5.1. INTRODUCTION

Sulphuric acid is most frequently used for the removal of undesirable scale and rust in metal finishing industries, heat exchangers, cleaning of boilers and pickling of iron and steel [1-4]. Corrosion inhibitors are often used to inhibit corrosion of apparatus caused by acid medium in many industrial operations [5]. Most of the well-known acid inhibitors are organic compounds such as those containing nitrogen, sulphur, oxygen atoms and aromatic rings [6-12]. These substances in general are effective through adsorption on the metal surface. Compounds containing both nitrogen and sulphur groups generally give rise to satisfactory inhibition efficiency in the case of iron corrosion in acid medium [13-15]. The efficiency of these inhibitors depends on chemical composition and structure of the inhibitors and the state of the metallic surface [16, 17].

A few investigations have been reported on the use of drugs as corrosion inhibitors. Rhodanine azosulpha drugs have been reported to be corrosion inhibitors for the corrosion of 304 stainless steel in HCl medium [18]. They showed good corrosion inhibition by parallel adsorption on the surface of steel due to the presence of more than one active center in the inhibitor. Some antibacterial drugs viz., ampicillin (AMP), cloxacillin, flucloxacillin and amoxicillin have been studied as inhibitors [19]. The corrosion inhibition of the mild steel in HCl medium by four sulpha drugs viz., sulfaguanidine, sulfamethazine, sulfamethoxazole and sulfadiazine was reported using weight loss and galvanostatic polarization techniques [20].

Imatinib was developed in the late 1990s by biochemist Nicholas Lydon, a former researcher for Novartis and oncologist, Brian Druker of Oregon Health & Science University (OHSU). Imatinib marketed by Novartis as Gleevec (U.S.) or Glivec (Europe/Australia/Latin America). It is a tyrosine-kinase inhibitor used in the treatment of multiple cancers, most notably Philadelphia chromosome-positive (Ph+) chronic myelogenous leukemia (CML) [21, 22]. Like all tyrosine-kinase inhibitors, imatinib works by preventing a tyrosine kinase enzyme. It occupies the tyrosine kinase active site, leading
to a decrease in activity [23, 24]. It is a white to off-white to brownish or yellowish tinged crystalline powder. Its molecular formula is C\textsubscript{29}H\textsubscript{31}N\textsubscript{7}O,CH\textsubscript{4}SO\textsubscript{3} and its molecular weight is 589.7. *Imatinib mesylate* is soluble in aqueous buffers \(\leq\) pH 5.5 but is very slightly soluble to insoluble in neutral/alkaline aqueous buffers. The chemical structure of *IMT* is shown in Fig. 5.1.

In the light of the above, present work is to study the inhibitive performance of *imatinib mesylate* (*IMT*) on the corrosion of mild steel in 0.25 M sulphuric acid using gravimetric measurements and potentiodynamic polarization studies. Thermodynamic parameters such as adsorption heat, adsorption entropy and adsorption free energy were obtained from the experimental data of the inhibition process at different temperatures, and pre-exponential factor at various inhibitors concentrations were calculated. The effect of activation energy on the corrosion rate of mild steel was discussed. The adsorbed film containing the investigated compound has been identified by FT-IR spectroscopy and SEM analysis. The inhibition mechanism has been discussed based on the electron orbital density distribution of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of *IMT* molecule. Optimization of temperature, fluid velocity and concentration of the inhibitor has been made and correlated the results obtained with the Box-Wilson statistical method.

![Chemical structure of IMT](image)

