Research Article

# Corrosion Inhibition of Indoloimidazole Derivative on Mild Steel in HCl

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**Abstract**
The corrosion inhibition of mild steel in 1M HCl 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 s tudied in the range of 303 K – 343 K. potentiodynamic polarization results shows that the inhibitor act as mixed type in 1M HCl. The adsorption of the inhibitor on the mild steel surface follows Langmuir and Tempkin adsorption isotherms at 303K. Molecular madeling has been conducted to correlate the corrosion inhibition properties with the calculated quantum chemical parameters.

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## 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 highlights the successful use of indoloimidazole derivative as corrosion inhibitors for mild steel in 1M HCl and its excellent inhibition efficiency. 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.

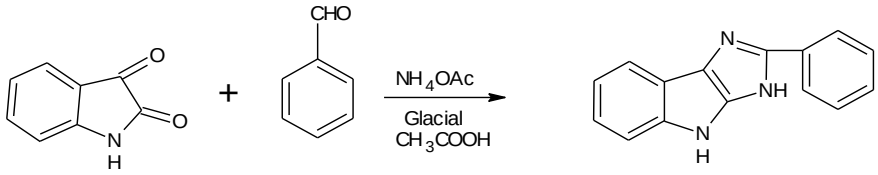
## Experimental Work

### *Materials and methods*

Mild steel coupons with the composition of C–0.07%, P–0.008%, Mn–0.34%, Fe –remaining 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 hours 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 recrystallized with methanol.




**Scheme** **DPI**

1M HCl solutions was prepared by the dilution of analytical grade HCl with double distilled water respectively. The concentration of inhibitors used was 11ppm, 15ppm and 21ppm in both the acids. 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. This study gives details about the nature of adsorption and activation energy.
Electrochemical impedance spectroscopy (EIS) & Tafel polarization were conducted in an electrochemical measurements unit (Model stat [10V, 30mA], IVIUM). The EIS measurements were made at corrosion potentials over a frequency range of 10 KHz to 0.01 Hz 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 1 mV/sec.

From the Nyquist plot ($Z_{real}$ vs $Z_{imaginary}$), electrochemical resistance $R_{ct}$ and double layer capacitance $C_{dl}$ were obtained. From the plot of potential E vs log I, the corrosion potential ($E_{corr}$), the corrosion current ($I_{corr}$), $b_c$ and $b_a$ were obtained.

## Results and discussion

### *Weight loss measurements*

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

**Table 1** Effect of concentration on the inhibition efficiency of DPI in 1M HCl from weight loss measurements

| Concentration (ppm) | Weight loss (g) | Corrosion rate (mpy) | Inhibition efficiency (%) |
|---|---|---|---|
| Blank | 0.0729 | 1028.2 | - |
| 11 | 0.0232 | 327.2 | 68.2 |
| 15 | 0.0191 | 269.3 | 73.8 |
| 21 | 0.0135 | 190.4 | 81.5 |

The adsorption plays an important role in inhibition. **Figures 1 and 2** 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 $R^2$ value for DPI. The results indicate that the $R^2$ values were very close to unity indicating strong adherence of adsorption which fits to the Langmuir and Temkin adsorption isotherm.

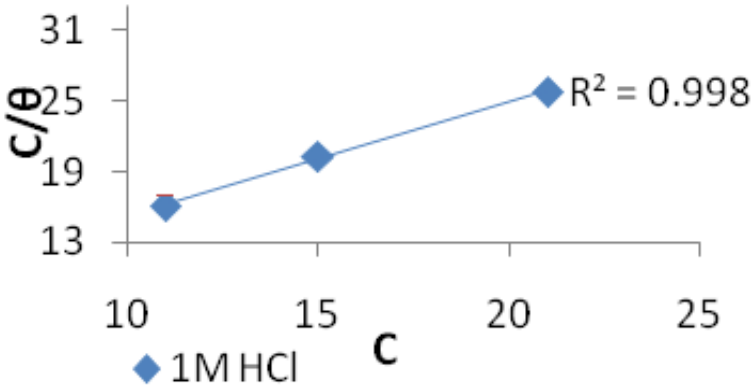



**Figure 1** Langmuir plots of inhibitor DPI

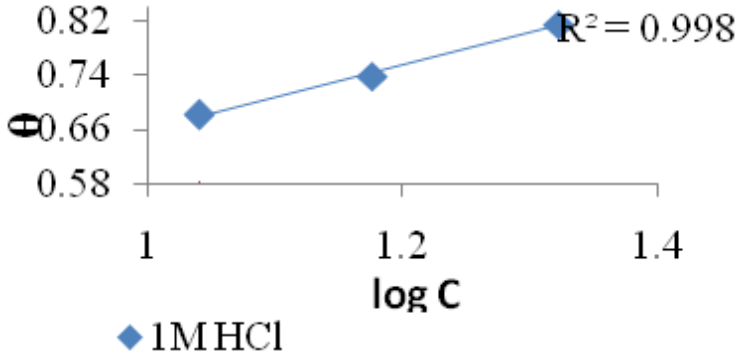



**Figure 2** Temkin plots of inhibitor DPI

***Effect of Temperature and Thermodynamic Parameters***

**Table 2** shows the effect of temperature on the corrosion rate of mild steel in 1M HCl 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 HCl from weight loss

