Experimental and DFT Investigation on the Corrosion Inhibition of Mild Steel by 1, 2, 3- triazole Regioisomers in 1M hydrochloric Acid Solution

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The inhibition effect of new isomers of the triazole derivative family, namely 1-[(4-ethyl-2-phenyl-4,5dihydro-1,3-oxazol-4-yl)methyl]-4-phenyl-1H-1,2,3-triazole (Ph4) and 1-[(4-ethyl-2-phenyl-4,5dihydro-1,3-oxazol-4-yl)methyl]-5-phenyl-1H-1,2,3-triazole (Ph5), on mild steel corrosion in 1 M HCl was synthesized and evaluated using weight loss, electrochemical polarization, and impedance spectroscopy. The Ph4 compound was the best rust inhibitor and its inhibitory efficiency increased with increasing concentration, reaching 95% at 10⁻³ M. The polarization curves indicated that Ph4 and Ph5 are mixed-type inhibitors. EIS diagram appears a single capacitive loop, where diameter increases gradually as the inhibitors concentration. The change in the substitution phenyl from position 5(Ph5) to position 4 (Ph4) in the triazole ring increased the inhibitory effect of the triazole compounds. The effect of temperature on the corrosion behavior of mild steel indicated that the inhibitory efficiency of both inhibitors decreased with increasing temperature in the range308-338K. The DFT study correlated well with the experimental results.

Keywords: oxazole-triazole; corrosion inhibition; mild steel; electrochemical impedance spectroscopy (EIS); density functional theory (DFT)

1. INTRODUCTION

Corrosion is one of the major problems affecting the economy and safety, especially for the use of metals and alloys. Steel is used in a wide range of industries and machinery, but its main drawback is corrosion. The corrosion of steel is an area of focus that has received special attention for industrial concern [1]. Organic inhibitors are being used in many industrial processes to protect the materials from deterioration due to corrosion, particularly in many aggressive acidic media. The organic molecules decrease the corrosion rate in the acidic medium by adsorbing on the surface of the steel[2-3]. These inhibitors contain some heteroatoms such as oxygen (O), nitrogen (N), phosphorus (P), sulfur (S), and multiple bonds, enabling adsorption on the surface of metal [4-5]. New environmental restrictions have resulted in the use of environmentally acceptable substitution compounds, known as "green inhibitors". For instance, triazole derivatives have been proven to be effective as corrosion inhibitors in many corrosive systems [6-7]. Many triazole derivatives containing N and O are corrosion inhibitors that are eco-friendly [8-9]. A series of oxazoline-triazole derivatives were synthesized in the laboratory to investigate their anti-corrosive behavior on mild steel in 1 M hydrochloric acid (HCl).

Triazole derivatives have been evaluated as effective corrosion inhibitors in various media by several investigators. , Many researchers[10-12]reported the corrosion inhibition efficiencies of two triazole derivatives for mild steel in 1.0 M HCl. They concluded that all the molecules showed good inhibition with a slight difference in the efficiencies, which was due to their chemical structures and the presence of a variety of active sites that allow good adsorption on the metal surface. Similarly, Authors studied the function of 1,2,4-triazole based Schiff base on the corrosion of mild steel in 0.5M HCl[13].

The present paper investigated the corrosion inhibition of two isomers, 1-[(4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazol-4-yl)methyl]-5-phenyl-1H-1,2,3-triazole (Ph5) and 1-[(4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazol-4-yl)methyl]-4-phenyl-1H-1,2,3-triazole (Ph4) on mild steel in 1M HCl using weight loss, Tafel polarization and electrochemical impedance spectroscopy (EIS) techniques. The experimental results are complemented by theoretical calculations using density functional theory (DFT). The chemical formulas of both inhibitors are outlined in Table 1.