**Fig. 5.1:** Chemical structure of *IMT*. 
5.2. RESULTS AND DISCUSSION

5.2.1. Gravimetric measurements

The corrosion rate (CR) and inhibition efficiency IE (%) obtained from gravimetric measurements of mild steel in the absence and in the presence of various concentrations of IMT at different temperatures and rotational speeds of the specimen in 0.25 M H₂SO₄ solutions after 6 h of immersion are presented in Table 5.1. The data in Table 5.1 revealed that the addition of IMT decreases markedly the corrosion rate of mild steel. The IE (%) increases as the concentration of added IMT is increased at all temperatures, and when the concentration reached to 5 mM, IE (%) of IMT reached a high values of 89.78 at 70 ºC and 1800 rpm, which represents the excellent inhibitive ability of IMT. This is due to the fact that, adsorption and the degree of surface coverage of the inhibitor on the mild steel increases with the inhibitor concentration, thus the mild steel surface gets efficiently separated from the medium.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Concentration (mM)</th>
<th>1800 (rpm)</th>
<th>2000 (rpm)</th>
<th>2200 (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CR (mg cm⁻² h⁻¹)</td>
<td>IE (%)</td>
<td>CR (mg cm⁻² h⁻¹)</td>
<td>IE (%)</td>
</tr>
<tr>
<td>blank</td>
<td>4.89</td>
<td>-</td>
<td>5.09</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>2.66</td>
<td>45.54</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.50</td>
<td>48.82</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.69</td>
<td>65.27</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.24</td>
<td>74.52</td>
<td>1.32</td>
</tr>
<tr>
<td>blank</td>
<td>6.16</td>
<td>-</td>
<td>6.32</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>2.99</td>
<td>51.41</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.74</td>
<td>55.51</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.80</td>
<td>70.79</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.35</td>
<td>78.08</td>
<td>1.41</td>
</tr>
</tbody>
</table>
To assess the effect of temperature on corrosion and corrosion inhibition process, gravimetric experiments were performed at different temperatures (30 - 80 ºC) in the absence and the presence of various concentrations of the inhibitor during 6 h of immersion and at various rotational speeds (1800 - 2100 rpm) of the specimen. The results are presented in Table 5.1. From the Fig .5.2 it is shown that, the \( CR \) increases with increasing the temperature in the absence of the inhibitor. However, this increase seems slightly in presence of the \( IMT \). The relationship between the corrosion rate (\( CR \)) of mild steel and temperature (T) can be expressed by the Arrhenius equation. The apparent
The activation energy for the corrosion process can be obtained from the following Arrhenius equation:

\[
CR = k \exp \left( -\frac{E_a^*}{RT} \right)
\]

(5.1)

where \(E_a^*\) is the activation energy, \(k\) is the pre-exponential constant, \(R\) is the universal gas constant and \(T\) is the absolute temperature. Using Eq. (5.1), and from a plot of the log \(CR\) versus \(1/T\) (Fig .5.3), the values of \(E_a^*\) and \(k\) at various concentrations of \(IMT\) were computed from slopes and intercepts, respectively and the values are given in Table 5.2. The lower value of \(E_a^*\) at higher inhibitor concentration was due to the slow rate of inhibitor adsorption [25]. Putilova [26] has reported that these types of inhibitors are effective at higher temperatures. It was reported that, the inhibition efficiency of ampicillin on the corrosion of mild steel in 0.1 M H\(_2\)SO\(_4\) solution was decreased with increase in temperature [27]. The inhibition efficiency of \(IMT\) increases with temperature, because the addition of \(IMT\) to the acid solution decreases the activation energy. The reduction of the activation energy in the presence of \(IMT\) may be attributed to the chemisorption of the \(IMT\) on metal surface [28, 29]. The increase of \(IE\) (%) with temperature is explained with the change in the adsorption character. In the present case physisorption has been observed at a lower temperature and transforms into chemisorption at higher temperature [30]. The adsorbed inhibitor molecules block significantly some of the active sites on the steel surface which is energetically inhomogeneous. The inhibitor adsorbs at the active sites of the metal surface have the lowest \(E_a^*\) and other active sites of higher \(E_a^*\) will take part in the subsequent corrosion process [31]. The values of enthalpy and entropy of activation can be calculated from the alternative form of Arrhenius equation as follows:

\[
k = \frac{RT}{Nh} \exp \frac{\Delta S_a^*}{R} \exp \frac{-\Delta H_a^*}{RT}
\]

