Corrosion inhibition of indoloimidazole derivative on mild steel in H$_2$SO$_4$

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Abstract— The corrosion inhibition of mild steel in 0.5M H$_2$SO$_4$ by indoloimidazole derivative namely, (3,4-dihydro-2-(phenyl)imidazo[4,5-b]indole) (DPI) has been studied using weight loss, potentiodynamic polarization, electrochemical impedance and quantum chemical studies. Inhibition was found to increase with increasing concentration of the inhibitor. The effect of temperature on the corrosion behavior of mild steel was studied in the range of 303 K-343 K. Potentiodynamic polarization results show that the inhibitors act as mixed type in 0.5M H$_2$SO$_4$. The adsorption of the inhibitors on the mild steel surface follows Langmuir and Temkin adsorption isotherms at 303K.

Molecular modeling has been conducted to correlate the corrosion inhibition properties with the calculated quantum chemical parameters.

Index Terms — acidic medium, corrosion inhibition, impedance, indoloimidazole, polarization, quantum studies, weight loss

1 INTRODUCTION

Corrosion of mild steel is a fundamental academic and industrial concern that has received considerable amount of attention. However, most equipment in industries is usually corroded owing to the general aggression of acid solutions. Some of the important fields of application of acid solutions in industries being acid pickling of iron and steel, chemical cleaning, ore production and oil well acidification. Thus, the use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [1]. Most of the efficient organic compounds acting as inhibitors have oxygen, sulphur, nitrogen atoms and multiple bonds through which they adsorb on metal surface [2]. Several works have studied the influence of organic compounds containing nitrogen on the corrosion of steel in acidic media. Adsorption of these compounds on metal surface depends on: (i) nature and charge of the metal, (ii) the type of electrolyte and (iii) the chemical structure of the inhibitor [3].

The present work also study the corrosion inhibition of mild steel using three different techniques: weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The effect of temperature on the corrosion behavior was also investigated. The quantum chemical study was employed to explain the experimental results obtained in this study and to give insight into the inhibition action of DPI on the mild steel.

2 MATERIALS AND METHODS

Mild steel coupons with the composition of C-0.07%, P-0.008%, Mn-0.34%, Fe – balance and size 3.5cm x 1.5cm x 0.5cm were used for weight loss investigation. The mild steel rod with an exposure area of 0.28 cm$^2$ was used for potentiodynamic polarization and impedance techniques. The coupons were prepared for the studies following ASTM procedure [4].

3,4-dihydro-2-(phenyl)imidazo[4,5-b]indole (DPI) was synthesized [5] by refluxing the equal amount of Isatin and benzaldehyde for 4 - 5 h at 40-60 0 C in the presence of ammonium acetate and glacial acetic acid. The reaction mixture was cooled and the precipitate obtained was filtered and recrystalized with methanol.

Scheme: Synthesis of DPI

0.5M H$_2$SO$_4$ solutions were prepared by the dilution of analytical grade H$_2$SO$_4$ with double distilled water respectively. The concentration of inhibitors used was 11 ppm, 15 ppm and 21 ppm. The loss of weights in different temperatures (303K, 313K, 323K, 333K and 343 K) using thermostat to study the inhibition efficiency of inhibitor at higher temperatures.

Electrochemical impedance spectroscopy (EIS) & Tafel polarization were conducted in an electrochemical measurements unit (Model stat [10V, 30 mA], IVIUM). The EIS measurements were made at corrosion potentials over a frequency range of 10 KHz to 0.01Hz with signal amplitude of 10 mV. The Tafel polarization measurements were made after EIS for a potential range of -200 mV to +200 mV with respect to open circuit potential at a scan rate of 1mV/sec.

From the Nyquist plot (Z$\text{real}$ VS Z$\text{imaginary}$), electrochemical resistance Rct and double layer capacitance Cdl was calculated. From the plot of potential E vs log I, the corrosion potential (E_{corr}), the corrosion current (I_{corr}), bc and ba were obtained.

3 RESULTS AND DISCUSSION

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Weight loss measurements

The inhibition efficiency with different concentrations (11ppm, 15ppm, 21ppm) of the inhibitor DPI on the mild steel in 0.5M H₂SO₄ has been evaluated by weight loss measurements and the results are given in the Table 1.