Abbreviation	Structural formula
Ph4	$Ph \rightarrow Et N = N \\ O \rightarrow V \rightarrow Ph$
	1-[(4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazol-4-yl)methyl]-4-phenyl-1H- 1,2,3-triazole
Ph5	Ph Ph Ph Ph N=N Ph Ph 1-[(4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazol-4-yl)methyl]-5-phenyl-1H-
	1,2,3-triazole

Table 1. Names and chemical structures of the organic compounds investigated.

2. EXPERIMENTAL

2.1. Material Preparation and Inhibitors

The chemical composition of mild steel used in this study was as follows (wt %): 0.21 C, 0.38 Si, 0.05 Mn, 0.05 S, 0.09 P, and 0.01 Al and balanced Fe. Prior to immersion, the steel specimens were pre-treated by grinding with different grades of emery papers from 180 up to 1500, washed with acetone and rinsed in distilled water, and then dried at room temperature before use.

The inhibitors were added to freshly prepared 1 M HCl in the concentration range of 10^{-6} to 10^{-3} M. The aggressive solution was prepared by dilution of analytical grade 37% HCl with distilled water.

2.2. General procedure for the Synthesis

The action of phenylacetylene on 4-(azidomethyl)-4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazole, determinedat 120 °C in a small amount of toluene with stirring for 48 h, yielded two position isomers called regioisomers that were separated by chromatography on silica gel column[14], as shown in flowing Equation.



1H-NMR (CDCl3, δ ppm): 1.01 (t, 3H, CH2CH3); 1.76 (q, 2H, CH2CH3); 4.22, 4.41 (AB, 2H, J = 9.16 Hz, CH2O), 4.54 and 4.64 (AB, 2H, J = 13.97Hz, CH2N), 7.25-7.91 (m, 10 Harom), 7.86 (s, 1Htriazole).

1H-NMR (CDCl3, δ ppm) : 0.54 (t, 3H, CH2CH3) ; 1.33 (q, 2H, CH2CH3) ; 3.94, 4.64 (AB, 2H, J = 9.16 Hz, CH2O) , 4.35 (S, 2H, CH2N), 6.85-6.55 (m, 10 Harom), 7.35 (s, 1Htriazole).

2.3. Electrochemical techniques

Electrochemical measurements were performed using a three-electrode cell. A mild steel sample including an electrode, platinum wire as the counter-electrode, and a saturated calomel electrode (SCE) as the electrode reference were used at room temperature. The working electrode was immersed in the test solution (1M HCl without or with the inhibitors) for 30min until a stable potential was reached before measurement. The electrochemical experiments of the potentiodynamic curves were performed with a (Potentiostat Radiometer-analytical PGZ 100, Lyon, France)[15] and controlled with Voltamaster 4 analysis software. The soft-steel electrode was maintained at open circuit conditions (OCP) and then polarized at –800 mV for 10 min. After this analysis, the potential was scanned at the anode. The anodic and cathodic polarization curves were recorded at a scan rate of 1 m/Vs with a small amplitude A.C.

signal of 10 mV and the applied frequency ranged from 100 KHz to 10mHz) with five points per every 10 degrees. The computer programs automatically controlled the measurements [16-18].

2.4. Gravimetric Measurements

The gravimetric measurements of 50 mL solutions were performed in a cell equipped with a thermostatic-controlled condenser. The mild steel specimens had a rectangular shape, with a length of 2 cm, width of 1 cm, and thickness of 0.2 cm, and were immersed vertically for 6 hours in the corrosive solution in both the absence and presence of inhibitors. At the end of the tests, the specimens were washed with distilled water and then weighed [19-20].

2.5. Theoretical Study

Theoretical calculations of the investigated molecules were performed using DFT (density functional theory) with the Yang–Parr non local correlation functional (B3LYP) with 6-31G (d,p) basis set by Gaussian 09 program[21]. The symmetry constraints were neglected for full geometry optimizations. The optimized molecular structures and some electronic properties, such as energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), and energy gap (ΔE) between LUMO and HOMO surfaces, were calculated [22].