(5.2)

where \(h\) is Planks constant, \(N\) is Avogadro’s number, \(\Delta S_a^*\) is the entropy of activation, \(\Delta H_a^*\) is the enthalpy of activation. Plots of log \((CR/T)\) versus \(1/T\) gave straight lines (Fig .5.4) with a slope of \((-\Delta H_a^*/2.303R\) and an intercept of \([\log (R/Nh) + \Delta S_a^*/2.303R]\) from which the values of \(\Delta H_a^*\) and \(\Delta S_a^*\) were calculated and are listed in Table 5.2. The \(\Delta H_a^*\) values obtained from the slope of Eq. (5.2) and those values calculated from the equation, \(\Delta H_a^* = E_a^* - RT\) are in good agreement with each other. The positive values of \(\Delta H_a^*\) both in the absence and presence of inhibitor reflect the endothermic nature of mild steel dissolution process [32]. The negative values of \(\Delta S_a^*\) obtained indicate that the activated
complex in the rate determining step represents an association rather than dissociation, means that decrease in the disorder of the system due to the adsorption of inhibitor molecule on to the metal surface [33-35].

Table 5.2: Activation parameters for mild steel in 0.25 M sulphuric acid medium in the absence and presence of IMT at 1800 rpm

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>$k$ (mg cm$^{-2}$ h$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_a^* = E_a^* - RT$</th>
<th>$\Delta S_a^*$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>814704</td>
<td>30.52</td>
<td>27.84</td>
<td>28.00</td>
<td>-140.73</td>
</tr>
<tr>
<td>1</td>
<td>8090</td>
<td>20.53</td>
<td>17.79</td>
<td>17.92</td>
<td>-179.09</td>
</tr>
<tr>
<td>2</td>
<td>1122</td>
<td>15.64</td>
<td>12.88</td>
<td>12.95</td>
<td>-195.52</td>
</tr>
<tr>
<td>4</td>
<td>144</td>
<td>11.38</td>
<td>8.64</td>
<td>8.60</td>
<td>-212.91</td>
</tr>
<tr>
<td>5</td>
<td>46</td>
<td>9.25</td>
<td>6.52</td>
<td>6.40</td>
<td>-221.91</td>
</tr>
</tbody>
</table>

Fig. 5.2: Variation of $CR$ of mild steel as a function of temperature and concentration of IMT at 1800 rpm.
Fig. 5.3: Plot of log $CR$ versus $1/T$ for the corrosion of mild steel in 0.25 M H$_2$SO$_4$ containing various concentrations of IMT at 1800 rpm.

Fig. 5.4: Alternative Arrhenius plots for mild steel dissolution in 0.25 M H$_2$SO$_4$ the absence and presence of different concentrations of IMT at 1800 rpm.
5.2.3. Effect of rotational speed

The corrosion measurements were carried out at different rotational speed of the specimen (1800 - 2000 rpm). From Fig. 5.5, it is clear that the \( IE (\%) \) is maximum at 70\(^\circ\)C, 1800 rpm and at 5 mM IMT. Further, \( IE (\%) \) increases with increasing rotational speed at all temperatures up to 1800 rpm. However, beyond 1800 rpm \( IE (\%) \) decreases at all concentrations. Therefore, an optimum velocity is necessary for uniform distribution of an inhibitor.

![Graph](image.png)

**Fig. 5.5:** Variation of CR of mild steel as a function of rotational speed and concentration of IMT at 70 \(^\circ\)C.

5.2.4. Adsorption isotherm

The dependence of the degree of surface coverage (\( \theta \)) as function of concentration (C) of the inhibitor was tested graphically by fitting it to various isotherms to find the best isotherm which describes this study. Langmuir adsorption isotherm was found to be the best description for IMT on mild steel. According to this isotherm, \( \theta \) is related to the inhibitor concentration, C and adsorption equilibrium constant \( K_{ads} \) via [36]:

\[
\frac{C}{\theta} = \frac{1}{K_{ads}} + C
\]  

(5.3)

The plot of \( C/\theta \) versus C gave a straight line (Fig. 5.6) with a slope close to unity confirming that the adsorption of IMT on mild steel surface in sulphuric acid obeys the Langmuir adsorption isotherm. According to Langmuir adsorption isotherm, there is no
interaction between the adsorbed inhibitor molecules, and the energy of adsorption is independent on the degree of surface coverage (θ). Langmuir isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site occupies one adsorbed species. The equilibrium adsorption constant, $K_{ads}$, is related to the standard Gibb’s free energy of adsorption ($\Delta G_{ads}$) with the following equation:

$$K_{ads} = \frac{1}{55.5} \exp \left( - \frac{\Delta G_{ads}}{RT} \right)$$

(5.4)

where 55.5 is the concentration of water in solution (mol L$^{-1}$), R is the universal gas constant and T is the absolute temperature. The enthalpy and entropy of adsorption ($\Delta H_{ads}$ and $\Delta S_{ads}$) can be calculated using the equations (5.6).

