

Corrosion inhibition of indoloimidazole derivative on mild steel in H₂SO₄

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Abstract— The corrosion inhibition of mild steel in 0.5M H₂SO₄ 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 H₂SO₄. The adsorption of the inhibitors on the mild steel surface follows Langmuir and Tempkin 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].

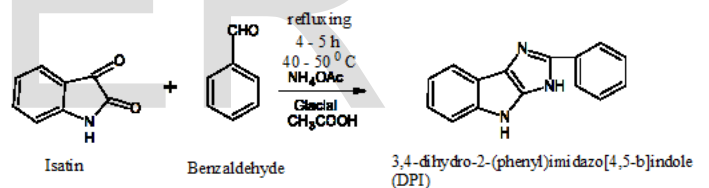
The present work also study the corrosion inhibition of mild steel using three different techniques: weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The effect of temperature on the corrosion behavior was also investigated. The quantum chemical study was employed 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 cm² was used for potentiodynamic polarization and impedance techniques. The coupons were prepared for the studies following ASTM proce-

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dure [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 °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: Synthesis of DPI

0.5M H₂SO₄ solutions were prepared by the dilution of analytical grade H₂SO₄ 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_{real} VS $Z_{imaginary}$), electrochemical resistance R_{ct} and double layer capacitance C_{dl} was calculated. 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.

3 RESULTS AND DISCUSSION

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

Conc (ppm)	Weight loss (g)	Corrosion rate (mpy)	Inhibition efficiency (%)
Blank	0.0452	637.5	-
11	0.0179	252.4	60.3
15	0.0161	227	64.4
21	0.0144	203.1	68.1

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

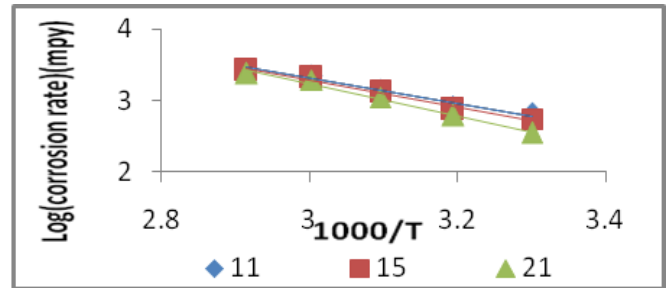
Table 2 shows the effect of temperature on the corrosion rate of mild steel in 0.5M H₂SO₄ in the absence and presence of DPI by weight loss measurements. It can be seen that the weight loss increases with the temperature which is due to the adsorption and desorption of inhibitor molecules continuously 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

Temp (°C)	Weight loss (g)	Corrosion rate (mpy)	Inhibition efficiency (%)
303	0.0157	664.3	66.38
313	0.0245	1036.6	58.89
323	0.0493	2086	51.71
333	0.1151	4870.3	44.98
343	0.1937	8196.1	36.13

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 ΔH^0_{ads} and the entropy of adsorption ΔS^0_{ads} obtained are given in Table 4. The positive value of ΔH^0_{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 ΔH^0_{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].

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



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.

Figure 2: Langmuir plots of inhibitor, DPI

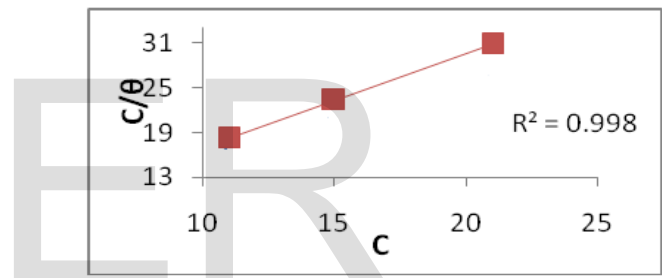
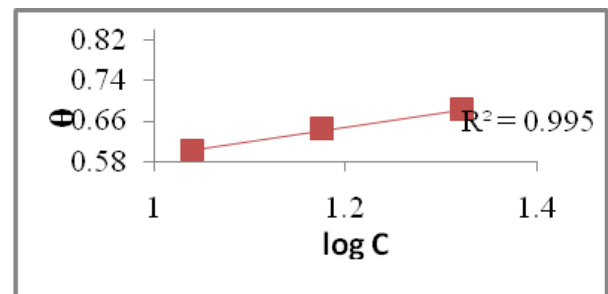


Figure 3: Temkin plots of inhibitor, DPI



The ΔG^0 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 3: Activation energy for DPI in 0.5M H₂SO₄

Conc (ppm)	Ea (kJmol ⁻¹)
Blank	43.03
11	53.94
15	54.67
21	56.67

Table 4: Thermodynamic parameters for DPI in 0.5M H₂SO₄

Conc in ppm	ΔG ⁰ (kJ mol ⁻¹)	-ΔS ⁰ _{ads} (J/mol/K)	ΔH ⁰ _{ads} (kJ mol ⁻¹)
11	4.91	66.02	24.86
15	4.40	67.28	24.91
21	4.16	73.63	26.52

EIS measurements

Inhibition efficiencies and other calculated impedance parameters for DPI in 0.5M H₂SO₄ were represented in Table 5. Figures 4 show the Nyquist plots for mild steel in 0.5M H₂SO₄ 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].