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic Polarization Studies



Figure 1. Potentiodynamic polarization plots for mild steel in 1M HCl containing different concentrations of Ph4 and Ph5.

Potentiodynamic polarization curves for mild steel with different concentrations of Ph4 and Ph5 are presented in Figure 1.Both anodic and cathodic curves of the current potential were extrapolated to their intersection at E_{corr} [23-24].

The cathodic currents significantly decreased in the presence of the studied compounds compared to the blank solution, shifting E_{corr} toward negative potentials (Figure 1), which suggests that Ph4 and Ph5 considerably reduced the hydrogen evolution reaction.

The electrochemical parameters such as current density i_{corr} , corrosion potential E_{corr} , and cathodic Tafel slope β_c obtained from the polarization measurements are listed in Table 2. The inhibition efficiency $IE_{pp}(\%)$ was calculated by the following equation. The $IE_{PP}\%$ values were calculated using the following equation [25].

$$IE_{PP}\% = \frac{i_{corr} - i'_{corr}}{i_{corr}} * 100$$

where i_{corr} and i'_{corr} are the corrosion current densities values without and with inhibitor, respectively

Table 2. Polarization parameters and the inhibition efficiency of mild steel corrosion in 1M HCl containing different concentrations of Ph4 and Ph5 at 298 K

Medium	Concentration (M)	E _{corr} (mV/SCE)	i _{corr} (µA.cm ⁻²)	-βc (mV. dec ⁻¹)	IE _{pp} (%)
1M HCl	0	-456	1072	176	
Ph4	10-6	-484	337	173	68
	10-5	-449	334	175	67
	10-4	-467	66	173	94
	10-3	-461	44	184	96
	10-6	-450	382	191	64
Ph5	10-5	-442	289	160	73
	10-4	-475	103	173	90
	10-3	-457	75	180	93

The experimental values showed that the current density of corrosion (i_{corr}) values decreased progressively with increasing concentration of both inhibitors. Furthermore, the inhibition efficiency (IE) increases with the increasing of inhibitor concentration. Current densities, after addition of inhibitor, indicate an anodic dissolution delay of the mild steel and the reduction of hydrogen ions. A change in the E_{corr} value was observed in the presence of Ph4 and Ph5. if the displacement $E_{corr} > 85$ mV, the inhibitor acts as a cathodic or anodic inhibitor; if the displacement $E_{corr} < 85$ mV, the inhibitor is considered a mixed type inhibitor [26]. In the present study, the maximum shift in the E_{corr} value compared to the blank was 28 mV for Ph4 and 19 for Ph5, indicating that the inhibitors studied are mixed inhibitors, as shown in Figure 1.

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3.2. Electrochemical Impedance Spectroscopy (EIS)

In order to improve the results extracted from gravimetric and polarization measurements, Nyquist plots for mild steel before and after the addition of different concentrations of Ph4 and Ph5 inhibitors at 298 K in 1M HCl solution are studied and given in Figure 2. The impedance spectra exhibit one single capacitive loop indicating that the corrosion of steel is mainly controlled by the charge transfer process[27-28]. The diameter of the capacitive loop increased gradually with increasing concentrations of both inhibitors indicating that the charge transfer resistance increased and the adsorbed inhibitor formed a more compact monolayer on the metal surface with an increasing amount of inhibitor [21].



Figure 2.Nyquist diagrams for mild steel in 1M HCl containing different concentrations of Ph4 and Ph5.

The representative equivalent electrical circuit demonstrating adsorption of compounds Ph4 and Ph5 is shown in Figure 3. This circuit includes a resistor electrolyte (R_s) and a constant phase element (CPE), used in place of the capacitance of the double layer (C_{dl}) to account for surface inhomogeneities [29-30], positioned parallel to a charge transfer resistor (R_{ct}).



Figure 3. Electrical equivalent circuit used to fit the EIS data of the interface mild steel/1M HCl solution without and with investigated inhibitors.