$$\ln K_{ads} = \ln \left( \frac{1}{55.5} \right) - \frac{\Delta G_{ads}}{RT}$$

(5.5)

$$\ln K_{ads} = \ln \left( \frac{1}{55.5} \right) - \frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R}$$

(5.6)

Using Eq. (5.6), the values of $\Delta H_{ads}$ and $\Delta S_{ads}$ were evaluated from the slope and intercept of the plot of $\ln K_{ads}$ versus 1/T (Fig. 5.7). The values of $\Delta G_{ads}$, $\Delta H_{ads}$ and $\Delta S_{ads}$ are listed in Table 5.3. It shows that, the increase in $K_{ads}$ with increasing temperature indicates increase in the extent of adsorption with temperature [37]. The negative values of $\Delta G_{ads}$ ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface [38]. Generally, the values of $\Delta G_{ads}$ around - 20 kJ mol$^{-1}$ or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption), while those around - 40 kJ mol$^{-1}$ or higher indicate charge sharing or transfer from organic molecule to vacant 3d orbital of the metal to form co-ordinate type of bond (chemisorption) [39, 40]. In the present study, $\Delta G_{ads}$ values are more negative than - 20 kJ mol$^{-1}$ suggest that, the adsorption process of IMT on mild steel surface is a typical chemisorption [41]. The value of $\Delta H_{ads}$ is another criterion to confirm the mode of adsorption. Generally, an exothermic adsorption process signifies either physisorption or chemisorption or mixture of both while an endothermic process signifies chemisorption [42]. In the present case, the calculated value of $\Delta H_{ads}$ is 9.41 kJ mol$^{-1}$ indicating chemisorption of IMT on metal surface. In fact, it is well known that adsorption is an exothermic phenomenon accompanied by a decrease in entropy [43]. In aqueous solution, the adsorption of organic molecule is generally accompanied with desorption of water.
molecules. The adsorption of an organic adsorbate at the metal-solution interface is considered a ‘‘substitutional adsorption’’ phenomenon [44]. Therefore, the positive values of $\Delta H_{ads}$ and $\Delta S_{ads}$ related to ‘‘substitutional adsorption’’. The values of $\Delta H_{ads}$ and $\Delta S_{ads}$ can also be calculated by using following equation:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$$

(5.7)

Using Eq. (5.7), the plot of $\Delta G_{ads}$ versus T gives a straight line with a slope of $-\Delta S_{ads}$ and intercept of $\Delta H_{ads}$. The values obtained are well correlated with those obtained from Eq. (5.6).

Table 5.3: Thermodynamic parameters for adsorption of IMT on mild steel in 0.25 M sulphuric acid at different temperatures and at 1800 rpm

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$R^2$</th>
<th>$K_{ads}$ (L mol$^{-1}$)</th>
<th>$\Delta G_{ads}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_{ads}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_{ads}$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>0.982</td>
<td>909.1</td>
<td>-28.18</td>
<td>9.41$^a$</td>
<td>120.27$^a$</td>
</tr>
<tr>
<td>323</td>
<td>0.990</td>
<td>1086.9</td>
<td>-29.56</td>
<td>9.39$^b$</td>
<td>120$^b$</td>
</tr>
<tr>
<td>343</td>
<td>0.993</td>
<td>1111.1</td>
<td>-30.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>0.998</td>
<td>1282.1</td>
<td>-31.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$values obtained from Eq. (5.6), $^b$values obtained from Eq. (5.7)

Fig. 5.6: Langmuir’s adsorption isotherm plots for the adsorption of IMT in 0.25 M H$_2$SO$_4$ on the surface of mild steel at A-313 K, B-323 K, C-333 K and D-343 K at 1800 rpm.
5.2.5. Potentiodynamic polarization measurements