| Temperature (°C) | Weight loss (g) | Corrosion rate (mpy) | Inhibition efficiency (%) |
|---|---|---|---|
| 303 | 0.0083 | 351.2 | 80.74 |
| 313 | 0.0146 | 617.7 | 70.39 |
| 323 | 0.0259 | 1095.9 | 64.67 |
| 333 | 0.0458 | 1937.9 | 51.38 |
| 343 | 0.0571 | 2416.1 | 47.23 |

Arrhenius plot is shown graphically in **Figure 3**. From the slopes of the plots, $E_a$ were calculated and tabulated in **Table 3**. The higher value of $E_a^0$ for mild steel in an inhibitor presence compared to that in its absence is attributed to its physical adsorption. The enthalpy of $\Delta H_{ads}^0$ and the entropy of adsorption $\Delta S_{ads}^0$ obtained are given in the Table 3. The positive value of $\Delta H_{ads}^0$ 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 $\Delta H_{ads}^0$ 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].

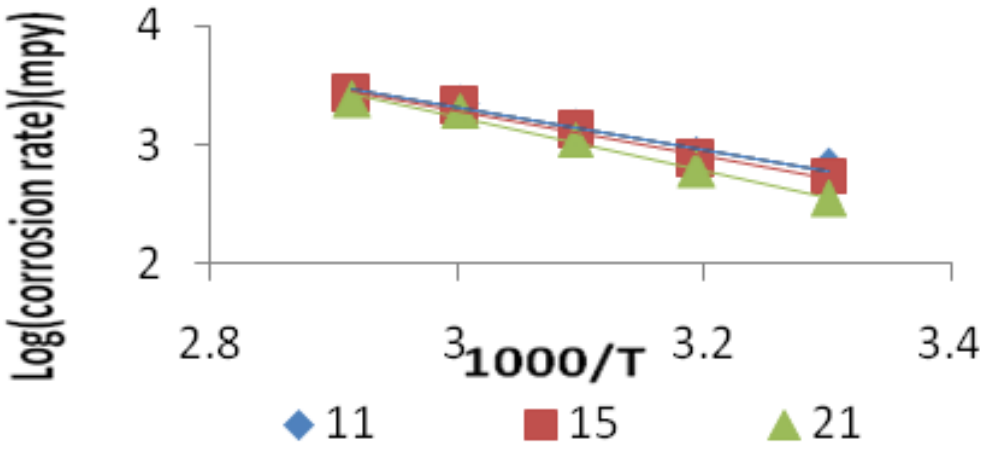



**Figure 3** Arrhenius plots for mild steel in 1M HCl

**Table 3** Activation energy values from Arrhenius plots in 1M HCl

| Conc in ppm | $E_a$ ($kJmol^{-1}$) | $-\Delta S^o$ (J/mol /K) | $\Delta H^o$ (kJ $mol^{-1}$) | $-\Delta G^o$ (kJ/mol) |
|---|---|---|---|---|
| Blank | 21.52 | - | - | - |
| 11 | 33.66 | 59.25 | 23.74 | 5.55 |
| 15 | 35.99 | 65.85 | 25.49 | 5.43 |
| 21 | 43.36 | 91.48 | 33.62 | 6.05 |

The $\Delta G^o$ values obtained for DPI (Table 3) in 1M HCl 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.

***EIS measurements***

Inhibition efficiencies and other calculated electrochemical parameters for DPI in 1M HCl were represented in **Table 4. Figures 4** show the Nyquist plots for mild steel in 1M HCl with and without inhibitor at various concentrations of DPI. The values of $R_{ct}$ is a measure of electron transfer across the surface and inversely proportional to the corrosion rate [8]. The increase in $R_{ct}$ values are attributed to the formation of the protective film of the inhibitor on the metal/solution interface [2] thereby increase in the efficiency of DPI. The decrease in $C_{dl}$ values can be attributed to decrease in local dielectric constant and/or increase in thickness of the electrical double layer. This suggests that the inhibitor molecules inhibit the corrosion rate by adsorption at the metal/solution interface [9].