Table 1: Effect of concentration on the inhibition efficiency of DPI in 0.5M H₂SO₄ from weight loss measurements

<table>
<thead>
<tr>
<th>Conc (ppm)</th>
<th>Weight loss (g)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0452</td>
<td>637.5</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>0.0179</td>
<td>252.4</td>
<td>63.0</td>
</tr>
<tr>
<td>15</td>
<td>0.0161</td>
<td>227</td>
<td>64.4</td>
</tr>
<tr>
<td>21</td>
<td>0.0144</td>
<td>203.1</td>
<td>68.1</td>
</tr>
</tbody>
</table>

The result shows that as the inhibitor concentration increases, the corrosion rate decreases and the inhibition efficiency increases. This implies that the inhibitor acts through the adsorption on mild steel surface and formation of a barrier layer between the metal and corrosive medium [6].

Effect of Temperature and Thermodynamic Parameters

Table 2 shows the effect of temperature on the corrosion rate of mild steel in 0.5M H₂SO₄ in the absence and presence of DPI by weight loss measurements. It can be seen that the weight loss increases with the temperature which is due to the adsorption and desorption of inhibitor molecules continuously occur at the metal surface and equilibrium exists between two processes at a particular temperature.

Table 2: Effect of temperature on the inhibition efficiency of DPI in 1M H₂SO₄ from weight loss measurements

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Weight loss (g)</th>
<th>Corrosion rate (mpy)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.0157</td>
<td>664.3</td>
<td>66.38</td>
</tr>
<tr>
<td>313</td>
<td>0.0245</td>
<td>1036.6</td>
<td>58.89</td>
</tr>
<tr>
<td>323</td>
<td>0.0493</td>
<td>2086</td>
<td>51.71</td>
</tr>
<tr>
<td>333</td>
<td>0.1151</td>
<td>4870.3</td>
<td>44.98</td>
</tr>
<tr>
<td>343</td>
<td>0.1937</td>
<td>8196.1</td>
<td>36.13</td>
</tr>
</tbody>
</table>

Arrhenius plot is shown graphically in Figure 1. From the slopes of the plots, Ea were calculated and tabulated in Table 3. The higher value of Ea for mild steel in an inhibitor presence compared to that in its absence is attributed to its physical adsorption. The enthalpy of ΔH₀_ads and the entropy of adsorption ΔS₀_ads obtained are given in Table 4. The positive value of ΔH₀_ads for corrosion of mild steel in the presence and absence of the inhibitor reflect the endothermic nature of the metal dissolution process. The increase in ΔH₀_ads with increase in the concentration of the inhibitor for mild steel corrosion reveals that decrease in mild steel corrosion rate is mainly controlled by kinetic parameters of activation [7].

Adsorption Isotherm

The adsorption plays an important role in inhibition. Figures (2 and 3) shows the plot of C/θ Vs C and the plot of θ as a function of log C respectively and linear relationship was obtained with R² value for DPI. The results indicate that the R² values were very close to unity indicating strong adherence of adsorption which fits to the Langmuir and Temkin adsorption isotherm.

Table 3: Activation energy for DPI in 0.5M H₂SO₄

The ΔG₀ values obtained for DPI (Table 4) in 0.5M H₂SO₄ was less than -20 KJ / mol indicating that the adsorption was physisorption. Physical adsorption was a result of electrostatic attraction between charged species in the bulk of the solution. The calculated values are negative which ensures the spontaneity of the adsorption.

Table 4: Adsorption Isotherm for DPI in 0.5M H₂SO₄

Figure 1: Arrhenius plot for mild steel in 0.5M H₂SO₄

Figure 2: Langmuir plots of inhibitor, DPI

Figure 3: Temkin plots of inhibitor, DPI
Polarization curves for mild steel in 0.5M H2SO4 without and with inhibitor at different concentration are shown in Figure 5. It has been reported that when the change in $E_{corr}$ values are not less than 80 mV, a compound can be recognized as an anodic (or) a cathodic type of inhibitor [8]. Analysis of $E_{corr}$ values (Table 5) shows that the largest displacement of the potentials was about 28 mV for 0.5M H2SO4. Therefore the inhibitors act as mixed type of inhibitor. The values of ba and bc are both influenced by the presence of inhibitors which suggest that these are mixed type of inhibitor. $I_{corr}$ was found to decrease as the concentration of the inhibitor increases. This confirms the inhibitory action of the indoloimidazole derivatives on metal surface.