Potentiodynamic polarization curves obtained for the mild steel in 0.25 M sulphuric acid at various concentrations of IMT ranging from 1 mM to 5 mM are shown in Figs. 5.8a and 5.8b. It can be observed that the addition of IMT at all the studied concentrations decreased the anodic and cathodic current densities, and resulted in significant decline in the $I_{corr}$. This indicates that IMT shifted to smaller $I_{corr}$ values in both anodic and cathodic branches of the curves, thus, acting as a mixed-type inhibitor [45], and the decrease is more pronounced with the increase in the inhibitor concentration. By comparing polarization curves in the absence and in the presence of various concentrations of IMT, it is observed that, increase in concentration of the inhibitor shift the corrosion potential ($E_{corr}$) in the positive direction and reduces both anodic and cathodic process [33, 46].
**5.2.6. Molecule structure and inhibition mechanism**

The adsorption of *IMT* molecule in sulphuric acid may be due to the interaction between iron atom and cyclic molecular π-orbital. The incompletely filled 3d orbital of iron could bond with highest occupied molecular orbital (HOMO) [47] of the *IMT* molecule, while the filled 4s orbital of the former could interact with the lowest
unoccupied molecular orbital (LUMO) of the latter. This type of interaction has been explained in other documents [48, 49]. The electron density distributions of HOMO and LUMO of IMT are shown in Fig. 5.9a and 5.9b. From this it can be seen that the larger HOMO (Fig. 5.9a) electron density at amide group and benzene ring are more feasible to interact with 3d orbital of iron, while the pyrimidine ring is having larger LUMO (Fig. 5.9b) electron density and could take priority of interaction with completely filled 4s orbital of iron. Both interactions lead to strong binding between iron and IMT and it evidence the negative value of $\Delta G_{\text{ads}}$, and it increases with concentration. Another important factor is that, IMT having approximate planar structure with larger molecular weight than usual inhibitors and this allows the molecule to have more functional groups which are in favor of corrosion inhibition.

**Fig. 5.9a:** Structure of molecular orbital plots of IMT (HOMO orbital density).

**Fig. 5.9b:** Structure of molecular orbital plots of IMT (LUMO orbital density).
5.2.7. FT-IR Analysis

The FT-IR analysis of IMT before and after interaction with iron was carried out between 400 and 4,000 cm\(^{-1}\) and the spectra are shown in Figs. 5.10a and 5.10b, respectively. The peak at around 3000 - 3050 cm\(^{-1}\) was assigned to C-H stretching, C=O and N-H stretching frequencies are shown at 1659 cm\(^{-1}\) and 3435 cm\(^{-1}\), respectively. On comparing the spectrum of pure IMT with the spectrum of adsorbed IMT molecule over iron, it is observed that shifting of C=O stretching frequency from 1659 to 1629 cm\(^{-1}\) and disappearance of N-H stretching frequency indicating the interaction between the surface of mild steel and IMT [50].

![FT-IR spectrum of pure IMT before interaction with iron at optimum conditions.](image)

**Fig. 5.10a:** FT-IR spectrum of pure IMT before interaction with iron at optimum conditions.
5.2.8. Morphological investigation

The protective layer that formed on the metal surface was characterized by SEM analysis. Morphologies of mild steel in the absence and presence of optimum concentration of IMT at 70 °C are shown in Figs. 5.11a – 5.11c. It can be seen from Fig. 5.11a that the mild steel sample before immersion seem smooth. Inspection of Fig. 5.11b reveals that the mild steel surface after immersion in uninhibited 0.25 M sulphuric acid for 6 h shows an aggressive attack of the corroding medium on the steel surface. The corrosion products appeared very uneven and lepidoteralllike morphology and the surface layer is rather rough. In contrast, in the presence of IMT there is an adsorbed film on the metal surface (Fig. 5.11c)
Fig. 5.11: SEM images of mild steel in 0.25 M H$_2$SO$_4$ after 6 h immersion at 70 °C and at 1800 rpm (a) Before immersion (polished) (b) without inhibitor (c) with 5 mM IMT.
5.2.9. Application of Box-Wilson statistical method to the experimental results

In general, the purpose of an experimental design is to find useful relationships between controllable variables and observed response. The calculations were performed using \( CR \) obtained from mass loss measurements. A second order polynomial mathematical model is employed to the present work using the following equation [51].