**Table 4** Electrochemical parameters for the corrosion of mild steel in 1M HCl with and without DPI

| Conc in ppm | Impedance Studies | | | Potentiodynamic Polarization Studies | | | | |
|---|---|---|---|---|---|---|---|---|
| | $R_{ct}$ (ohm) | $C_{dl}$ (F) x$10^{-5}$ | Inhibition efficiency (%) | $I_{corr}$ (A/cm$^2$) | $E_{corr}$ (V) | $b_a$ (V/dec) | $b_c$ (V/dec) | Inhibition efficiency (%) |
| Blank | 9.9 | 5.55 | - | 0.001734 | -0.4676 | 0.044 | 0.0750 | - |
| 11 | 55.06 | 3.06 | 82.0 | 0.000478 | -0.4912 | 0.054 | 0.0124 | 72.4 |
| 15 | 73.71 | 4.08 | 86.6 | 0.000416 | -0.4902 | 0.073 | 0.0134 | 76.0 |
| 21 | 84.04 | 2.40 | 88.2 | 0.000280 | -0.4965 | 0.047 | 0.1030 | 83.9 |

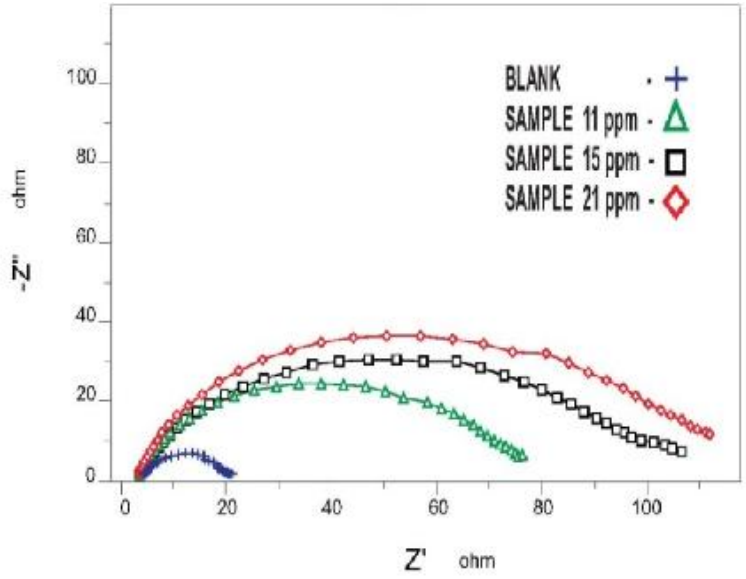



**Figure 4** Nyquist plot of DPI in 1M HCl

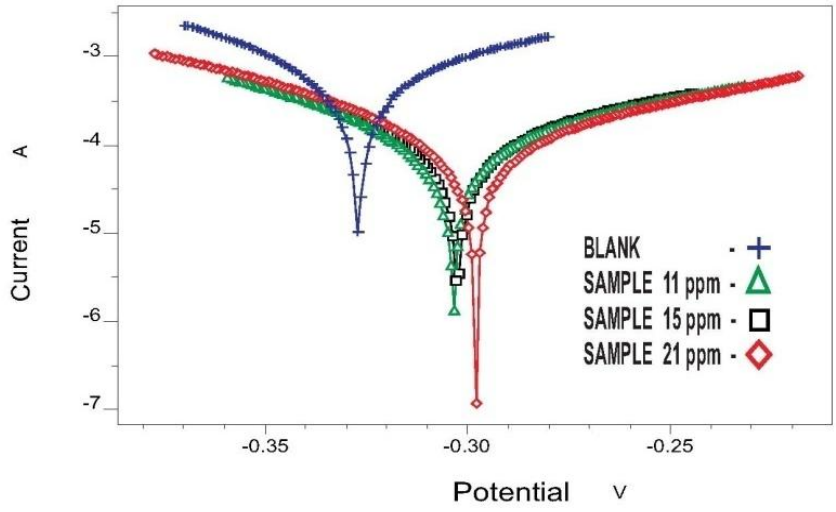



**Figure 5** Polarization Curves of DPI in 1M HCl

***Polarization measurements***

The values of electrochemical parameters associated with polarization measurements, such as corrosion potential ($E_{corr}$), corrosion current densities ($I_{corr}$), Tafel slopes ($b_a$ and $b_c$) and calculated inhibition efficiency (IE %) were listed in Table 4. Polarization curves for mild steel in 1M HCl 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 4) shows that the largest displacement of the potentials was about 28 mV for 1M HCl. Therefore the inhibitors act as mixed type of inhibitor. The values of $b_a$ and $b_c$ 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.