The charge transfer resistance (R_{ct}) values were calculated from the difference in impedance at low and high frequencies [31]. The efficiency of the corrosion inhibition (IE_{imp} %) was calculated using the following equation:

$$IE_{R_{ct}}\% = \frac{R_{ct} - R'_{ct}}{R_{ct}}$$

Where R_{ct} and R'_{ct} are the charge transfer resistance values without and with the both studied inhibitors, respectively.

The Impedance parameters for the corrosion of mild steel in 1M HCl including the solution resistance (R_s), charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and *IE_{imp}* values are presented in Table 3.

Table	3.Characteristic	parameters	evaluated	from	the	impedance	diagram	in	the	absence	and	the
	presence of Ph4	and Ph5 in	1M HCl.									

Medium	Concentration (M)	$\frac{R_s}{(\Omega.cm^2)}$	$\frac{R_{ct}}{(\Omega.cm^2)}$	$\frac{C_{dl}}{(\mu F.cm^{-2})}$	IE _{imp} %
1M HCl	0	2.1	23	152	
Ph4	10-6	1.2	186	93	88
	10-5	2.1	336	72	93
	10-4	1.5	499	54	95
	10-3	0.8	669	53	97
	10-6	1.8	87	130	74
Ph5	10-5	1.2	209	95	89
	10-4	0.1	347	35	93
	10-3	1.1	404	33	94

From the calculated parameters in Table 3, the transfer of the charge resistance increased with increasing inhibitor concentration, which indicates an increase in the efficiency of the corrosion inhibition [32-35]. The EIS diagrams obtained with and without the inhibitors resemble half circles. The transfer of charge process, according to this result, controls the corrosion of mild steel. The C_{dl} capacity values decreased with increasing concentration for each inhibitor, potentially due to the molecule adsorption on the mild steel surface generating an insoluble barrier film from the acid solution. All compounds improved the transfer resistance loading R_{ct} and decreased in the double layer capacity C_{dl} in acid medium.

The results obtained for every concentration of Ph4 and Ph5 studied showed that these molecules reduce the corrosion rate of the metal surface in 1 M HCl. The values of the corrosion rate of mild steel decreased when the concentration of the inhibitor increased. Moreover, the efficiency of these inhibitors was greater for Ph4 than for Ph5.

3.3. Effect of Temperature

Temperature is an important factor that can change the behavior of a material in a corrosive environment, modifying the inhibitor-metal interaction in a given medium. Inhibitors protect the metal against acid attacks. Our experiments revealed a decrease in the power inhibitor by increasing the temperature. Few molecules retain their powers of inhibition with increasing temperature [36]. The temperature study was performed at different temperatures between 308 and 338 K using the weight loss technique in the absence and presence of the optimal concentration (10^{-3} M) for both compounds in 1 M HCl medium. The obtained results are calculated and listed in Table 4.

	1M HCl		Ph4		Ph5		
Temperature	W _{corr} (mg.cm ⁻² h ⁻¹)	IE%	<i>W_{corr}</i> (mg.cm⁻²h ⁻¹)	IE%	<i>W_{corr}</i> (mg.cm⁻²h⁻¹)	IE%	
308	0,852	-	0,039	95	0,059	93	
318	1,690	-	0,090	95	0,130	92	
328	3,860	-	0,320	92	0,424	89	
338	6,154	-	0,603	90	1,070	82	

Table 4. Corrosion parameters values for mild steel in 1M HCl without and with different inhibitors at 10⁻³M after 2 h immersion period.

The corrosion rates increased with temperature, which implies the reduction in the inhibitory efficiency. The rate of corrosion increased markedly with increasing temperature due to the higher dissolution of mild steel at higher temperatures, which could cause desorption of the studied inhibitors from the mild steel surface[37-38].