\[
CR = b_0 + \sum_{i=1}^{p} b_i X_i^2 + \sum_{i}^{p} \sum_{j}^{p} b_{ij} X_i X_j
\]  

(5.8)

Where \( b_0, b_i, b_{ii} \) and \( b_{ij} \) are constants. The relationships between the coded variables and the corresponding real variables are as follows:

\[
X_{\text{coded}} = \frac{X_{\text{actual}} - X_{\text{centre}}}{X_{\text{centre}} - X_{\text{minimum}}} \times \sqrt{p}
\]  

(5.9)

Where \( X_{\text{actual}} \) is \( X_1 \) (temperature in °C), \( X_2 \) (velocity in rpm) and \( X_3 \) (inhibitor concentration in mM), \( X_{\text{centre}} = (X_{\text{min.}} + X_{\text{max.}})/2 \) for the given ranges, and \( p \) is the number of variables. The number of experiments (\( N \)) was estimated as follows:

\[
N = 2^p + 2p + 1
\]  

(5.10)

Rewriting Eq. (5.8) for the three variables in the present work as follows:

\[
CR = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_1 x_2 + b_5 x_1 x_3 + b_6 x_2 x_3 + b_7 x_1^2 + b_8 x_2^2 + b_9 x_3^2
\]  

(5.11)

The design of the coded data has the properties that \( \sum x_i = \sum X_i X_j = 0 \) and, \( \sum x_i^2 = 0.933 \) then Eq. (5.11) was rearranged as follows:

\[
B_0 = b_0 + 0.933 \times b_7 + 0.933 \times b_8 + 0.933 \times b_9
\]  

By substituting \( b_0 \) into Eq. (5.11) one obtains,

\[
CR = B_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_1 x_2 + b_5 x_1 x_3 + b_6 x_2 x_3 + b_7 (x_1^2 - 0.933) + b_8 (x_2^2 - 0.933) + b_9 (x_3^2 - 0.933)
\]  

(5.12)

\[
b_i = \frac{\sum (CR) - B_0}{\sum x_i^2}
\]  

(5.13)

The \( CR \) can be calculated from Eq. (5.12) after substituting \( B_0 \) and \( b_i \). Table 5.4 shows coded and real variables, \( CR \) calculated and errors which were conducted according to Box-Wilson method and the experimental response were represented by the measured \( CR \). The analysis of variance F-value was used for testing the significance of each effect in Eq. (5.12). The values of degree of freedom (\( \gamma = N - 10 \)) and the experimental error variance (\( S^2 = \sum_i (e_i^2/\gamma) \)) are 5 and 0.14633, respectively.
Chapter five

The estimated variance of coefficients, \( S_0^2 = S_f^2 / \sum X_i^2 \) was determined. The values are presented in Table 5.5. By using \( F_{0.95} \), after substituting the values of \( B_0 \) and \( b_i \) in Eq. (5.12), it can be rearranged as,

\[
CR = 2.917 + 0.689TX_1 + 0.365X_2 - 0.788X_3 + 0.168X_4X_2 - 0.468X_5X_3 - 0.180X_6X_3 + 0.057(X_1^2 - 0.933) + 0.031(X_2^2 - 0.933) - 0.059(X_3^2 - 0.933)
\] (5.14)

This equation represents the best form of mathematical model which correlates the \( CR \) with three variables in terms of the coded variables. The real values were determined using Eq. (5.14) as follows:

\[
CR = 2.736 \times 10^{-4}T^2 + 0.0225C^2 - 0.4425 \times 10^{-6}V^2 + 0.5490T + 2.3266C + 0.0303V + 0.0100TC - 2 \times 10^{-4} TV - 0.00135CV - 37.372
\] (5.15)

An equivalent in terms of actual variables will be more useful in the estimation of \( CR \) of mild steel in sulphuric acid medium and \( IMT \) at any desired conditions. The optimum conditions of variables in case of \( IMT \) were obtained by taking the first derivative of Eq. (5.15) for the dependent variables which were taken with respect to \( T \), \( V \) and \( C \).
<table>
<thead>
<tr>
<th>Run No</th>
<th>Coded variables</th>
<th>Real variables</th>
<th>$^{a}CR$, mg cm$^{-2}$ h$^{-1}$</th>
<th>$^{b}CR$, mg cm$^{-2}$ h$^{-1}$</th>
<th>$e_{r}$, mg cm$^{-2}$ h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_1$</td>
<td>$X_2$</td>
<td>$X_3$</td>
<td>$X_1$, °C</td>
<td>$X_2$, rpm</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>30.00</td>
<td>2000</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>50.00</td>
<td>1800</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>50.00</td>
<td>2200</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>50.00</td>
<td>2000</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>50.00</td>
<td>2000</td>
</tr>
</tbody>
</table>