Table 5: Electrochemical parameters for the corrosion of mild steel in 0.5M H2SO4 with and without DPI

<table>
<thead>
<tr>
<th>Conc in ppm</th>
<th>$IE%$</th>
<th>Blank</th>
<th>11</th>
<th>15</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>62.70</td>
<td>66.80</td>
<td>67.40</td>
<td></td>
</tr>
</tbody>
</table>

**Quantum chemical Studies**

Quantum chemical calculation has been wildly used to study reaction mechanism and to interpret the experimental results as well as to resolve chemical ambiguities. It is an ap-
approach to investigate reaction mechanism on the molecule and electronic structure level. It is proved to be a very useful theoretical tool for studying inhibition mechanism and behavior. There are many reports on quantum chemical studies of an inhibitor [10].

The calculated values of the quantum chemical parameters obtained using the Hartree-fock/Density Functional theory (HF-DFT) by Becke 3 Lee Yang Parr (B3LYP) method with 6-31G basis set of GAUSSIAN 09 program are represented in the Table 6.

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>C₁₅N₃H₁₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>E&lt;sub&gt;HOMO&lt;/sub&gt; (eV)</td>
<td>-4.9239</td>
</tr>
<tr>
<td>E&lt;sub&gt;LUMO&lt;/sub&gt; (eV)</td>
<td>-0.7964</td>
</tr>
<tr>
<td>ΔE(eV)</td>
<td>-4.1275</td>
</tr>
<tr>
<td>Dipole Moment (µ)</td>
<td>4.6596</td>
</tr>
<tr>
<td>Global Hardness (η)</td>
<td>2.0638</td>
</tr>
<tr>
<td>Global Softness (σ)</td>
<td>0.2423</td>
</tr>
<tr>
<td>Electronegativity (χ)</td>
<td>2.8602</td>
</tr>
</tbody>
</table>

Absolute softness (σ) is defined as the reciprocal of the hardness. η and σ are calculated using the energies of the HOMO and LUMO orbital of the inhibitor molecules are related to the ionization potential (I) and the electron affinity (A) respectively, by the following reactions [13].

\[
(\eta) = \frac{I - A}{2} \\
(\sigma) = \frac{2}{I - A}
\]

where, I = E<sub>HOMO</sub> and A = E<sub>LUMO</sub>

The global softness (σ) for the investigated inhibitor suggests that the molecules are strongest inhibitor.

The dipole moment is another important electronic parameter that results from no uniform distribution of charges on the various atoms in a molecule. The results indicate that both values of the energy gap, ΔE = E<sub>HOMO</sub>-E<sub>LUMO</sub> as well as that of the dipole moment µ, favour indoloimidazole derivative DPI implying effectiveness as a corrosion inhibitor. The value of dipole moment probably increases the adsorption between the chemical compound and metal surface [6]. Other indicator is absolute electronegativity (χ), is a chemical property that describes the ability of a molecule to attract electron towards itself in a covalent bond, while the absolute hardness is measured by the energy gap between the lowest unoccupied and highest occupied molecular orbital.

The inhibitor efficiency increases as the molecular weight, molecular volume and molecular area of the molecules increases, due to the increase of the contact area between the molecule and surface [14, 15, 16, 17]. Small ionization energy indicates high reactivity of the atoms and molecules. Hereby,
the theoretical values also justify the experimental results.

4 CONCLUSION

The following conclusions are derived from the present work on DPI as corrosion inhibitor for mild steel in 0.5M H$_2$SO$_4$ over certain range of concentration at various temperatures by non-electro chemical, electro chemical and quantum chemical studies.

- The inhibition efficiency increases with increase in the concentration of these inhibitors but decreases with rise in temperature. The inhibitive action of DPI is due to the presence of heteroatom and aryl group.
- The adsorption of the investigated compound found to follow the Langmuir and Temkin adsorption isotherm indicating that the inhibition process occurs via adsorption.
- The Tafel constants obtained from the potentiodynamic polarization curves indicate that the investigated compound was mixed type inhibitor in 0.5M H$_2$SO$_4$.
- The theoretical findings reveal that the differences of inhibiting molecule efficiencies can be explained in terms of the value of sum of electron charge of nitrogen atoms.

REFERENCES