3.4. Thermodynamic parameters of the activation corrosion process

The Arrhenius plots (Ln W_{corr}) versus 1000/T resulted in straight lines with a slope of (-Ea /R) are presented in Figure 4.



Figure 4. Arrhenius plots for mild steel in 1 M HCl in the absence and in presence of 10⁻³ M of Ph4 and Ph5.

The Arrhenius plot of Ln (I_{corr}/T) versus 1000/T shown in Figure 5 which gave straight lines with slope $\Delta H^*/R$ and intercept (Ln R/N.h + $\Delta S^*/R$) from which ΔH^* and ΔS^* values were calculated.



Figure 5. Transition-state plots for C-steel in 1 M HCl in the absence and presence of 10⁻³ M of Ph4 and Ph5.

To obtain more details on the corrosion process, activation kinetic parameters, such as activation energy (E_a), enthalpy (ΔH^*), and the entropy (ΔS^*) were calculated from the Arrhenius equation (Eq.1) and summaries in Table 5. its alternative formulation called transition state equation (Eq. 2) [39-40]

$$W_{corr} = A \exp\left(-\frac{E_a}{RT}\right) (1)$$
$$W_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right) (2)$$

where W_{corr} is the corrosion rate, E_a is the apparent activation energy, R is the gas constant, A is the Arrhenius pre-exponential factor, N is Avogadro's number, h is Plank's constant, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation.

Table 5. Activation parameters for mild steel in 1 M HCl in the absence and in the presence of Ph4 and
Ph5 at the optimal concentration of 10^{-3} M at different temperatures

Medium	$E_a(kJ.mol^{-1})$	$\Delta H^*(kJ.mol^{-1})$	$\Delta S^*(kJ.mol^{-1}.K^{-1})$
1M HCl	58.580	55.899	-64.958
Ph4	82.047	79.360	-14.705
Ph5	85.374	82.693	-1.0123

The activation energy E_a for both compounds were lower in the presence of the inhibitor suggesting an increase in the barrier's energy during the process of corrosion; therefore, the dissolution of the metal surface sites will be more difficult [41-42]. The positive sign of ΔH^* was attributed to the endothermic nature of the mild steel dissolution process [43]. The increase in ΔS^* is usually interpreted as an increase in disorder as the reactants are converted to the activated complexes [44].

3.5. Adsorption Isotherm

The Ph4 and Ph5 adsorption process was subsequently evaluated to better understand its inhibitory mechanism. Surface coverage values (θ) at various concentrations were provisionally adapted to the Langmuir Isotherm, which was interpreted by the following equation [45]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh}$$

Where θ is the surface coverage degree as a function of the inhibitor concentration, K is the equilibrium constant of the adsorption process and C_{inh} is the inhibitor concentration.



Figure 6: Langmuir isotherm for the mild steel in 1M HCl with different concentrations of Ph4and Ph5 at 298K

As shown in Figure 6, the plot of C/θ versus C results in a linear correlation and the free adsorption energy ΔG^* was estimated by the following equation:

$$K = \frac{1}{55.5} exp\left(-\frac{\Delta G_{ads}^0}{RT}\right)$$

Table 6. Activation parameters for mild steel in 1M HCl in the absence and in the presence of Ph4 and Ph5 at different concentrations

Inhibitors	K	ΔG^0_{ads} (kJ.mol ⁻¹)
Ph4	3,38.105	-41,5
Ph5	2,98.105	-41,1

The negative and low value of the free enthalpy of adsorption ΔG_{ads}^0 (Table 6) indicates that the inhibitor was adsorbed spontaneously at the surface of the mild steel. This type of isotherm generally corresponds to chemisorption [45], implying the absence of interactions between the species adsorbed on the surface of the electrode [46].

3.6. Quantum Chemical Calculations

To explain the experimental findings and to investigate a possible correlation between experimental results and the electronic properties of the tested compounds, quantum chemical calculations were calculated to determine the adsorption and inhibition mechanism of Ph4 and Ph5. The values of the quantum chemical parameters were determined using DFT at B3LYP/6-31G (d,p). The optimized molecular structures of Ph4 and Ph5 are presented in Table 7.