$^{a}CR$ obtained by experiments and $^{b}CR$ calculated by using Eq. (5.15)
Table 5.5: Analysis of variance of variable effects for IMT on mild steel

<table>
<thead>
<tr>
<th>Effect</th>
<th>$\sum X_i^2$</th>
<th>$\sum CR \times X_i$</th>
<th>$b_i = \frac{\sum_{i=1}^{15} X_i \times (CR)_i}{\sum X_i^2}$</th>
<th>$S_i^2 = S_i^2 / \sum X_i^2$</th>
<th>F-value</th>
<th>$F_{0.95}=0.0661$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_0$</td>
<td>15.0</td>
<td>43.76</td>
<td>B.</td>
<td>2.917</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$X_1$</td>
<td>14.0</td>
<td>9.64</td>
<td>$b_1$</td>
<td>0.689</td>
<td>0.0105</td>
<td>45.363 S</td>
</tr>
<tr>
<td>$X_2$</td>
<td>14.0</td>
<td>5.11</td>
<td>$b_2$</td>
<td>0.365</td>
<td>0.105</td>
<td>12.735 S</td>
</tr>
<tr>
<td>$X_3$</td>
<td>14.0</td>
<td>-11.03</td>
<td>$b_3$</td>
<td>-0.788</td>
<td>0.0105</td>
<td>59.364 S</td>
</tr>
<tr>
<td>$X_1X_2$</td>
<td>8.0</td>
<td>1.34</td>
<td>$b_4$</td>
<td>0.168</td>
<td>0.0183</td>
<td>1.533 S</td>
</tr>
<tr>
<td>$X_1X_3$</td>
<td>8.0</td>
<td>-3.74</td>
<td>$b_5$</td>
<td>-0.468</td>
<td>0.0183</td>
<td>11.948 S</td>
</tr>
<tr>
<td>$X_2X_3$</td>
<td>8.0</td>
<td>-1.44</td>
<td>$b_6$</td>
<td>-0.180</td>
<td>0.0183</td>
<td>1.771 S</td>
</tr>
<tr>
<td>$U_1$</td>
<td>12.93</td>
<td>0.730</td>
<td>$b_7$</td>
<td>0.057</td>
<td>0.0113</td>
<td>0.282 S</td>
</tr>
<tr>
<td>$U_2$</td>
<td>12.93</td>
<td>0.40</td>
<td>$b_8$</td>
<td>0.031</td>
<td>0.0113</td>
<td>0.084 S</td>
</tr>
<tr>
<td>$U_3$</td>
<td>12.93</td>
<td>-0.77</td>
<td>$b_9$</td>
<td>-0.059</td>
<td>0.0113</td>
<td>0.312 S</td>
</tr>
</tbody>
</table>

$^a U_i = X_i^2 - 0.933$, S: Significant; NS: Not Significant
5.3. CONCLUSIONS

Results obtained from the experimental data shows *IMT* as effective inhibitor for the corrosion of mild steel in 0.25 M H$_2$SO$_4$. The adsorption of *IMT* was found to obey the Langmuir adsorption isotherm. The lower values of activation energy in the presence of *IMT* than those in its absence, and the higher values of Gibbs free energy indicated that the adsorption of *IMT* on mild steel in 0.25 M sulphuric acid is chemisorption. The corrosion rate in the presence and in the absence of inhibitor decreased with increasing rotational speed up to 1800 rpm and then it began to increasing. The adsorbed film containing the investigated compound was identified by SEM analysis and FT-IR spectroscopy. The experimental results obtained were well correlated with the Box-Wilson statistical method. The designed equation (5.15) based on Box-Wilson statistical method is applicable at any desired conditions with the given ranges of variables.
REFERENCES


Chapter five