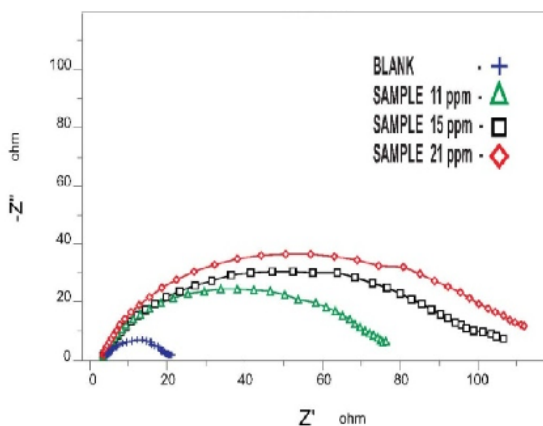


Figure 4: Nyquist plot of DPI in 0.5M H₂SO₄

Polarization measurements

The values of electrochemical parameters associated with polarization measurements, such as corrosion potential (E_{corr}), corrosion current densities (I_{corr}), Tafel slopes (ba and bc) and calculated inhibition efficiency (IE %) were listed in Table 5.

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

Conc in ppm	Blank	11	15	21	
Impedance Studies	R _{ct} ohm	18.51	54.27	57.2	57.42
	C _{dl} F x 10 ⁻⁵	4.63	3.13	3.64	3.68
	IE %	-	65.9	67.6	67.8
Potentiodynamic Polarization Studies	I _{corr} μA/cm ²	1682	627	558	549
	E _{corr} V	-0.4708	-0.4957	-0.4969	-0.4922
	ba V/dec	0.0370	0.0540	0.0516	0.0476
	bc V/dec	0.099	0.142	0.144	0.142
	IE %	-	62.70	66.80	67.40

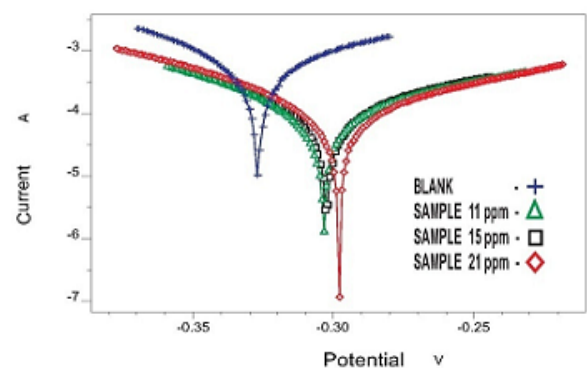


Figure 5: Polarization Curves of DPI in 0.5M H₂SO₄

Quantum chemical Studies

Quantum chemical calculation has been widely used to study reaction mechanism and to interpret the experimental results as well as to resolve chemical ambiguities. It is an ap-

proach 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].

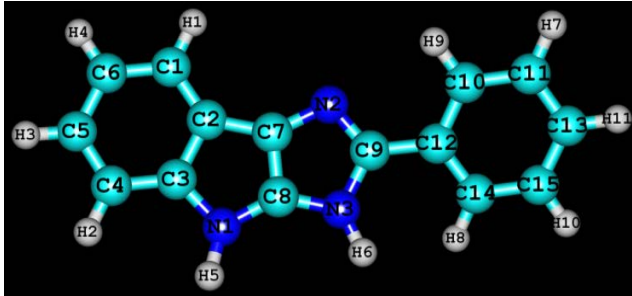


Figure 6: Optimized geometry for DPI

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.

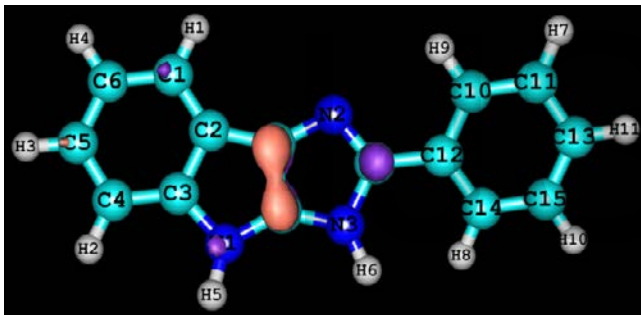


Figure 7: HOMO density distribution for DPI

Figure 6 - Figure 8 shows the optimized geometry, the HOMO density distribution and the LUMO density distribution for DPI molecule obtained with DFT at B3LYP/6-31G basic set of GAUSSIAN 09.

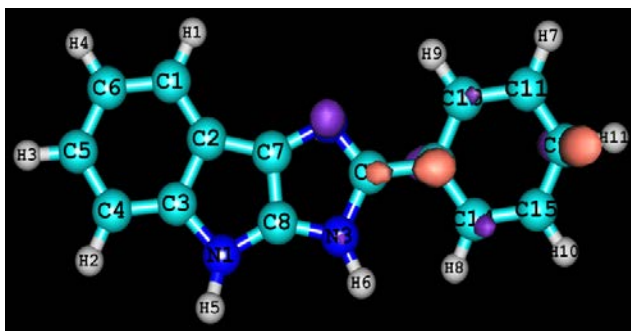


Figure 8: LUMO density distribution for DPI

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 $E_{\text{HOMO}} - E_{\text{LUMO}}$ [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 $\Delta E/2$ 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.

Table 6: Quantum chemical parameters obtained by Gaussian 09

Molecular Formula	$\text{C}_{15}\text{N}_3\text{H}_{11}$
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

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].

$$\begin{aligned}(\eta) &= (I - A) / 2 \\(\sigma) &= 2 / (I - A)\end{aligned}$$

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

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, $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$ 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, 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 H₂SO₄ 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 H₂SO₄
- 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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