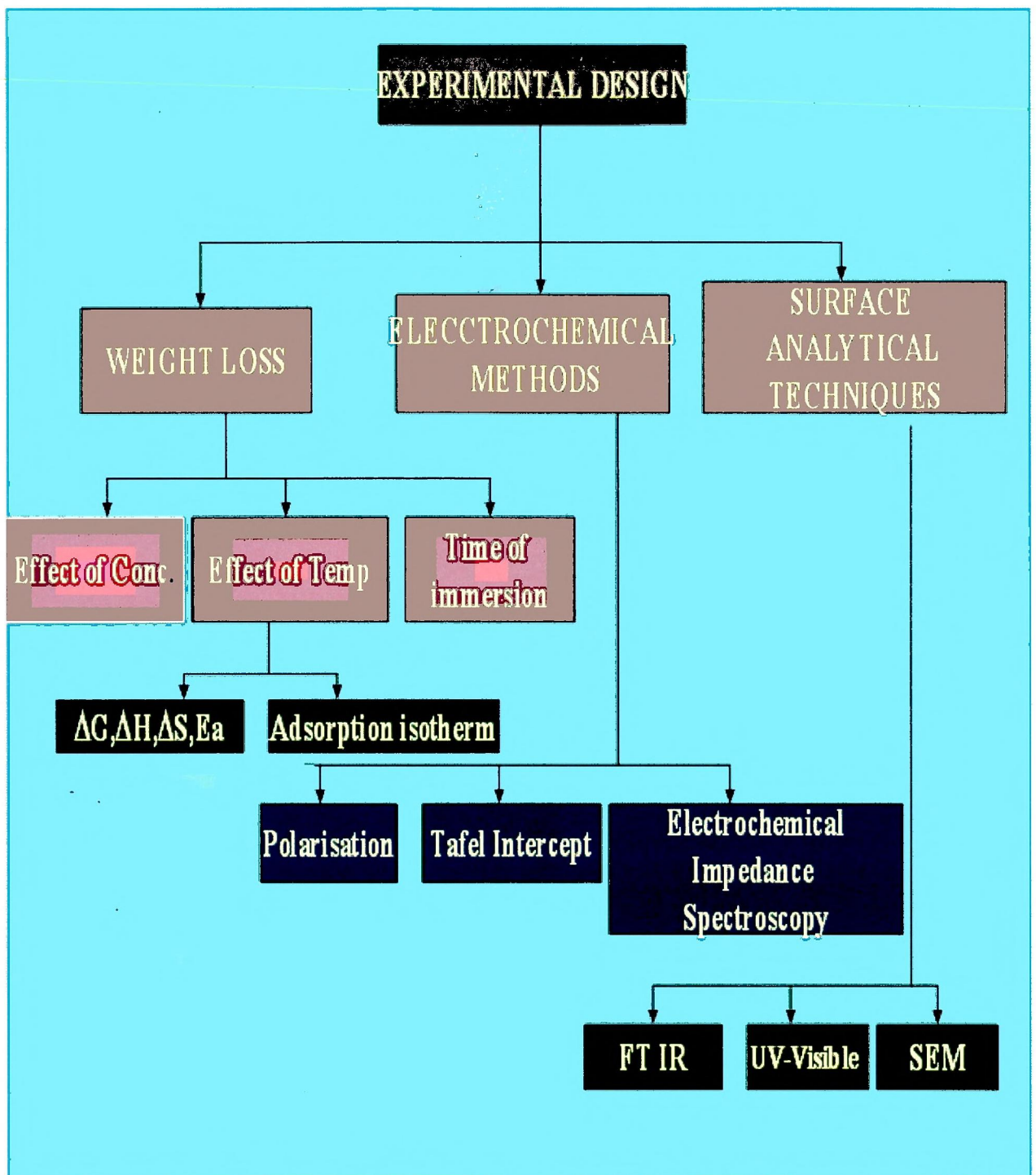


Figure - 14 a