 Table 7. Optimized molecular structures of neutral compounds 1, 2 and 3 with HOMO and LUMO orbitals



The total energy (ΔE), the ionization potential (*I*), the electron-affinity (*A*), the number of transferred electrons (ΔN) the electronegativity (χ) and the global hardness (η) were calculated using the following equations, as listed in Table 8[47-48]:

A=-E_{LOMO} ; I=-E_{HUMO} ;
$$\chi = \frac{I+A}{2}$$
 ; $\eta = \frac{I-A}{2}$
 $\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}$; $\Delta E = E_{LUMO} - E_{HOMO}$

where E_{HOMO} is the highest occupied molecular orbital energy, E_{LUMO} is the lowest unoccupied molecular orbital energy, $\chi_{Fe}=7$ eV and χ_{inh} denote the absolute electronegativity of iron and the inhibitor molecule, respectively, and $\eta_{Fe}=0$ eV and η_{inh} denote the absolute hardness of iron and inhibitor molecule, respectively[49-50].

Inhibitor	Phas	Еномо	E lumo	ΔE	μ	A	Ι	η(ev)	X	ΔN
S	e	(ev)	(ev)	(ev)	(D)	(ev)	(ev)	•	(ev)	
Ph4	G	-	-	4,845	3,121	1,184	6,030	2,423	3,607	0,700
		6,0302	1,1843	9	1	3	2	0	3	1
	А	-	-	4,928	3,121	1,257	6,185	2,464	3,721	0,665
		6,1855	1,2572	4	1	2	5	2	4	3
Ph5	G	-	-	5,320	5,450	1,170	6,490	2,660	3,830	0,595
		6,4901	1,1701	1	7	1	2	0	2	8
	А	-	-	5,334	5,450	1,263	6,597	2,667	3,930	0,575
		6,5976	1,2632	4	7	2	6	2	4	4

Table 8. The calculated quantum chemical parameters of the investigated inhibitors

The charge transfer rate ΔN describes the electron donation tendency inside of a set of inhibitors. According to Lukovits[51], if ΔN is less than 3.6, the effectiveness of the inhibition increases with increasing electron donor capacity at the steel or electrolyte. The values obtained from ΔN in Table 8 are all lower than 3.6. The difference between the HOMO and LUMO energy levels of the molecules, $\Delta E = E_{LUMO} - E_{HOMO}$, is another important descriptor that must be considered [52-53]. The energy gap describes the energy needed to perform the first excitation, so the efficiency of the inhibition of corrosion is inversely proportional to the value of the gap. The results of our study, as outlined in Table 8, show that the number of transferred electrons ΔN obtained with Ph4 was higher than Ph5, which strongly align with the experimental study. In addition, the energy gap values follow the order ΔE (Ph4) $< \Delta E$ (Ph5), which is in accordance with the order of inhibition efficiency of our compounds EI% (Ph4) < EI% (Ph5).

4. CONCLUSION

The triazole regioisomers reveal excellent protective qualities for protection of mild steel against corrosion in 1M HCl medium and the inhibition efficiency reached an optimum value at 10^{-3} M. The inhibition efficiency of Ph4 was less than that of Ph5, which shows that substitution plays an important role in the inhibition efficiency. The adsorption of both Ph4 and Ph5 molecules onto the surface of the mild steel in the 1 M HCl solutions fit the Langmuir isotherm model.

The polarization measurements indicate that both compounds can be classified as mixed type inhibitors. The inhibitory action of the added inhibitors can chemically adsorb on the surface of mild steel. EIS measurement results indicate that the resistance of steel increased considerably and its capacitance decreased with increasing inhibitor concentration. The quantum chemical parameters demonstrate the efficiency obtained by gravimetric study, Tafel polarization, and the EIS method.

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