***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 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].
**Figures 6 - 8** show the optimized geometry, the HOMO density distribution and the LUMO density distribution for DPI molecule obtained with DFT at B3LYP/6-31G level of theory. The calculated values of the quantum chemical parameters obtained using the Hatree-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 5**.

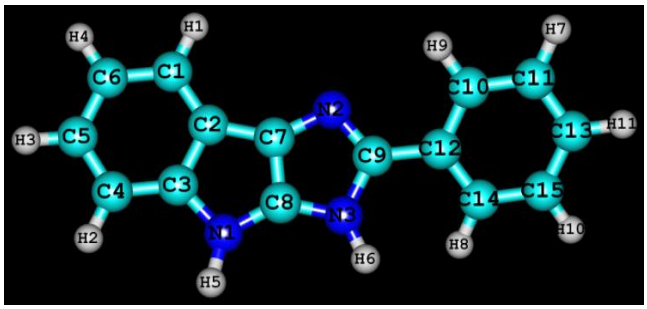



**Figure 6** Optimized geometry for DPI

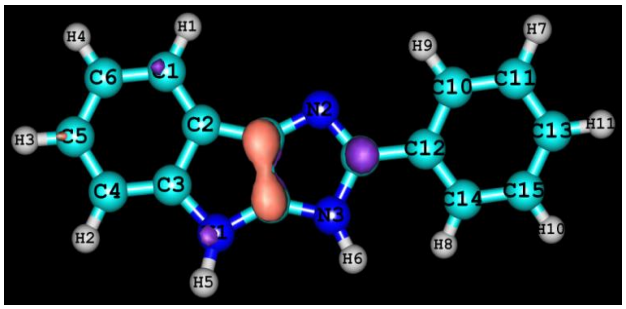



**Figure 7** HOMO density distribution for DPI

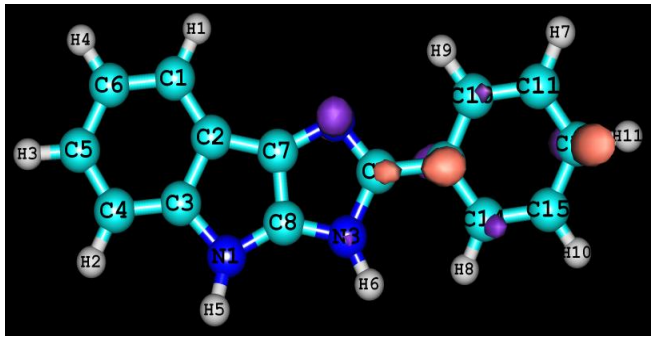



**Figure 8** LUMO density distribution for DPI

**Table 5** Quantum chemical parameters obtained by Gaussian 09

| Molecular Formula | $C_{15}N_3H_{11}$ |
|---|---|
| $E_{HOMO}$ (eV) | -4.9239 |
| $E_{LUMO}$ (eV) | -0.7964 |
| ΔE(eV) | -4.1275 |
| Dipole Moment (μ) | 4.6596 |
| Global Hardness (η) | 2.0638 |
| Global Softness (σ) | 0.2423 |
| Electronegativity (χ) | 2.8602 |

The increasing values of $E_{HOMO}$ facilitate the adsorption of the inhibitor. The negative sign of $E_{HOMO}$ value obtained and other thermodynamic parameters indicates that the data obtained supports physical adsorption mechanism [6]. The $E_{LUMO}$ indicates the ability of the molecule to accept the electrons. Therefore, the lower value of $E_{LUMO}$ the more apparent it is that the molecule would accept the electrons. The energy gap was calculated by $E_{HOMO}$ - $E_{LUMO}$ [11].

A soft molecule is more reactive than a hard molecule because a hard molecule has a larger energy gap [12]. The global hardness η is approximated as ΔE/2 and can be defined under the principle of chemical hardness and softness (HSAB). These parameters also provide information about the reactive behavior of molecules and represented in Table 6.

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].

**(η) = I - A / 2**
**(σ) = 2 / I – A**

where, $I = -E_{HOMO}$ and $A = -E_{LUMO}$

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, $\mathbf{\Delta E = E_{HOMO}-E_{LUMO}}$ 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 - 17]. Small ionization energy

indicates high reactivity of the atoms and molecules. Hereby, the theoretical values also justify the experimental results.

## Conclusion

The following conclusions are derived from the present work on DPI as corrosion inhibitor for mild steel in 1 M HCl 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 potentiodymamic polarization curves indicate that the investigated compound was mixed type inhibitor in 1M HCl.

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.

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